Microstructure and thermodynamics of polymer and surfactant systems

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Microstructure and Thermodynamics of Polymer and Surfactant Systems

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ABSTRACT

Polymer and surfactant systems have found numerous applications in the chemical and specialty chemical industry. Investigation on the binding interaction between surfactant and polymer is fundamentally important for the successful formulation of home care and pharmaceutical products. For the binding interaction between surfactant and polymer, two types of classification are commonly used, i.e. (a) charged polymer and oppositely charged surfactant, and (b) uncharged polymer and all types of surfactant. In this thesis, the interaction between uncharged polymers and surfactants were systematically studied using the isothermal titration calorimetric (ITC), surfactant selective electrode (EMF), and laser light scattering (LLS) techniques, where the results provide the necessary information for the discovery of appropriate binding mechanisms.

Sodium dodecyl sulfate (SDS) is one of the most common anionic surfactant, which contains a hydrophilic head of sulfate anion and a hydrophobic dodecyl alkyl chain. When the concentration exceeds the critical micelle concentration (CMC), SDS monomers self-assemble to form micelles in order to minimize the Gibbs free energy (ΔG_m). However, the micellization behavior of SDS depends on temperature and solvent quality. From the ITC thermogram, not only the surfactant micellization thermodynamics, but also the CMC can be determined. In addition, we proposed for the first time the determination of effective micellar charge fraction (β) from ITC measurements for the ionic surfactant micellization process. In aqueous solution, the CMC remains constant for the temperature range of 18 to 31 °C, but the micellization enthalpy (ΔH_m) increases with temperature. Addition of glycols as co-solvents results in the initial reduction of the CMC, followed by an increase, while ΔH_m continued to

increase. The solvent mixtures become less polar with the addition of glycols, which reduces the non-ideality of SDS solution.

The interaction between SDS and different molecular weights of poly(ethylene glycol) (PEG or PEO) was studied by ITC. No interaction between SDS and PEG occurs when the PEG molecular weight is lower than 400 Da. With increasing polymer molecular weight to 900 Da, the binding interaction is observed and the polymer induced mixed micelles are formed, where PEG is dehydrated and solubilized into the mixed micellar core. When the molecular weight is increased to 3500 Da, ion-dipole association produces necklace-like SDS/PEG mixed micelles at high SDS concentrations, where the previously dehydrated PEG is re-hydrated and wrapped around the SDS micelles. The equilibrium of the polymer-induced micellization at low SDS concentrations and the ion-dipole association at high SDS concentrations dominates the binding interaction. When the polymer molecular weight exceeds 11,000 Da, the binding interaction becomes independent of polymer molecular weight. To examine the effect of polydispersity index (PDI) on the binding interaction, the ITC studies between SDS and the different PEG mixtures were conducted and the results revealed that the binding isotherms are independent of PDI.

Solvent quality affects not only the polymer conformation but also the binding isotherms between surfactant and polymer. The shift in the solvent quality can be achieved by varying temperature or by the addition of less polar solvents. With increasing temperature, the hydrogen bonds are partially destroyed and this lowers the solubility of the PEG in water. However, the lower critical solution temperature (LCST) for PEG is greater than 80 °C, thus poly(propylene glycol) (PPG) was used instead of PEG for the investigation of temperature effect since it possesses an LCST that is achievable experimentally. At temperatures lower than the LCST, the binding

interactions for SDS and PPG are identical to that of PEG/SDS system. However, at temperatures greater than the LCST, insoluble PPG chains are directly solubilized by SDS surfactant micelles. Near the LCST, the binding mechanism is controlled by the equilibrium between the solubilization of oily PPG domains at low SDS concentrations and polymer-induced micellization at high SDS concentrations. Addition of glycols, such as ethylene glycol, propylene glycol and glycerol, results in the decrease in solvent polarity and solvent quality of PEG based on their different solubility parameters, δ . From the ITC thermograms, it was evident that the polymer-induced micellization is transformed into chain solubilization with the addition of less polar solvent due to the decrease in the polymer desolvation process. The effect of decreasing solvent quality has the following trends; propylene glycol > ethylene glycol > glycerol.

The binding interaction between SDS and amphiphilic polymers was also investigated. For the hydrophobic modified water-soluble polymer, titration of SDS micellar solution into hydrophobic ethoxylated urethane (HEUR) and titration of HEUR into SDS micellar solutions revealed different binding mechanisms. For the former, non-cooperative binding occurs at very low SDS concentration as evident from EMF data. However, due to the weak enthalpy change, the non-cooperative binding process was not detectable by ITC. At critical aggregation concentration (CAC), cooperative binding begins to dominate the binding interaction as evident from ITC and EMF studies. The binding is controlled by polymer-induced micellization at low SDS concentrations and ion-dipole association at high SDS concentrations. After the saturation concentration C_2 , the binding interaction ceases. The free SDS monomer concentration during the whole binding process can be monitored by the EMF measurements using SDS selective electrode and the binding

isotherm can be calculated from the EMF and ITC data. The combination of EMF and ITC provide a complete characterization of the binding isotherms. CAC is independent of polymer concentration, but the saturation concentration C_2 strongly depends on the polymer concentration. With increasing SDS concentration, SDS molecules displace some of the HEUR end-groups in addition to being bound on PEO segments. These substituted end-groups are then solubilized by free SDS micelles as physical cross-linkers to produce larger aggregates in aqueous solution as confirmed by LLS measurements. The hydrophobic modification strongly affects the non-cooperative binding at very low SDS concentration. Due to the more hydrophobic HEUR, the CAC of HEUR/SDS system is lower than that of PEO/SDS system. However, long HEUR backbone and urethane groups as well as the non-cooperative binding at lower SDS concentration give rise to negligible effect of polymer end-groups on the cooperative binding process. We observed that the polymer molecular weight do not significantly affect the cooperative binding process. When titrating HEUR into a SDS micellar solution, HEUR chains directly bind to SDS micelles via the ion-dipole association. It was observed that polymer molecular weight, polymer and surfactant concentrations altered the binding enthalpies. We proposed for the first time the concept of basic binding segment for polymer-surfactant interaction based on the ITC measurements.

For the interaction between surfactant and amphiphilic block copolymers, SDS and PEP-type [P and E represent poly(oxypropylene) and poly(oxyethylene), respectively] Pluronic-R triblock copolymers in aqueous solution were investigated by ITC. Beyond the CAC, PEP/SDS aggregation complexes are formed through the polymer-induced micellization process, where SDS monomers first bind to the PPO segments followed by the binding to PEO segments. The polymer segments are

dehydrated and solubilized into the hydrophobic core of the mixed micelles. The formation of PEP/SDS aggregation complex is an entropic driven process, where the CAC is independent of polymer molecular weight, but is weakly dependent on the polymer concentrations and strongly dependent on polymer composition. An increase in the length of PPO segments results in the reduction of the CAC. With further increase in the SDS concentration, these dehydrated PEO segments are first rehydrated, which is then accompanied by the rehydration of PPO segments. At the saturation concentration C_2 , the polymer chains are bound to the surface of SDS micelles through ion-dipole associations. C_2 shifts to higher values with increasing polymer concentration.

For the interaction between HASE latex and different types of surfactants, strong binding interactions are evident, since the cloudy solution becomes clear with the addition of surfactants. However, the types of surfactant strongly affect the binding mechanism. For anionic surfactant, the non-cooperative hydrophobic binding at low surfactant concentration dominates. However, the cooperative hydrophobic binding at high surfactant concentration controls the formation of mixed micelle at CAC before the CMC of the surfactant, where the cloudy solution becomes clear. When the HASE latex is cross-linked, anionic surfactant only binds non-cooperatively to the latex and cause it to swell. For cationic surfactant, electrostatic interaction occurs at very low surfactant concentration and gives rise to phase separation. With further increase in the cationic surfactant concentration, non-cooperative hydrophobic and cooperative hydrophobic interactions dominate at low and high surfactant concentrations respectively. After the formation of mixed micelles at CAC, which is lower than the CMC of the cationic surfactant in water, the cloudy solution becomes clear. In addition, counterion condensation plays an important role in the binding

interaction between HASE latex and ionic surfactant. For nonionic surfactant, free surfactant micelles are formed in solution first due to its very low CMC value. After that, HASE latexes are directly solubilized into the surfactant micellar core.

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List of Publications

- 1) **Dai, S.**; Tam, K. C.; Wyn-Jones, E.; Jenkins, R. D. Isothermal Titration Calorimetry and Electromotive Force Studies on Binding Interactions of Hydrophobic Ethoxylated Urethane and Sodium Dodecyl Sulfate: Effects of Polymer Molecular Weights and End-capped Groups, *The Journal of Physical Chemistry B*, 2004, 108, 4979-4988.
- 2) **Dai, S.**; Tam, K. C. Isothermal Titration Calorimetric Studies on the Temperature Dependence of Binding Interactions between Polypropylene Glycols and Sodium Dodecyl Sulfate, *Langmuir*, 2004, 20, 2177-2183.
- 3) **Dai, S.**; Tam, K. C. Isothermal Titration Calorimetry Studies of Binding Interactions between Polyethylene Glycol and Ionic Surfactant, *The Journal of Physical Chemistry B*, 2001, 105, 10759-10763.
- 4) **Dai, S.**; Tam, K. C.; Jenkins, R. D. Binding Characteristic of Hydrophobic Ethoxylated Urethane (HEUR) and an Anionic Surfactant: Microcalorimetry and Laser Light Scattering Studies, *The Journal of Physical Chemistry B*, 2001, 105, 10189-10196.
- 5) **Dai, S.**; Tam, K. C.; Li, L. Isothermal Titration Calorimetry Studies on Interactions of Ionic Surfactant and Poly(oxypropylene)-Poly(oxyethylene)-Poly(oxypropylene) Triblock Copolymers in Aqueous Solutions, *Macromolecules*, 2001, 34, 7049-7055.
- 6) **Dai, S.**; Tam, K. C.; Jenkins, R. D. Microstructure of Dilute Telechelic Associative Polymer in Sodium Dodecyl Sulfate Solutions, *Macromolecules*, 2001, 34, 4673-4675.

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List of Symbols and Abbreviations

A_2	Second virial coefficient
AFM	Atomic force microscopy
C	Concentration
C^*	overlap concentration
C_2	Saturation concentration for polymer-surfactant systems
CAC	Critical aggregation concentration
C_m	Critical micellization concentration of surfactant in polymer solution
CMC	Critical micellization concentration
CTab	Cetyltrimethylammonium bromide
D	Diffusion coefficient
D_0	Diffusion coefficient at infinite dilute solution
DLS	Dynamic light scattering
dn/dC	Refractive index increment
DoTab	Dodecyltrimethylammonium bromide
DP	Degree of polymerization
E	Cell potential
EG	Ethylene glycol
EMF	Electromotive force
F	Faraday constant (9.65×10^4 C/mol)
GPC	Gel permeation chromatography
GR	Glycerol
HASE	Hydrophobically modified alkali soluble emulsion
HEUR	Hydrophobic ethoxylated urethane
HLB	hydrophile-lipophile balance
I	Light intensity
IEP	Isoelectric point
ISE	Ion selective electrode
ITC	Isothermal titration calorimetry
K	Equilibrium constant
k_B	Boltzmann constant (1.38×10^{-23} J/K)

k_D	Diffusion second virial coefficient
L_c	Contour length
LCST	Lower critical solution temperature
LLS	Laser light scattering
M_n	Number-averaged molecular weight
M_w	Weight-averaged molecular weight
MW	Molecular weight
n	Refractive index
N_A	Avogadro constant (6.02×10^{23} /mol)
N_{agg}	Aggregation number
NMR	Nuclear magnetic resonance
$P(q)$	Internal structure factor
PAA	Poly(acrylic acid)
PDI	polydispersity index
PEG	polyethylene glycol
PEO	Poly(ethylene oxide)
PG	Propylene glycol
PMAA	Poly(methacrylic acid)
PPG	polypropylene glycol
PPO	Poly(propylene oxide)
q	scattering vector
R	gas constant (8.31 J/molK)
REPES	Regularized positive exponential sum
R_F	Root mean end-to-end distance
R_g	Radius of gyration
R_h	Hydrodynamic radius
R_θ	Excess Rayleigh ratio at scattering angle θ
$S(q)$	Static structure factor
SANS	Small angle neutron scattering
SAXS	Small angle X-ray scattering
SDS	Sodium dodecyl sulfate
SLS	Static light scattering
SPC	Photon correlation spectroscopy

ST	Surface tension
T	Temperature
TEM	Transmission electronic microscopy
T_k	Krafft point
UCST	Upper critical solution temperature
V	Volume
ΔF	Helmholtz free energy
ΔG	Gibbs free energy
ΔH	Enthalpy
ΔS	Entropy
θ	Scattering angle
ϕ	Volume fraction
$[\eta]$	Intrinsic viscosity
χ	Flory parameter
Γ	Decay rate
α	Activity
β	Effective micellar charge fraction
ε	Dielectric constant
η	Viscosity
λ	Wavelength
μ	Chemical potential
τ	Relaxation time

Chapter 1 Introduction

1.1 Background

Mixtures of water-soluble polymers and surfactants not only have many current or future applications, such as in pharmaceutical formulations, personal care products, food products, household and industrial detergents, paints and coatings, drilling and enhanced oil recovery fluids, they but also are of fundamental interests to researchers that seek to elucidate intermolecular interaction and hydrophobic aggregation phenomena [Jonsson et al. 1998; Kwak 1998; Malmsten 2002]. Such mixtures produce many intriguing and unusual properties, and these have attracted increasing attention in commercial research laboratories and academic institutions. The earlier study on the formation and existence of lipo-protein aggregates in biological fluids could be traced to more than 100 years ago. Until the middle of 1950s, a number of studies on the interactions between proteins or acidic polysaccharide and synthetic ionic surfactants were carried out. It was confirmed that electrostatic forces played an important role in the binding interaction between natural ionic macromolecules and ionic surfactants, in addition to short-range hydrophobic attractions. The binding of charged surfactants onto water-soluble polymer chains results in the conformational change of natural macromolecular chains. In the last 40 years, extensive studies on water-soluble synthetic polymers and surfactants (ionic and nonionic) were conducted, and this has resulted in a significant advancement in the understanding of binding isotherms and theoretical interpretations of binding interactions [Goddard and Ananthapadmanaban 1993].

Surfactants contain both hydrophobic and hydrophilic groups. When the solution concentration exceeds the critical micelle concentration (CMC), micelle-like structure is first produced, driven by the increase in entropy. Different types of

micelles or aggregates can be achieved by varying surfactant types, surfactant concentrations and solvent quality [Jonsson et al. 1998]. Depending on the charge characteristics of the hydrophilic group, surfactants can be classified into anionic, cationic and nonionic, which gives rise to differences in the conformation of the surfactant micelle, the aggregation number as well as the CMC value. By introducing additives such as salt or organic molecules, the aggregation properties of surfactants can be altered [Rosen 1980].

Water-soluble polymers are a class of polymers that are readily solubilized in aqueous environment. They consist of both homopolymer and amphiphilic polymers. One category of water-soluble homopolymers are the uncharged polymers which can form hydrogen bond with water, such as polysaccharide, polyethylene glycol (PEG), poly(N-isopropyl acrylamide) (PNIPAM), etc. These uncharged polymers are water-soluble when the temperature is lower than their lower critical solution temperature (LCST). The other category of water-soluble homopolymers are polyelectrolytes, such as DNA, protein, neutralized polyacrylic acid (PAA), protonated poly[2-(diethylamino)ethyl methacrylate] (PDEAEMA), etc [Hara 1993; Hashidzume et al. 2002; Radeva 2001]. For amphiphilic polymers, they possess hydrophobic and hydrophilic segments. One type of amphiphilic polymer is achieved by hydrophobic modification of hydrophilic homopolymers, such as hydrophobically modified polyethylene oxide (HEUR). The other type of amphiphilic polymer is the block copolymer containing hydrophobic and hydrophilic segments, such as PEG related Pluronic block copolymers, PEG-*b*-PS (polystyrene), PEG-*b*-PEA (poly(ethyl acrylate)) [Alexandridis and Hatton 1995; Dai et al. 2004b; Tam and Tiu 1996; Yu and Eisenberg 1996; Yu and Eisenberg 1998]. For amphiphilic polymers in aqueous solution, they exhibit similar properties as surfactants. For example, they can

aggregate each other to form micelles at concentration exceeding the CMC, depending on the hydrophile/lipophile balance (HLB) [Hamley 1998; Webber et al. 1997].

However, mixtures of surfactant and water-soluble polymer exhibit aggregation properties that are totally different from their individual components in solution. The interactions depend strongly on the nature of the polymer and the surfactant. It is customary to classify polymer/surfactant interactions according to the charges on the polymer and surfactant system. For system of oppositely charged polymers and surfactants, long range electrostatic attractions between these opposite charged pairs of polymers and surfactants dominate the polymer/surfactant interactions at low surfactant concentrations, which commonly produces phase separation at the isoelectric point (IEP) [Kwak 1998; Wang and Tam 2002]. After all the charged groups are neutralized, the hydrophobic interaction begins to dominate and gives rise to the structure reorganization at high surfactant concentrations. For system of uncharged polymer and charged surfactant, hydrophobic attraction and ion-dipole interactions are the main driven forces for the binding interactions depending on the characteristics of polymer and surfactant. [Goddard and Ananthapadmanaban 1993; Kwak 1998]. In addition, the binding isotherms and microstructures of the polymer and the surfactant-bound polymer complex are also affected by temperature, organic or inorganic additives and solvent polarity.

In polymer-surfactant binding system, two critical values are commonly used to describe the binding interactions between surfactant and polymer; the critical aggregation concentration (CAC) indicating the onset of binding and the saturation concentration (C_2) signifying the completion of binding. In the past, many different techniques have been used to measure these critical values accurately, such as surface

tension (ST), viscosity, conductivity, dye solubilization and fluorescence probe, nuclear magnetic resonance (NMR), surfactant selective electrode (EMF), calorimetry, and small angle neutron scattering (SANS) [Goddard and Ananthapadmanaban 1993]. However, the binding interactions at concentration regime between CAC and C_2 are still not well understood and the thermodynamics of such interactions are not fully developed. In order to further elucidate the nature of polymer/surfactant systems, a detailed study on the interaction between various uncharged water-soluble polymers and surfactants using more precise and sensitive research tools is needed.

1.2 Objectives and Scope

The objectives of this study are to provide a molecular-level understanding on the binding isotherms and the binding mechanisms for various uncharged water-soluble polymers and surfactants. Isothermal titration calorimeter (ITC), laser light scattering (LLS) and electromotive force (EMF) were utilized to elucidate the binding behavior of these polymer/surfactant systems. The temperature and the solvent quality effects on the surfactant micellization were first examined. After that, the binding of sodium dodecyl sulfate (SDS) and different molecular weights of polyethylene glycol (PEG) and polypropylene glycol (PPG) were examined at different temperatures. The effect of polymer polydispersity and solvent polarity on the binding behaviors was investigated. In addition, the interaction between SDS and hydrophobically modified polyethylene oxide (HEUR) with different molecular weights and hydrophobic modification groups were carried out. At the same time, binding between SDS and amphiphilic block copolymers were also studied. Finally, the interaction between surfactant and colloidal latex were examined, and from these studies, we seek to obtain new insights into the interaction between uncharged polymer and ionic

surfactants, and to correlate these interactions to the microstructures of the polymer/surfactant complexes.

1.3 Overview of the Thesis

From this study, it has been observed that the binding interaction between SDS and water-soluble polymers are dependent on the polymer molecular weight, molecular weight distribution, co-solvent and temperature. The hydrophobic modification lowers the CAC values and increases the binding capacity. Studies on the interaction between latex and different types of surfactants indicate that surfactant type can alter the binding mechanisms. In this thesis, the theories on surfactant and polymer solutions as well as the previous studies on polymer/surfactant interactions are reviewed in the **Literature Review** section (Chapter 2). The theories of related research techniques are also briefly documented in this section. In the **Material and Experimental** section (Chapter 3), the materials used, the sample preparation, and the equipment details are described. In the section of **Results and Discussion** (Chapters 4 to 10), the experimental results are analyzed, discussed and interpreted. The key findings are highlighted and the comparisons with the theoretical predictions are made. The binding isotherms and the binding mechanisms are derived. In the **Conclusion** section (Chapter 11), the major original findings in this study are summarized and future research work is recommended.

Chapter 2 Literature Review

The literature review is divided into three separate parts. The first part summarizes the self-assembly behavior of surfactants in solutions. The second outlines the basic properties of polymer solutions. The third section reviews the recent development on the interaction between polymers and surfactants.

2.1 Self-Assembly of Surface Active Agents

2.1.1 Formation of surfactant micelles

In colloidal and interface science, the term amphiphile indicates that one part of molecule has affinity for the solvent while the other does not. In solution, amphiphilic molecules can spontaneously self-organize into a variety of structures, depending on temperature and concentration [Moroi 1992]. The simplest and best understood structure of an amphiphilic aggregate is the spherical micelle. Surface active agents or surfactants comprising of small molecules with both hydrophobic and hydrophilic groups are the most common amphiphilic molecules. In aqueous solution, the less soluble hydrophobic groups migrate to the air-water interface with the hydrophobes extending towards the air. Thus, addition of surfactants into water results in a decrease in the surface tension. At the critical micelle concentration (CMC), a change in the slope of the surface tension vs. concentration curve is observed. Beyond the CMC, surfactant molecules self-assemble to produce a micro-phase where the hydrophobes sequester themselves inside the aggregates and the polar hydrophilic groups orient themselves toward the aqueous phase. For sodium dodecyl sulfate (SDS) in aqueous solution, spherical micelles are produced at a CMC of ~ 8 mM [Rosen 1980]. Generally, the occurrence of a CMC is the results of two

competing factors; the hydrophobic interaction which transfers hydrophobes from water into the oily core of the micelles and the repulsive interaction among surfactant head groups. Hence, the growth in the micelle size as well as the aggregation number has a specific upper limit. Beyond the CMC, addition of more surfactant molecules simply increases the amount of surfactant micelles rather than further growth in the size of micelles.

However, the self-assembly behavior of amphiphile requires schizophrenic molecules that possess strong polar and non-polar groups. The non-polar tail groups could be a hydrocarbon or a fluorocarbon with a carbon number of more than eight, while the polar head groups could be ionic or nonionic. When these functional groups are not schizophrenic enough to serve as effective amphiphilic segments, phase separation occurs instead of micellization.

Since the formation of surfactant micelle is a physical process, the size and conformation of the micelle could be changed by varying the amphiphilic groups, concentrations of inorganic or organic additives, temperature, pressure, and pH. Among these factors, temperature plays a significantly important role in the behavior of amphiphilic molecules. The temperature where the surfactant solubility equals to the CMC is called the Krafft point, T_k . At temperatures lower than T_k , the surfactant precipitates from solution as a hydrated crystal when excess surfactant is added to the solution. When the temperature exceeds T_k , surfactant micelles are formed. The T_k of homologous ionic surfactants have been reported to increase with increasing alkyl hydrophobic segments [Moroi 1992].

2.1.2 Critical micelle concentration, Aggregation number and Micelle structure

Since the physiochemical properties differ at conditions below and above CMC, a variety of experimental techniques can be used to determine the CMC, such as electrical conductivity, surface tension, light scattering, refractive index, and surfactant selective electrodes. Among these factors that affect the CMC values, the structure of surfactant, the organic/inorganic additive and the temperature play major roles. The CMC of surfactant in aqueous media decreases as the hydrophobic character of the surfactant increases. It decreases by half with the addition of one methylene group to a straight chain of alkyl hydrophobic group for ionic surfactants and by one-tenth of previous value by introducing two more methylene groups for nonionic surfactants [Rosen 1980]. Ionic surfactants always possess a much higher CMC than nonionic surfactants containing equivalent hydrophobic segment. With increasing amount of hydrophilic head segments, the CMC increases. The presence of counter-ions in ionic surfactant solutions does significantly alter the CMC, where an increase in the binding of counter-ions results in the decrease in the CMC. The extent of the binding of counter-ion increases with an increase in the polarity and valency of the counter-ion, and decreases with an increase in the hydrated radius of the counter-ion. Addition of electrolyte into surfactant solutions reduces the CMC since the electrostatic repulsion between surfactant head groups is shielded, while the presence of small amount of organic molecules may produce a marked change in the CMC. If the organic molecules are polar, such as alcohol and amide, the CMC is reduced due to the adsorption and solubilization of organic molecules that are incorporated into the micellar core. However, when the amount of the organic molecules is high, the water structure is modified resulting in changes in the polarity and solubility of the surfactants. Since urea, formamide, guanidinium salt could destroy the water

structure, the hydration of hydrophilic groups increase, thereby increasing the CMC. Water structure promoters such as xylose and fructose will result in a decrease in the CMC. Dioxane and ethylene glycol could increase the CMC because they decrease the solubility of water and thus increase the solubility of monomeric surfactants.

The effects of temperature on surfactant micellization are often quite complex. An increase in the temperature reduces the hydration of the hydrophilic group, which favors micellization. However, temperature increase also leads to the disruption of the water structure surrounding the hydrophobic moieties, which is unfavorable for micellization. The balance between these two factors controls the micellization behavior of surfactants. It was reported that the CMC for nonionic surfactant decreased with temperature, reaching a minimum at $\sim 50\text{ }^{\circ}\text{C}$, where it increases again.

Micellar aggregation number could be determined by light scattering, pulsed-gradient NMR, fluorescent probes, and other techniques [Evans and Wennerstrom 1999]. The aggregation number increases with the increase in the length of hydrophilic groups of surfactant molecules, while it decreases with an increase in the cross-sectional area of the hydrophobic groups or volume of hydrophobic groups. Addition of electrolyte increases the aggregation number of ionic surfactants. However, higher temperature produces a smaller and larger aggregation number for ionic and nonionic surfactant respectively.

Although the common structure for most surfactant micelles is spherical, by varying the surfactant molecular parameters (hydrophobic volume, chain length and head group area) and intensive variables (temperature and ionic strength), elongated cylindrical or rod-like, lamellar and vesicles can also be obtained as shown in Figure 2.1 [Evans and Wennerstrom 1999; Rosen 1980].

Figure 2.1 Amphilic aggregate structures. [Evans and Wennerstrom 1999]

The Gibbs free energy for the self-assembly micellization of surfactant in dilute solution is comprised of three terms; a favorable hydrophobic contribution, an unfavorable surface term (electrostatic repulsion, hydration and steric hindrance), and an unfavorable packing or the geometry term (no head groups in the core).

For dilute solution where the interactions between micelles are negligible, the surfactant parameter N_s could be used to predict the microstructure and the shape of the surfactant micelles [Evans and Wennerstrom 1999; Rosen 1980].

$$N_s = \frac{V_H}{l_c a_0} \quad (2.1)$$

where V_H is the volume occupied by the hydrophobic groups in the micellar core with a value of $[0.027(n_c + n_{Me})] \text{ nm}^3$, where n_c is the total number of the carbon atoms per chain and n_{Me} is the number of methyl groups, which is twice the size of a methylene group. If there is more than one hydrophilic chain, the total surfactant parameter

should be the sum of all the individual surfactant parameters. The length of the hydrophobic groups in core, l_c possesses a maximum value of $[0.15 + 0.127n_c]$ nm depending on the extension of the chains, where the 0.15 nm comes from the van der Waals radius of the terminal methyl group minus half of the bond length while 0.127 is the bond length of the carbon-carbon projected onto the direction of the chain in the *trans* configuration. For linear saturated carbon chain, l_c is approximately 80 % of the fully extended chain. The parameter a_0 is the cross-section area occupied by the hydrophilic groups at the micelle-solution interface. For ionic surfactant, a_0 depends on both electrolyte and surfactant concentration, but is not sensitive to the external condition for nonionic surfactants. For spherical micelles, N_s has a value of 0 to 1/3; while N_s for cylindrical micelles varies from 1/3 to 1/2; whereas the lamellar structure possesses a N_s value of 1/2 to 1, and for inverse micelle, N_s is larger than 1. As the surfactant concentration is increased, the structure sequence for ionic surfactants is spherical-cylindrical- hexagonal-lamellar, while the shape changes from spherical to lamellar for nonionic surfactants.

2.1.3 Micelle association models

Micelles are the simplest and most thoroughly characterized self-organizing system. A stepwise addition process of a monomer S to the aggregate S_{n-1} as shown below can describes their aggregation in general,

with the equilibrium constant K_n of,

$$K_n = \frac{[S_n]}{[S][S_{n-1}]} \quad (2.2)$$

However, this requires all the association equilibrium constants K_i to be determined at every step resulting in the formation of monomers to micelles. Hence, in a micellar

solution, several approximate models have been developed to describe the surfactant micellization behaviors [Moroi 1993].

The isodesmic model assumes that K_n is independent of n . It is a continuous process that does not show an abrupt transition at the concentration of micelle formation (CMC). Since this model is based on the assumption that K_n is independent of n , it does not include the process of cooperativity.

The phase separation model assumes that aggregates with large n dominate all other intermediate aggregates except for the monomers. This assumption implies strong cooperativity because once aggregates are formed, and it becomes more favorable to add another monomer until an optimum aggregation number is reached. In the pseudo-separate phase, the surfactant possesses a chemical potential μ^o (micelle) in the aggregate given by the expression;

$$\mu^o(\text{micelles}) = \mu^o(\text{solvent}) + RT \ln[S] \quad (2.3)$$

where monomers and aggregates coexist in equilibrium and $[S]$ is the CMC in the unit of molar ratio. The standard Gibbs free energy of micelle formation, ΔG_{mic}^o represents the chemical potential difference between a monomer in the micelle and in dilute solution, i.e.

$$\Delta G_{mic}^o = \mu^o(\text{micelle}) - \mu^o(\text{solvent}) = RT \ln CMC \quad (2.4)$$

For the closed-association model, it assumes that one aggregation number N dominates for the equilibrium with monomers in solution,

The total surfactant concentration can be expressed by,

$$[S]_T = N[S_N] + [S] = NK_N[S]^N + [S] \quad (2.5)$$

Hence, the CMC can be expressed by the Equation (2.6),

$$CMC = (N^2 K_N)^{-1/(N-1)} (1 + N^{-1}) \quad (2.6)$$

When the N is sufficiently large, the Gibbs free energy of micellization is given by,

$$\Delta G_{mic}^0 = -\frac{RT}{N-1} \ln(K_N N^2) = RT \ln CMC \quad (2.7)$$

For ionic surfactants, the counter-ions C^+ are also involved in the formation of micelles. The association behavior of ionic surfactant could be described by the equilibrium reaction shown below,

Thus, a modified form of the Gibbs free energy of micellization shown in Equation (2.7) can be derived;

$$\Delta G_{mic}^0 = (2 - \kappa)RT \ln CMC = (1 + \beta)RT \ln CMC \quad (2.8)$$

where $\kappa = P/N$ is the degree of counterion dissociation or $\beta = (1 - \kappa)$ is the degree of counter-ion binding. For a completely ionized micelle $\kappa = 1$, and for a neutral micelle $\kappa = 0$. Thus, this model describes the micelles as a charged entity consisting of N surfactant molecules and (N-P) counter-ions with a net charge of $(-P)$.

2.1.4 Thermodynamics of micelle formation

At equilibrium, the surfactant chemical potential μ_s is uniform throughout the system and can be obtained by focusing on the free monomers in solution. By neglecting activity coefficient correction,

$$\mu_s = \mu_s^0(solvent) + RT \ln[S] \quad (2.9)$$

At concentration lower than the CMC, $[S] = [S]_T$ and the surfactant chemical potential increases logarithmically with concentration. When the concentration is much larger than the CMC, where $[S] \ll [S]_T$,

$$[S] = [S]_T^{1/N} (NK_N)^{-1/N} \quad (2.10)$$

and thus,

$$\mu_s = \mu_s^o(\text{solvent}) + \frac{RT}{N} \ln[S]_T - \frac{RT}{N} \ln(NK_N) \quad (2.11)$$

Thus, the surfactant chemical potential remains constant above the CMC up to very high values of the total concentration. In the case of ionic surfactants, the chemical potential should include the contributions from both ions, where;

$$\mu_{sc} = \mu_s^- + \mu_c^+ = \mu_{sc}^o(\text{solvent}) + RT \ln[S^-][C^+] \quad (2.12)$$

The relative contributions of enthalpy could be determined from the temperature dependence of the CMC. From the Gibbs-Helmholtz expression, an equation for the enthalpy of micelle formation can be derived, where;

$$\Delta H_{mic}^o = -T^2 \left(\frac{\partial \left(\frac{\Delta G_{mic}^o}{T} \right)}{\partial T} \right)_p = -RT^2 \left(\frac{\partial (\ln CMC)}{\partial T} \right)_p \quad (2.13)$$

For ionic surfactants, a coefficient of (2-κ) is required in above expression.

After determining the values of ΔG_{mic}^o and ΔH_{mic}^o , by applying the second law of thermodynamics as described by Equation (2.14), the entropy associated with the surfactant micellization ΔS_{mic}^o could be calculated.

$$T\Delta S_{mic}^o = \Delta H_{mic}^o - \Delta G_{mic}^o \quad (2.14)$$

For the formation of surfactant micelles, the Gibbs free energy of micellization is comprised of several components [Dai and Tam 2003; Moroi 1992], i.e.;

$$\Delta G_{mic} = \Delta G(HP) + \Delta G(\text{contact}) + \Delta G(\text{packing}) + \Delta G(HG) \quad (2.15)$$

where $\Delta G(HP)$ is the Gibbs free energy derived from the dehydration of hydrophobic segment from the water phase into the hydrophobic micellar core, which contributes

to the negative energy to the total Gibbs free energy. If n_c is the carbon number in the alkyl segment, then,

$$\Delta G(HP) = -3.0(n_c - 1) - 9.6 \quad (2.16)$$

where 3.0 kJ/mol is the Gibbs free energy contribution for one CH_2 group and 9.6 kJ/mol is the Gibbs free energy contribution for one CH_3 group. It is clear that the ΔG_{mic} decreases with increasing carbon number. The calculated $\Delta G(HP)$ value represents a complete transfer of alkyl segments from the water phase into the hydrophobic micellar core. However, considerable solvent exposure exists at the micellar surface and the solvent contact per mole of surfactant molecules decreases with increasing size of micelles, and this decrease is the source of cooperative formation of surfactant micelles. $\Delta G(\text{contact})$ is attributed to the solvent hydrocarbon contact in the micelles, which yields a positive contribution to the total micellization Gibbs free energy. The value is proportional to the area of micelles A_{mic} given by;

$$\Delta G(\text{contact}) = B \frac{A_{\text{mic}}}{N} \quad (2.17)$$

where B is a constant and N is the aggregation number. In addition, when a surfactant monomer enters a micelle, its head group will be located at the micellar surface, which restricts the conformational freedom of the hydrocarbon segments. The segments will become stretch within the micelles than in bulk liquid due to the combined effects of the micelle-solvent interactions and the constraints from neighboring segments. This packing effect gives rise to the positive Gibbs free energy contribution of $\Delta G(\text{packing})$. At the same time, the interactions between the surfactant head groups contribute positively to the micellization Gibbs free energy $\Delta G(\text{HG})$. The contribution of this part for nonionic surfactants is not as significant as ionic surfactant. For the nonionic surfactants with hydrophilic PEG segment, the repulsion

will increase with the length of PEG segment. Hence, the ΔG_{mic} increases with increasing length of PEG segment.

2.1.4 Isothermal titration calorimetry and surfactant selective electrode system

Many techniques, such as surface tension (ST), viscosity, electrical conductivity, electrophoresis, laser light scattering (LLS), isothermal titration calorimetry (ITC) and electromotive force (EMF), have been developed to study the surfactant micellization behaviors. However, ITC and EMF are probably two techniques recently introduced to study the micellization behavior of surfactant systems [Xu 2001]. The basic theories of ITC and EMF are briefly reviewed.

Calorimetric analysis is a common research method for studying thermodynamic properties by measuring the enthalpy changes (ΔH). A detailed classification of calorimetric methods can be found in a monograph by Hemminger [Hemminger 1994]. The “micro”- prefix in microcalorimetry refers to a calorimetric measurement that is able to measure heat changes as low as 1 μW . There are many types of microcalorimeters used in thermodynamics studies. Depending on their applications and the method of study, they include flow, titration, and dilution calorimeters. ITC is a technique that combines thermochemical and analytical applications, where the enthalpy change in a chemical reaction as a function of the amount of titrant is quantified. Based on the power compensation technique, the heat flow is measured more accurately. Hence, it yields more precise thermodynamic information. When micellar surfactant solution is titrated into water, the enthalpy and CMC associated with the demicellization can be directly determined from ITC measurements [Dai and Tam 2003]. Figure 2.2 shows a typical ITC thermogram of a nonionic surfactant.

Figure 2.2 (a) The ITC raw heat signals and (b) the ITC thermogram of Triton X-305 dilution in water at 298 K and 1 atm. [Dai and Tam 2003]

EMF is an electrochemical method that is receiving increasing attention in several research laboratories, which measures the electromotive force between the surfactant and reference electrodes. For instance, pH meter is based on recording the $[H^+]$ dependence of the EMF values using a H^+ selective glass electrode. By using different ion-selective electrodes (ISE), the concentration of a certain ion in dilute solution can be obtained from EMF measurements. For ionic surfactant, EMF method can be applied to monitor the surfactant monomer concentration via the surfactant ion-selective electrode, which is an electrochemical sensor that responds selectively to the concentration or activity of ionic surfactant in solution. The design and the development of the surfactant ISE can be found elsewhere [Xu 2001].

The half-cell for EMF studies on surfactant solution consisting of one surfactant ion-selective electrode (for example SDS selective electrode) and one reference electrode (for example Br^- electrode) is described:

Based on Nernst equation,

$$EMF_{cell} = E_{ISE} - E_{Br^-} = E^0 - \frac{RT}{nF} \ln \left(\frac{a_{DS^-}}{a_{Br^-}} \right) \quad (2.18)$$

where EMF_{cell} , E_{ISE} and E_{Br^-} are the EMF of cell, ISE electrode and Br^- reference electrode respectively, E^0 is the cell standard potential, R the gas constant, T the absolute temperature, n the charge of the ion ($n = 1$ for this case), F the Faraday constant, a_{DS^-} and a_{Br^-} are the activity of the DS^- and Br^- in solution respectively. If the SDS and Br^- concentrations are C_{DS^-} and C_{Br^-} respectively,

$$EMF_{cell} = E^0 - \frac{RT}{F} \ln \left(\frac{C_{DS^-} \gamma_{DS^-}}{C_{Br^-} \gamma_{Br^-}} \right) \cong E^0 - \frac{RT}{F} \ln \left(\frac{C_{DS^-}}{C_{Br^-}} \right) \quad (2.19)$$

where γ_{DS^-} and γ_{Br^-} are the activity coefficients of DS^- and Br^- respectively. For monovalent ions with the same charge, their activity coefficients are approximately equal. Due to the fact that the NaBr concentration inside the SDS ISE electrode is similar to that in the sample solution,

$$EMF_{cell} = E^0 + \frac{RT}{F} \ln C_{Br^-} - \frac{RT}{F} \ln C_{DS^-} = E^1 - \frac{RT}{F} \ln C_{DS^-} \quad (2.20)$$

Since the SDS ISE is only selective to the monomeric SDS molecules in solution, a transition will be observed near the CMC. In addition, the monomeric SDS concentration also can be determined based on above equation if we know the EMF value in solution. Figure 2.3 shows a typical EMF measurement using the SDS selective electrode.

Figure 2.3 EMF measurements using the SDS selective electrode system. [Xu 2001]

Comparison between anionic and cationic surfactant electrodes revealed that SDS electrode may be less reliable and reproducible than cationic surfactant electrodes since it may exhibit a curved or “S-shaped” calibration curve [Kwak 1998]. In addition, with increasing surfactant concentration, Eq. 2.20 should be used with caution since the activity contribution becomes significant especially in salt-free solution.

2.2 Physical Properties of Polymer Solutions

Unlike small molecules, polymer molecules consist of many identical or different repeating units. These repeating units are called monomers and the number of the repeating units is called the degree of polymerization (DP). These monomers are linked to each other by covalent bond to produce a macromolecule. If only one kind of repeating unit is present, the polymer is called homopolymer, however if there are more than one kind of repeating units, the polymer is termed as copolymer. Block copolymer refers to the copolymer where each kind of monomers form a block and these blocks are linked together [Flory 1953; Young 1991]. In solutions, homopolymer may display different conformations based on the polymer characteristics, solvent properties, temperatures, and organic/inorganic additives [Teraoka 2002]. In addition to the above properties, block copolymers always display amphiphilic properties in selective solvents [Webber et al. 1997]. Due to the theoretical importance and extensive applications of water-soluble polymers, detailed understanding on the behavior of the polymer in different solvent environment is desired. In the subsequent sections, the physical properties of dilute polymer solutions are reviewed.

2.2.1 Conformations of polymer chain in solution

A polymer chain in the solution changes its shape incessantly. An instantaneous shape of a polymer chain in solution is called conformation. If both ends of the linear polymer chain are stretched to its full extension, the distance between the ends is called the contour length. The contour length is proportional to the DP or the molecular weight of the linear polymer. In solution, this kind of fully stretched conformation is highly unlikely. The chain is usually rather crumpled and takes a conformation of a random coil. In addition, for real polymer chains in the form of random coil, two monomers cannot occupy the same space due to the excluded volume, which plays an important role in the properties of polymer solution [Flory 1953; Yang 1991].

(a) Ideal chain and Gaussian chain

Random chain does not take into account the excluded volume effect and this implies that the polymer chains can walk randomly in solution. As for a random walk chain or the ideal chain, the dimension or the size of a polymer molecule can be assessed using the end-to-end distance and the radius of gyration. Consider a linear chain consisting of N bonds of the length b . If the position of the joints are denoted by $\mathbf{r}_i$ ($i = 0, 1, 2, \dots, N$) and the two ends of the i th bond are $\mathbf{r}_{i-1}$ and $\mathbf{r}_i$, the end to end vector distance $\mathbf{R}$ is defined as:

$$\vec{R} \equiv \vec{r}_N - \vec{r}_0 \quad (2.21)$$

where $\mathbf{R}$ is the difference for each configuration of the chain. Since the chain ends are not necessary extended outward, the end-to-end distance $\mathbf{R}$ does not always span the largest dimension of the chain, hence its average length is a good measure of the overall chain dimension. The root-mean-square end-to-end distance R_F of the chain is

the root-mean-square of $\mathbf{R}$, and the whole chain can be regarded as roughly being contained in a sphere of diameter R_F (Figure 2.4), where

$$R_F^2 = \langle \tilde{\mathbf{R}}^2 \rangle \equiv \langle (\tilde{\mathbf{r}}_N - \tilde{\mathbf{r}}_0)^2 \rangle \quad (2.22)$$

Figure 2.4 Comparison of R_F and R_g for random polymers.

The root-mean-square radius of gyration R_g is the second moment from the center of mass of the chain. Roughly, the chain occupies a space of a sphere of radius R_g . The center of mass r_G of the chain is given by,

$$r_G = \frac{1}{N+1} \sum_{i=0}^N r_i \quad (2.23)$$

and assuming that the beads have same mass and connected by a negligible mass bonds, the R_g is then given by,

$$R_g^2 = \left\langle \frac{1}{N+1} \sum_{i=0}^N (r_i - r_G)^2 \right\rangle = \frac{1}{N+1} \sum_{i=0}^N \langle (r_i - r_G)^2 \rangle \quad (2.24)$$

Since mR_g^2 is the moment of inertia for rotational motion of the molecules around its center of mass, R_g is defined as the radius of gyration. In addition, the R_g can also be determined using the mean square distance between any two monomers for any conformation by:

$$R_g^2 = \frac{1}{2} \left\langle \frac{1}{(N+1)^2} \sum_{i,j=0}^N (r_i - r_j)^2 \right\rangle = \frac{1}{2(N+1)^2} \sum_{i,j=0}^N \langle (r_i - r_j)^2 \rangle \quad (2.25)$$

The comparison of R_F and R_g is shown in Figure 2.4.

Although R_F is defined for linear chain only, R_g can be defined for any chain structures. For ideal linear chain,

$$\begin{aligned} R_F^2 &= b^2 N, \\ R_g^2 &= \frac{1}{6} b^2 N \end{aligned} \quad (2.26)$$

However, in the real case, there is a restriction on the choice of bond angle. If the bond angle is $\pi - \theta$, then the above equation should be modified to following equation,

$$\begin{aligned} R_F^2 &= b^2 N \frac{1 + \cos \theta}{1 - \cos \theta} \\ R_g^2 &= \frac{1}{6} R_F^2 \end{aligned} \quad (2.27)$$

For the limit of N close to ∞ , all ideal chains become identical and follow the Gaussian distribution. A Gaussian chain is defined by extending the ideality to the short portion of the chain. In Gaussian chain, any two points r_1 and r_2 on the chain follow a Gaussian distribution, i.e.,

$$G(r_1, r_2, n) = \left(\frac{2}{3} \pi n b^2 \right)^{-3/2} \exp \left(- \frac{3(r_1 - r_2)^2}{2 n b^2} \right) \quad (2.28)$$

where the partial chain between the two points consists of n ($n < N$) segments with segment length b . For Gaussian chain, both R_g and R_F could be calculated using Equation 2.27.

(b) Real coil chain and rigid chain

As discussed previously, the excluded volume property makes the real polymer chains non-ideal. The dimension of real chain is different from that of ideal

chain of the same contour length. Even in the low concentration regime, the excluded volume does not disappear. By considering the excluded volume effect, the R_g of the real chain consisting of N monomers with bead size, b can be described by,

$$R_F \cong bN^\nu$$

$$R_g^2 = \frac{0.952}{6} R_F^2 \quad (2.29)$$

where the exponent ν is called the Flory exponent with a value of around 0.6. Real polymer chain with an excluded volume can also be modeled using the self-avoiding walk. From the model, the calculated relationship as shown in Equation (2.30) is similar to that of the Equation (2.29).

$$R_g = 0.4205bN^{0.5934} \quad (2.30)$$

However, there are semi-rigid polymers whose chains are not sufficiently flexible to form coil shape, and will instead form rigid chain conformation. The reason of the rigidity backbone may be due to several reasons, such as *p*-conjugation in the valence electrons of the main chain, bulky side groups, hydrogen bonding, and Coulomb repulsions. The rigidity of the backbone depends on solvent, temperature and organic/inorganic additives. In the limiting condition where the chain is straight, it is called a rod-like molecule, and otherwise it is called a worm-like molecule.

For the worm-like chain, the end- to-end distance R_F is obtained from,

$$R_F^2 = 2L_p \left[L_c + L_p (\exp(-L_c / L_p) - 1) \right] \quad (2.31)$$

where L_p is the persistence length and L_c is the contour length. When the $L_p \gg L_c$, the chain is either short or rigid,

$$R_F^2 = L_c^2 \left(1 - \frac{L_c}{3L_p} \right) \quad (2.32)$$

In the limit of above equation where $L_c/L_p \rightarrow 0$, the worm-like chain becomes a rod $L_c = R_F$. At the same time, when $L_p \ll L_c$, the chain is either long or flexible,

$$R_F^2 = 2L_p L_c \left(1 - \frac{L_p}{L_c} \right) \quad (2.33)$$

In the limit of above equation where $L_p/L_c \rightarrow 0$, the worm-like chain becomes an ideal chain.

The radius of gyration, R_g for worm-like chain can be described by,

$$R_g^2 = \frac{1}{3}L_p L_c - L_p^2 + 2 \frac{L_p^3}{L_c} \left(1 - \frac{L_p}{L_c} \left[1 - \exp(-L_c/L_p) \right] \right) \quad (2.34)$$

In the limit of short or rigid chain,

$$R_g^2 = \frac{1}{12}L_c^2 \left(1 - \frac{L_c}{5L_p} \right) \quad (2.35)$$

In the limit of the long or flexible chain,

$$R_g^2 = \frac{1}{3}L_p L_c \left(1 - \frac{3L_p}{L_c} \right) \quad (2.36)$$

(c) Concentration regime

For linear flexible polymer chains, each chain occupies a space of a sphere or a cubic of linear dimension, R_g . At low concentrations, these spheres or cubes are separated from each other. With increasing concentration, they become overcrowded and start to overlap each other. The overlap concentration C^* is defined as the concentration where the whole volume of the solution is packed by these spheres or cubes. The overlap concentration can be evaluated from,

$$\begin{aligned}
C^* &= \frac{M}{N_A} \left(\frac{3}{4\pi R_g^3} \right) \\
C^* &= \frac{M}{N_A} \left(\frac{1}{\sqrt{2} R_g} \right)^3 \\
C^* &= \frac{1}{[\eta]}
\end{aligned} \tag{2.37}$$

where M is the molecular weight and N_A the Avogadro constant and $[\eta]$ the intrinsic viscosity of polymer. When the concentration is below C^* , the solution is commonly referred to as dilute. When the polymer concentration exceeds C^* , it falls to the semi-dilute or concentrated regimes.

For the rod-like molecules, the concentration regimes are different from above. If the contour length is L_c , then

$$C^* = \frac{M}{A} L_c^{-3} \tag{2.38}$$

2.2.2 Thermodynamics of dilute polymer solution

When mixing a polymer and a solvent, the Gibbs free energy change is dependent on the solvent quality. If the Gibbs free energy decreases, the polymer will dissolve in the solvent, which is commonly referred to as a good solvent. Otherwise, the solvent is a poor solvent or a non-solvent in which the polymer is not soluble. The cross-link polymer swells in good solvent instead of being soluble in the solvent. This section reviews the polymer and solvent interactions from the viewpoint of thermodynamics.

Flory-Huggins mean field theory has been widely used to evaluate the dissolution of polymer in a solvent. The well-known lattice model forms the basis for the theoretical development for the interaction between the polymer and solvent molecules, where the arrangement of the polymer chains and solvents in a lattice is

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considered. The hypothesis consists of total n_{site} sites and each site could be occupied by either a monomeric unit of the polymer or a solvent molecule. Each polymer has N monomers and there are total of n_p polymer chains. The unfilled sites are occupied by the n_s solvent molecules. Then the volume fraction of the polymer ϕ is,

$$\phi = \frac{n_p N}{n_{\text{site}}} = \frac{n_{\text{site}} - n_s}{n_{\text{site}}} \quad (2.39)$$

The entropy of mixing is then determined from Flory-Huggins theory,

$$\Delta S_{\text{mix}} = -k_B n_{\text{site}} \left[\frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) \right] \quad (2.40)$$

If the interaction of the mixing for the solvent-solvent, solvent-polymer and polymer-polymer are represented by E_{ss} , E_{sp} and E_{pp} , then the χ parameter is defined by the following equation with Z as the lattice coordinate,

$$\chi = \frac{Z[2E_{ps} - (E_{ss} + E_{pp})]}{2k_B T} \quad (2.41)$$

A positive χ indicates a poor polymer-solvent interaction and a negative value of χ means the polymer-solvent contacts are preferred.

The Helmholtz free energy of the mixing can be described by Equation (2.42),

$$\Delta F_{\text{mix}} = n_{\text{site}} k_B T \left(\frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right) \quad (2.42)$$

and thus the chemical potential of a polymer chain in solution can be expressed by,

$$\Delta \mu = k_B T \left(\ln \phi + N(\chi - 1 + (1 - 2\chi)\phi + \chi\phi^2) \right) \quad (2.43)$$

For a polymer solution, the osmotic pressure π is given by,

$$\frac{\pi V}{n_{\text{site}} k_B T} = \frac{\phi}{N} - \ln(1 - \phi) - \phi + \chi\phi^2 \quad (2.44)$$

In dilute solution, the above equation can be simplified to,

$$\frac{\pi V}{n_{\text{site}} k_B T} = \frac{\phi}{N} + \left(\frac{1}{2} - \chi \right) \phi^2 + \frac{1}{3} \phi^3 + \dots \quad (2.45)$$

Since the mass concentration is related the volume fraction in the terms of

$$C = \frac{M n_{\text{site}}}{N_A N} \frac{\phi}{V} \quad (2.46)$$

then,

$$\frac{\pi}{N_A k_B T} = \frac{C}{M} + A_2 C^2 + A_3 C^3 + \dots \quad (2.47)$$

The second virial coefficient A_2 is a measure of the non-ideality of the solution. A positive A_2 deviates upward compared with that of the ideal solution, but negative A_2 deviates downward. The A_2 values could also evaluated using,

$$A_2 = \left(\frac{1}{2} - \chi \right) N_A \frac{V}{n_{\text{site}}} \left(\frac{N}{M} \right)^2 \quad (2.48)$$

A solvent with a positive A_2 is called a good solvent, while a negative A_2 is called a poor solvent. When $A_2 = 0$ the polymer solution is in the Θ condition, where χ is 0.5. At the Θ condition, the non-ideality of the polymer solutions is 0 and the polymer chain behaves like an ideal chain where both R_F and R_g increase with the molecular weight.

The quality of the solvent for a given polymer can be altered by changing the temperature or the mixing ratio of a good solvent to a poor solvent. When the temperature is changed, it is customary to draw a phase diagram consisting of a coexistence curve on a temperature-composition plain. In some phase diagrams of polymer solutions, they exhibit a critical temperature at the highest point of the coexistence curve, where this temperature is referred to as the upper critical solution temperature (UCST). At temperature exceeding the UCST, the solution is soluble and transparent, but at a temperature below the UCST, the solution phase separates. Each

phase maybe homogeneous, but it has different compositions. Polystyrene in cyclohexane has a UCST of 35 °C and poly(methyl methacrylate) (PMMA) has a UCST of 44 °C in acetonitrile. An invert phase diagram with a minimum temperature where the two phases coexist is called the lower critical solution temperatures (LCST). A polymer that is soluble in water due to hydrogen bonding usually has a LCST since the hydrogen bond can be destroyed at high temperatures. For example, poly(N-isopropyl acrylamide) has a LCST of ~ 30 °C [Wu and Zhou 1995]. With increasing temperatures, the second virial coefficient, A_2 changes from positive to zero and then to negative for LCST, while it changes from negative to zero to positive for UCST. In addition, very few polymers possess both UCST and LCST in solution. The cloud point method is commonly used to determine these two critical temperatures and the phase diagram. As the temperature crosses the coexistence curves, the solution becomes turbid, indicating the existence of a heterogeneous two phase. The cloud point could be determined by either naked eye detection or by photo-detectors, such as UV-vis spectrophotometer and light scattering. With increasing molecular weight, the UCST increases while the LCST decreases. As the solvent quality changes from good to poor, the random coil conformation changes to a globular shape to minimize the polymer-solvent contact and to maximize the polymer-polymer contact. When the chain length is sufficiently long, the abrupt transition of the coil-globular transition could be observed [Winnik et al. 1992; Wu and Zhou 1995; Wu and Zhou 1996].

2.2.3 Static and dynamic properties of dilute polymer solution

Light scattering has been widely used to study the polymer chain properties in solution [Brown 1993, Brown 1996; Chu 1991; Pecora 1985; Schmitz 1990]. Not

only weight averaged molecular weight M_w , radius of gyration R_g and second virial coefficient A_2 but also the hydrodynamic radius and the conformation of polymer chains in solutions could be determined from light scattering experiments. As an incident light beam I_i passes the polymer solution, the scattered light intensity I_s is recorded at different scattering angle θ . If the time-averaged scattered intensities is measured and analyzed, only information on time-averaged properties are obtained where this technique is commonly referred to as static light scattering (SLS). If the intensity fluctuations with time are recorded and analyzed based on the photon correlation spectroscopy (SPC), the temporal variations of the scattered radiation yield the familiar Doppler shift, and the broadening of the central Rayleigh line can be used to determine the dynamic properties of the system, and thus this technique is called as dynamic light scattering (DLS). Light scattering is a phenomenon of absorption and re-emission of the electromagnetic radiation. In a typical experiment, a dispersion of particles is illuminated by an incident beam. The direction of propagation of this beam is defined by an incident wave vector $\mathbf{k}$, with magnitude $k = 2\pi n/\lambda = n\omega_0/c$, where n is the medium refractive index and ω_0 is the circular frequency in vacuum. The radiation scattered under an angle θ with respect to the incident beam is characterized by a scattering wave vector: $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$. By taking into account $|\mathbf{k}_i| = |\mathbf{k}_s|$, the magnitude of $\mathbf{q}$ can be represented by the expression:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2.49)$$

(a) *Static properties*

For Rayleigh scattering, the intensity of scattered light for a small particle can be described by,

$$\frac{I_s}{I_i} = \frac{\pi^2 \alpha^2 \sin^2 \theta}{\lambda^4 \epsilon_0^2 r^2} \quad (2.50)$$

where α the polarizability of the particle, ϵ_0 the electric permittivity of vacuum. However, when the particle size is greater than $\lambda/20$, (e.g. high molecular weight polymer chain), the Rayleigh scattering is not suitable. In this condition, the light scattered from different points of the particles will reach the detector with different phases. The beams scattered from different points if coherent will lead to the phenomenon called intra-particle interference. Then the scattering intensity could be described by,

$$\frac{I_s}{I_i} = \frac{\pi^2 \alpha^2 \sin^2 \theta}{\lambda^4 \epsilon_0^2 r^2} \sum_{i,j=1}^N \exp[iq \cdot (r_i - r_j)] \quad (2.51)$$

For condition when the scattering volume contains several polymer chains, the inter-particle interference also contributes to the scattered intensity. However at low concentration, polymer chains are sufficiently far apart from each other, and the scattering intensity for the dilute polymer solution can be described by,

$$\frac{I_s}{I_i} = \frac{\pi^2 \alpha^2 \sin^2 \theta}{\lambda^4 \epsilon_0^2 r^2} n_p \sum_{i,j=1}^N \langle \exp[iq \cdot (r_i - r_j)] \rangle \quad (2.52)$$

where n_p is the number of polymer chains in the scattering volume and the static structure factor $S(q)$ is defined as the summation factor divided by N , the monomer number of the polymer chain.

$$S(q) = \frac{1}{N} \sum_{i,j=1}^N \langle \exp[iq \cdot (r_i - r_j)] \rangle \quad (2.53)$$

The local segment density, which corresponds to the number of monomers per unit volume, is defined as

$$\begin{aligned} \rho(\vec{r}) &= \sum_{m,i} \delta(\vec{r} - \vec{r}_{mi}) \\ \rho &= \langle \rho(\vec{r}) \rangle = n_p N / V \end{aligned} \quad (2.54)$$

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where the pair distribution function $\langle \rho(\mathbf{r})\rho(0) \rangle$ is called the autocorrelation function of the segment density. The static structure factor is related to the density autocorrelation function by,

$$S(q) = \frac{4\pi}{\rho} \int_0^\infty \langle \rho(\bar{r})\rho(0) \rangle \frac{\sin qr}{qr} r^2 dr = \frac{N_A N}{CM} \int_V \langle C(\bar{r})C(0) \rangle \exp(i\bar{q} \cdot \bar{r}) d\mathbf{r} \quad (2.55)$$

For a polymer chain with any conformation at low angle where $qR_g < 1$, the static structure can be approximated as,

$$S(q) = \frac{N}{1 + q^2 R_g^2 / 3} \quad (2.56)$$

In addition, the $S(q)$ for a Gaussian chain at any scattering angles can be determined from the Debye function $f_D(x)$ as defined by,

$$f_D(x) = 2x^{-2} [1 - x^{-2} (1 - \exp(-x^2))] \quad (2.57)$$

$$S(q) = N f_D(qR_g) \quad (2.58)$$

It is obvious that a plot of $S(q)$ as a function of q^2 at small q gives the radius of gyration for any conformation, but beyond that range, $S(q)$ depends on the conformation. The form factor or the internal structure factor $P(q)$ is defined as the ratio of $S(q)$ to $S(0)$. For Gaussian chain $R_g^2 = Nb^2/6$ and

$$P(q) = \frac{S(q)}{S(0)} = \frac{S(q)}{N} = f_D(qR_g) \quad (2.59)$$

For a hard sphere with the radius of R_s , $R_g^2 = 0.6R_s^2$,

$$P(q) = [3(qR_s)^{-3} (\sin(qR_s) - (qR_s) \cos(qR_s))]^2 \quad (2.60)$$

While for a rod with rod length of L , $R_g^2 = L^2/12$,

$$P(q) = \frac{2}{qL} \int_0^{qL} \frac{\sin z}{z} dz - \left(\frac{2 \sin(qL/2)}{qL} \right)^2 \quad (2.61)$$

For static light scattering on the polymer solutions, the molecular parameters can be determined from the well-known Zimm Plot as described by equation (2.62),

$$\frac{KC}{R_{\theta}} = \frac{1}{M_w} \left(1 + \frac{1}{3} q^2 R_g^2 \right) + 2A_2 C \quad (2.62)$$

where $K (=4\pi^2 n^2 (dn/dC)^2 / N_A \lambda^4)$ is an optical constant with N_A , n , and λ being the Avogadro's number, the solvent refractive index, and the wavelength of the light in vacuum, respectively. C is the polymer concentration in gram per milliliter and R_{θ} is the excess Rayleigh ratio at scattering angle θ . The refractive index increment of the polymer solutions, (dn/dC) , can be measured using a differential refractometer. The z -averaged radius of gyration R_g , the second virial coefficient A_2 and the weight average molecular weight M_w can be determined from the above equation by extrapolating to zero concentration and zero angle. Most of this information can be derived by constructing the Zimm plot.

(b) *Dynamic properties*

The center-of-mass diffusion and the viscosity are the main dynamic properties of a polymer solution. A small change in the thermodynamics, for instance A_2 , causes a large shift in the solution dynamic properties.

DLS takes into account the frequency broadening of the scattered light due to the transfer of a small amount of kinetic energy from the incident light. Hence, DLS examines the intensity fluctuations with time and correlates these fluctuations to the scattered properties. The intensity fluctuations can be caused by translational diffusion arising from the motion of particles themselves as they move in and out of the scattering volume, or by rotation of non-spherical particles while present in the scattering volume. In general, the term of correlation functions of dynamic variables are commonly used to describe the response of the scattering molecules to the

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incident light. At time t and a delay time τ , the intensity-intensity autocorrelation function is the average $\langle I(t)I(t+\tau) \rangle$, which is a function of τ . Under the ergodicity assumption of the intensity, the autocorrelation function can be expressed by,

$$\langle I(t)I(t+\tau) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T I(t)I(t+\tau) dt \quad (2.63)$$

When τ is 0, $\langle I(t)I(t+\tau) \rangle$ becomes $\langle I^2 \rangle$. When τ is close to ∞ , $\langle I(t)I(t+\tau) \rangle$ becomes $\langle I \rangle^2$ where $I(t)$ and $I(t+\tau)$ are irrelevant. The normalized intensity-intensity autocorrelation function $g_2(t)$ is related to the electric field autocorrelation function $g_1(t)$ by the Siegert relations with β the coherence factor,

$$g_2(t) = 1 + \beta (g_1(t))^2$$

$$g_2(t) \equiv \frac{\langle \Delta I(t) \Delta I(t+\tau) \rangle}{\langle \Delta I^2 \rangle} \quad (2.64)$$

In DLS, the dynamic structure factor $S(q, t)$ is defined as

$$S(q, t) = \left\langle \frac{1}{n_p} \sum_{m, n=1}^{n_p} \exp[i\vec{q} \cdot (\vec{r}_m(0) - \vec{r}_n(t))] \right\rangle \quad (2.65a)$$

Hence,

$$g_1(t) = \frac{S(q, t)}{S(q, 0)} \quad (2.65b)$$

For the dynamic structure factor, when the t is 0, it is the same as the static structure factor. Thus, $S(q, t) = g_1(t)$. The dynamic structure factor or the field correlation function for single particle is related to the decay rate Γ by,

$$S(q, t) = \exp(-\Gamma t) \quad (2.66)$$

The decay rate Γ is the inverse of the relaxation time t . However, for multiple decay processes, the summation in Equation (2.66) can be replaced by an integral, leading to the following expression:

$$g_1(t) = \int w(\Gamma) \exp(-\Gamma t) d\Gamma \quad (2.67)$$

where $w(\Gamma)$ is a continuous distribution function of decay rate Γ . For translational diffusion decay, the decay rate

$$\Gamma = Dq^2 \quad (2.68)$$

where D is the diffusion coefficient. Through the Stokes-Einstein equation, the hydrodynamic radius can be determined from the diffusion coefficient,

$$D = \frac{kT}{6\pi\eta R_h} \quad (2.69)$$

where k is the Boltzmann constant, T the absolute temperature, η the solvent viscosity and R_h the polymer hydrodynamic radius.

For linear chain, R_h is proportional to R_g or R_F . For a Gaussian chain, the relationship is $R_F > R_g > R_h$ due to the hydrodynamic interactions. The ratio of R_h/R_g , R_h/R_F , or R_F/R_g could be used to describe the chain conformations. For an ideal chain or the Θ condition, $R_h/R_g = 0.665$; $R_h/R_F = 0.271$ and $R_F/R_g = 2.45$. For polymers in good solvent, $R_h/R_g = 0.640$; $R_h/R_F = 0.255$ and $R_F/R_g = 2.51$. For a rod-like polymer, $R_h/R_g = 3^{0.5}/(\ln(L/b)-0.3)$; $R_h/R_F = 1/(2\ln(L/b)-0.3)$; and $R_F/R_g = 3.46$. For the hard sphere structure, $R_h/R_g = 1$ or greater.

2.2.4 The solution properties of various types of water-soluble polymers

Water-soluble polymers include two categories: hydrophilic polymers and amphiphilic polymers. In this section, the solution properties of several water-soluble polymers being examined in this thesis are briefly reviewed.

Polyethylene glycol (PEG or PEO) is one of the most common water-soluble polymers, and is miscible with water in all proportions at room temperature. However, it displays an inverse solubility-temperature relationship in water. The LCST is a function of both concentration and molecular weight. Above a molecular

weight of 50000 g/mol and a concentration of 0.3 wt%, the LCST is insensitive to the molecular weight and concentration, which is known to be in the range of ~ 90 - 100 °C [Amu 1982]. Addition of neutral salt or changing pH alters the solubility of PEO in water. The solubility decreases proportional to the salt concentration and decreases with increased anion and cation charge [Bailey and Callard 1959]. The LCST decreases linearly with salt concentration, but the effectiveness of salts in lowering the LCST does not conform to the ionic strength. The anion has the distinct effect of lowering the temperature. In addition, small hydrated ions are more effective than large hydrated ions in salting out the polymer from solution ($F^- > Cl^- > Br^- > I^-$). As for the effect of pH on the solubility of PEO, high hydroxyl ion concentrations markedly lower the LCST ($pH > 12$) and high concentrations of hydrogen ions appear to raise the LCST ($pH < 2$). The behavior is related to the strongly pH and salt dependent hydrogen-bonding effect [Bailey and Callard 1959]. For very dilute PEO aqueous solutions, it is observed from light scattering studies that the diffusion depends only on the molecular weight, and not on polymer concentration. The hydrodynamic radius R_h (nm) of PEO in water at 30 °C can be determined from following equation [Alami et al. 1996]:

$$R_h = 0.0145M_w^{0.571 \pm 0.009} \quad (2.70)$$

With increasing PEO concentration, light scattering study revealed that the aggregation are formed in PEO aqueous solution as the temperature is increased from 20 to 90 °C [Polik and Burchard 1983]. When the concentration exceeds the overlap concentration C^* , the solution is referred as semi-dilute solution. Light scattering indicates that diffusion depends on concentration and independent of molecular weight and at higher concentration, viscoelastic properties become dominant.

Polypropylene glycol (PPG or PPO) has similar structure as PEO, but is more hydrophobic. PPG is almost water-insoluble at room temperature except those with lower molecular weight ($MW < 2000$) [Dai and Tam 2004].

Due to the hydrophobicity of PPO, the tri-block copolymer comprising of PEO and PEO blocks shows amphiphilic properties in aqueous solution, which are known as polymeric surfactants with the commercial names of Pluronic (PEO-PPO-PEO) and Pluronic-R (PPO-PEO-PPO). Many studies have been conducted on the solution behaviors of Pluronic copolymers and two good reviews can be found in the literatures [Alexandridis and Hatton 1995; Chu and Zhou 1996]. For these copolymers, core-shell-like micelles are formed in aqueous solutions when the concentration is greater than the critical micelle concentration. With further increase in the concentration, different phase-diagrams are observed based on chemical composition, concentration and temperature. Due to the fact that the solubility of both PPO and PEO segments depends on temperature, the micellization and gelation behavior are strongly dependent on the temperature.

Relatively fewer studies have been reported on the Pluronic-R copolymer system [Liu et al. 1997; Mortensen et al. 1994]. For these polymers in aqueous medium, random network or micelles could be formed by varying the chemical composition, concentration as well as temperature. At condition where micelles are produced, the CMC is much higher and the aggregation number is much smaller than Pluronic copolymers. The details of the association behaviors of these copolymers can be found in the monograph by Chu [Chu 1995].

The incorporation of hydrophobic alkyl chains to both ends of polyethylene glycol yields another series of water-soluble amphiphilic polymer, which is commonly referred to as associative polymer. This system has found numerous

industrial applications due to its special rheological properties [Chassenieux et al. 1997], and the hydrophobically modified urethane ethoxylate (HEUR) is one such system that has been widely reported in the last twenty years. When the carbon number at the end-capped alkyl group is lower than 12, open association dominates and a 3-D network cluster is produced in aqueous solution. However, when the carbon number is greater than 12, closed association mechanism dominates. For $C_{16}H_{33}$ - end capped HEUR, flower-like micelles are formed in aqueous solution at polymer concentration greater than the CMC [Yekta et al. 1996]. From fluorescence spectroscopy, it is found that the CMC is extremely low (~ 0.01 wt%) and the aggregation number is ~ 20 . With further increase in the polymer concentration, the viscosity increases sharply due to the linkage of these individual micelles through bridging chains to produce a 3-D microgel structure in solution [Tam et al. 1998b]. A good review on the solution behaviors of HEUR in aqueous solution can be found in a monograph by Winnik [Winnik and Yekta 1997]. Addition of ethylene glycol into HEUR aqueous solution causes the structure reorganization due to the decrease in the solvent quality and polarity [Dai et al. 2003b].

2.3 Interactions between Polymers and Surfactants

By introducing surfactants into polymer solutions, the polymer properties and the surfactant micellization behaviors will be altered. Interactions between polymers and surfactants in aqueous solutions have attracted increasing attention because of their potential applications and complex behaviors. Numerous research groups have devoted their attention to advance the fundamental understanding of the physics governing these interactions. For water-insoluble polymer solution, addition of surfactant molecules could solubilize these water-insoluble chains at surfactant

concentration exceeding their CMC. The water-insoluble polymer chains are then dissolved into the hydrophobic core of surfactant micelles. However, for water-soluble polymers, the interactions are more complicated. In general, water-soluble polymer and surfactant interactions can be divided into two broad categories: (1) charged polymers and oppositely-charged surfactants, and (2) uncharged polymers and all types of surfactants [Karsa 2000]. For the system consisting of charged polymers and oppositely charged ionic surfactants, the electrostatic attractive interaction dominates the binding interactions rather than the hydrophobic interaction in solution [Goddard and Ananthapadmanaban 1993; Wang and Tam 2002]. However, for an uncharged water-soluble polymer chain, surfactant molecules could bind to the polymer chains depending on the characteristics of the surfactants driven by the decrease in Gibbs free energy. The previous research works on the polymer-surfactant interaction are summarized below:

2.3.1 Charged polymer and oppositely charged surfactant

For charged polymer and oppositely charged surfactant, the strong electrostatic attraction between these charged groups is evident and dominates the binding interaction at very low surfactant concentration. This usually results in the phase separation at isoelectric point (IEP), where the amounts of positive charges and negative charges are equivalent. However, such precipitates can be re-solubilized in excess amount of surfactants. [Wang and Tam 2002; Wang et al. 2003; Wang 2004]. The interaction between charged polymer and oppositely charged surfactant is generally accepted as an ion-exchange process [Goddard 1993; Lindman and Thalberg 1993]. When the charges are fully neutralized, phase separation appears in solution. With further increase in surfactant concentration, a second layer of bound surfactants may form on top of the first layer through hydrophobic association with

their ionic head groups extending outwards water. Thus, the excess external charges introduced by the second layer transform the insoluble complex into a soluble polyelectrolyte-like complex [Goddard 1993].

We can simply classify this system into two categories based on the charge of the surfactant. One category is the interaction of anionic surfactants, such as SDS, and positively charged polymers. Ohbu et al. reported the binding of SDS to cationic cellulose occurred at $\sim 1/20^{\text{th}}$ the CMC of SDS [Goddard 1993]. Bloor and coworkers examined the interaction between SDS and dendrimers and reported that the primary binding is due to the electrostatic attraction between anionic SDS head groups and the cationic polymer side groups. [Ghoreishi et al. 1999a; 1999c]. The electrostatic interaction was further confirmed to be the major driving force for the interaction of SDS and methylvinylimidazole/vinylpyrrolidone/vinyl acrylic acid copolymers [Li et al. 1999]. It has been also found that SDS can bind to positive charge sites on proteins in stoichiometric proportions, and this alters the conformation of the protein molecules from a random structure to a folded-helix surrounded by surfactant micelles [Rodenhiser and Kwak 1998; Shirahama 1998]. Wasserman et al. indicated that the aggregate formed via the electrostatic attraction has a highly organized structure which is controlled by the flexibility of polymer chain and hydrocarbon chain length of the surfactant from their ESR study [Wasserman et al. 2002]. Richetti et al. presented studied cationic guar/SDS mixtures and observed phase separation at low SDS concentration, which can be resolubilized with further addition of SDS, and this phenomenon is independent of polymer charge density and alkyl chain length of the surfactant [Anthony et al. 1998]. However, Merta et al. reported that the aggregate of cationic starch and SDS is dependent on the polymer charge density and

hydrocarbon chain length of the surfactant based on their small angle x-ray scattering (SAXS) studies [Merta and Stenius 1999; Merta et al. 2001].

The other category is the interaction of cationic surfactant and negatively charged polymer. For the system of sodium hyaluronate and cationic surfactant of the alkyl trimethylammonium bromide, the polymer-surfactant attraction is purely electrostatic [Linse et al. 1998]. The study on the interaction of different cationic surfactants and the sodium salt of poly(acrylic acid) (PAA) indicates that the binding driven by the electrostatic force occurs at very low surfactant concentration. [Cavasino et al. 2001; Kasaikin and Zakharova 1999; Kosmella et al. 1998; Yoshida and Dubin 1999; Wang and Tam 2002; Wang et al. 2003]. However, it was found from laser light scattering that the interaction between cetyltrimethylammonium bromide (CTab) and poly(acrylic acid) is due to both the electrostatic attraction and hydrophobic interaction [Fundin et al. 1997]. In addition, studies on binding of cationic surfactant to anionic cellulosic polymers revealed that the initial binding was driven by electrostatic interaction, and followed by clustering of surfactant and counterions on the binding sites [Rodenhiser and Kwak 1998]. Kwak and co-workers have conducted extensive studies on the binding of cationic surfactants to a series of anionic polyelectrolytes [Kwak 1998]. It was found that the binding is highly cooperative, and the flexibility and the distance between neighboring charged sites of the polymer chains are relevant factors affecting the binding behavior. The polymers with flexible backbones have stronger interaction with surfactants than those which are stiffer, and a longer separation distance between neighboring charges always lead to a lower cooperative binding [Goddard 1993; Kwak 1998]. The salt effect on the binding interaction was also examined and found that the addition of salt substantially reduces the affinity of binding. However, the addition of salt also increases the

steepness of the binding isotherms, i.e., the cooperativity [Kwak 1998]. In addition, the effect of charge density on the binding of cationic surfactant onto polyanions, such as PAA, poly(methacrylic acid) (PMAA), poly(vinyl sulfate) and carboxymethyl cellulose was reported [Chandar et al. 1988; Hayakawa and Kwak 1982; Hayakawa et al. 1983]. The effect of pH on the interactions between PAA and cationic surfactant is driven by electrostatic interaction at high pH but controlled by hydrogen bonding at low pH [Anghel et al. 2002; Yoshida and Dubin 1999]. However, some reported that the interactions between cationic surfactant and PAA or PMAA is driven by the hydrophobic interaction at low pH but the electrostatic interaction at high pH to form highly organized cubic structure of the polymer/surfactant aggregates [Katsuura et al. 2002; Kogej et al. 2002].

Figure 2.5 The binding mechanism of DoTab and PAA system (PAA fully neutralized). [Wang and Tam 2002]

Wang and Tam carried out systematical studies on the binding interactions between dodecyltrimethylammonium bromide (DoTab) and PAA at different degrees of neutralization using isothermal titration calorimetric technique [Wang and Tam 2002; 2004]. It is found that electrostatic interaction plays an important role in the binding interaction between DoTab and fully neutralized PAA as shown in Figure 2.5. The surfactant monomers bind onto the charged polymers via electrostatic interaction after the onset of the binding concentration, C_1 . When the electrostatic interaction ceases at C' , hydrophobic interactions begin to dominate up to the saturation concentration, C_2 . With further increase in the surfactant concentration beyond C_m , free DoTab micelles coexist with the polymer/surfactant complexes in solution.

Figure 2.6 The binding mechanism of DoTab and PAA system (PAA without neutralization). [Wang and Tam 2004]

However, the binding isotherm for DoTab and PAA without neutralization is quite different. Figure 2.6 reveals the binding mechanism for DoTab and PAA at low pH. Due to the hydrophobic character of PAA in acidic condition, the non-cooperative binding occurs at low DoTab concentration. With further increase in surfactant

concentration, more and more surfactants are bound on the polymer chains. The repulsion between these surfactant charged head groups expands PAA chains, which give rise to the structure reorganization induced by hydrogen bonding between the carboxylic acid groups. At higher surfactant concentration, the PAA chains are solubilized by the surfactant micelles. To summarize, different research studies have revealed different perspective on the binding of charged polymer and oppositely charged surfactant. However, a comprehensive understanding on the nature of the binding is still not available and more research is needed.

2.3.2 Uncharged polymer and all types of surfactant

Different from the charged polymer and oppositely charged surfactant, there is no electrostatic interaction between uncharged polymer and surfactant and no phase separation [Dai and Tam 2004]. The main driving force for this system comes from the entropy increase or hydrophobic interaction. In some cases, ion-dipole interaction between uncharged polymer and ionic surfactant also plays an important role for the binding interaction. The current understanding on the interaction between uncharged polymer and ionic surfactant is that segments of the polymer chains are wrapped around the micelle to form a complex that reduces the stress of the polymer/surfactant pair [Goddard and Ananthapadmanaban 1993]. However, the polymer chains only located at the surfactant micellar core of non-ionic surfactant so as to reduce the Gibbs free energy of the whole system. It seems that different types of surfactants have different binding capabilities. Generally, the binding capability of surfactant to uncharged polymer chain follows the order: anionic > nonionic $\geq$ cationic. The interactions between uncharged polymers and anionic surfactants have been well studied [Bloor et al. 1995a, 1995b; Couderc et al. 2001; Ghoreishi et al. 1999a, 1999b,

1999c; Li et al. 1999, 2000a, 2000b, 2000c, 2001; Rodenhiser and Kwak 1998; Thurn et al. 2002 Wan-Badhi et al. 1993]. It has been reported that anionic surfactants exhibit a strong cooperative interaction with uncharged water-soluble polymers such as PEO or polyvinylpyrrolidone (PVP), while such polymers do not interact with cationic surfactants. Cationic surfactant was found to only bind to extremely hydrophobic polymers such as the hydrophobically modified polymers [Goddard and Ananthapadmanaban 1993; Ghoreishi et al. 1999a, 1999b]. Recently, indications of interaction between PEO and cationic surfactants, such as dodecylammonium chloride and dodecylammonium bromide were reported [Shirahama 1998], and this may be due to the steric effect since these surfactants are smaller than that of DoTab. The features of binding between uncharged water-soluble polymers and charged surfactants can be described as follows: the binding of surfactant to polymer is a cooperative process while surfactant monomers do not individually bind onto polymer chains. Since the driving force for binding is a reduction in the contact area of alkyl chains of the surfactant and water, the higher the hydrophobicity of polymers, the more favorable is the binding process [Dai et al. 2001b, 2001c; Persson et al. 1994].

In addition, studies on the interaction between hydrophobically modified water-soluble polymers or amphiphilic polymers and surfactants have been carried out by several research groups [Dai et al. 2001b, 2001c, 2004a; Seng et al. 2000a, 2000b; Person et al. 1994; Tam et al. 2000; Wang and Olofsson 1995, 1998]. The modified groups could either be located at one or both ends of the polymer, or grafted onto the main polymer chains. In the solutions of these amphiphilic polymers, the hydrophobic groups induce the formation of hydrophobic microdomains (micelles). The pre-existence of such hydrophobic microdomains promotes the interaction between the polymer and surfactant molecules as well as the non-cooperative binding. These

polymers have the capacity to bind individual surfactant molecules to existing micellar core rather than cooperative binding for the pure water-soluble polymers, which yielding a smaller CAC. [Goddard and Ananthapadmanaban, 1993; Linse et al. 1998; Person et al. 1994; Rodenhiser and Kwak 1998; Seng et al. 2000a, 2000b]. The interaction between hydrophobically modified EHEC and SDS was studied using ITC [Wang and Olofsson 1995]. Two step binding was observed, a non-cooperative binding during the early stage of interaction, followed by a cooperative binding, which is similar to the one found in normal EHEC/SDS system. The early non-cooperative binding may be caused by the strong hydrophobicity induced by the hydrophobic microdomains along the polymer chains. With the addition of surfactants into the semi-dilute solution of these polymers, a significant shear thickening was observed with increasing surfactant concentration, which is followed by a shear-thinning. This is due to the fact that surfactant molecules not only bind to the polymer-micellar core, but also substitute some of the alkyl groups on the polymer chains.

In all the interactions between water-soluble polymers and surfactants, several critical concentrations are observed and these will be described below [Goddard 1993; Dai et al. 2001b; Seng et al. 2000a, 200b]. The CAC or T_1 corresponds to the surfactant concentration where the binding of surfactant to polymer commences, which refers to the onset of binding. The C_2 or T_2 refers to the surfactant concentration where the polymers are fully saturated by the surfactant [Goddard and Ananthapadmanaban 1993; Wang 1997; Wang 2004]. In addition, the surfactant critical micelle concentration in polymer solutions (C_m) is defined as the concentration where surfactant free micelles are formed in the presence of polymer. C_m as introduced by Wyn-Jones and co-workers is different from the CMC in the pure

water [Bloor et al. 1995a, 1995b; Ghoreishi et al. 1999a, 1999b, 1999c; Li et al. 1999]. They used a combination of the EMF and ITC to detect these critical values. C_m is sometimes smaller than C_2 and binding constant strongly affects these binding concentrations. However, the identifications of CAC and C_2 are not consistent with each other and more research is needed [Wang 1997].

The binding interactions are usually accompanied by enthalpy changes and this can be monitored by calorimetry. For example, the enthalpy of transfer of one mole of SDS from the micelle to PEO/SDS is about 2.5 kJ/mol [Goddard 1993]. Recently, ITC was used to investigate the binding of surfactant onto polymer since this is an extremely sensitive technique and it provides other useful information on the binding interactions. Not only the critical values could be determined from the ITC thermogram, but also the thermodynamics of the interactions can be quantified. Olofsson and co-workers have conducted extensive studies on PEO/SDS and cellulose/SDS systems using the ITC [Olofsson and Wang 1994, 1998; Thuresson et al. 1995; Wang and Olofsson 1995, 1998]. The critical concentrations were determined from the differential curve for titrating surfactants into polymer solutions and into water. The surfactant concentration where these two curves deviate is defined as CAC and when they merge with each other is defined as C_2 . After C_2 , surfactant micelles appear in the solution. For the PEO/SDS system, an exothermic peak followed a significant endothermic peak in the thermogram. The enthalpy curves obtained from the titration of SDS into other nonionic polymers such as ethyl (hydroxyethyl) cellulose (EHEC) and PPG showed similar features. In addition, Wyn-Jones and co-workers had conducted extensive research using ITC on surfactants and various types of polymeric systems [Bloor et al. 1995a, 1995b; Couderc et al. 2001; Ghoreishi et al. 1999a, 1999b, 1999c; Li et al. 1999, 2000a, 2000b, 2001; Rodenhiser

and Kwak 1998; Wan-Badhi et al. 1993]. The values of CAC and C_2 detected from microcalorimetry are in good agreement with the values obtained from the surfactant ion selective electrode measurements. For certain system, the surfactant free micelles were formed before the saturation concentration C_2 , during the range of C_m and C_2 , and there is a competition for the surfactant monomer to bind onto the polymer or to self-assemble.

Although several research groups have been working on polymer/surfactant systems, the binding mechanism between surfactant molecules and polymer chains is still not completely understood. There are several hypotheses on the binding mechanisms and the debates on these are continuing. It has been suggested that the polymer and surfactant interaction is driven by hydrophobic interaction, but others have proposed that the interaction is dominated by ion-dipole interaction [Kwak 1998]. The CAC and C_2 or C_m could be determined by various methods, but the lack of understanding on the binding mechanisms in the region between CAC and C_2 limits the effective use of polymer/surfactant system in product formulations. In addition, the binding interactions near the critical temperatures are still not well understood. Currently, the self-assembly of amphiphilic molecules in less polar solvents or the solvent mixtures is an active research field, and hence the binding interactions between surfactant and polymer system in the less polar solvent deserve more attention. The present study seeks to resolve some of these important issues.

Chapter 3 Materials and Experimental Details

3.1 Materials

In this study, the polymeric materials used could be divided into four categories. The first category is mono-dispersed water-soluble polymers, namely polyethylene glycol (PEG) and polypropylene glycol (PPG). Several polyethylene glycols of different molecule weights were obtained from Dow Chemicals (Danbury, CT). The rest of the polyethylene glycols and all polypropylene glycols with different molecular weights were purchased from SP² Scientific Polymer Products, Inc. (Ontario, NY). Gel permeation chromatography (GPC) results indicate that the polymers are mono-dispersed with the polydispersity index (PDI) of M_w/M_n of 1.05 to 1.08. The chemical structures of these polymers are shown below and the details of these polymers such as nomenclatures and molecular weights are listed in Table 3.1:

Nomenclature	M_n	PDI	Manufacturer
PEG-0.4K (PEG-8)	400	-	Dow
PEG-0.9K (PEG-20)	900	-	Dow
PEG-1.5K (PEG-32)	1450	-	Dow
PEG-3.5K (PEG-75)	3350	1.05	Dow
PEG-4.6K (PEG-100)	4600	1.07	Dow
PEG-8.0K (PEG-150)	8000	1.05	Dow
PEG-4K	4020	1.05	Sp2
PEG-7K	6770	1.08	Sp2
PEG-11K	11200	1.05	Sp2
PEG-20K	20400	1.06	Sp2
PPG-1K	1040	1.06	Sp2
PPG-2K	2040	1.05	Sp2
PPG-3K	2870	1.08	Sp2

Table 3.1 The specifications of the PEG and PPG used in this study. The commercial name of PEG from Dow is listed in parentheses.

In literature, the high molecular weight of PEG is known as poly(ethylene oxide) (PEO). The PEO used in this study was also obtained from Dow Chemicals with a viscosity-averaged molecular weight of 300000 Da (PEO750).

The second category of polymer is the hydrophobically modified water-soluble polymers. This kind of polymer bears a water-soluble backbone and both ends are capped with hydrophobic groups. The polymer used in this study is the hydrophobic ethoxylated urethanes (HEUR), which was synthesized by the Dow Chemicals and the synthesis details can be found in Jenkins [Jenkins 1991]. These samples have the chemical structures of;

where PEG segments of the nominal molecular weight of 8200 Da are linked through isophorone diisocyanate groups and R is the terminating hydrophobic linear alkyl end group ($\text{R} = \text{C}_n\text{H}_{2n+1}$). The molar masses of HEUR vary from 17500 to 100400 Da and M_w/M_n is around 1.5 to 1.7 from GPC. The details of these polymers are listed in Table 3.2.

HEUR Nomenclature	M _n	Hydrophobes	Manufacturer
HEUR-C ₁₆ 18K	17500	C ₁₆ H ₃₃	Dow
HEUR-C ₁₆ 34K	34200	C ₁₆ H ₃₃	Dow
HEUR-C ₁₆ 51K	51000	C ₁₆ H ₃₃	Dow
HEUR-C ₁₆ 68K	67600	C ₁₆ H ₃₃	Dow
HEUR-C ₁₆ 84K	84300	C ₁₆ H ₃₃	Dow
HEUR-C ₁₆ 100K	100400	C ₁₆ H ₃₃	Dow
HEUR-C ₁ 51K	50200	CH ₃	Dow
HEUR-C ₁₂ 51K	50700	C ₁₂ H ₂₅	Dow
HEUR-C ₁₆ 51K	51000	C ₁₆ H ₃₃	Dow

Table 3.2 The specifications of HEUR polymers used in this study.

The third category of the polymer is the tri-block copolymers of PPG-PEG-PPG. These polymers with a commercial name of Pluronic-R copolymer were obtained from BASF Corp. (Mount Olive, NJ). The details on these Pluronic and Pluronic-R copolymers have been documented in two separate monographs. [Alexandridis and Hatton 1995; Chu and Zhou 1996]. The chemical structure of these copolymers is shown below and the details on the molecular weight and the composition of the Pluronic-R copolymers are listed in Table 3.3. The M_w/M_n of these polymers varies from 1.3 to 1.5 as determined from GPC traces.

Nomenclature	M _n	m	n	Manufacturer
25R4	3600	19	33	BASF
17R4	2650	14	24	BASF
10R5	1960	8	22	BASF

Table 3.3 The specification of Pluronic-R block copolymers used in this study.

The fourth category of the polymer is the hydrophobically modified alkali soluble/swellable emulsion (HASE) latex. Both HASE latexes are synthesized by emulsion copolymerization at Dow Chemicals (formerly Union Carbide) and the synthesis details can be obtained from our previous publications [Dai 1999; Dai et al. 2000c, Tirtaatmadja et al. 1997b]. Alkali-soluble HASE latex is a comb-like polymer with the chemical structure as shown in Figure 3.1. On the methacrylic acid (MAA) and ethyl acrylate (EA) copolymer backbone, small amounts of hydrophobic moieties are grafted through a dimethyl *m*-isopropenylbenzyl isocyanate and a short PEO linkage, referred to as associative macromonomers (AM). The molar composition for MAA/EA/AM ($X:Y:Z$) $\sim 49/59/1$ and the degree of polymerization (DP) P of PEO in the branch chain is ~ 20 , where the hydrophobe is linear $-C_{16}H_{33}$ group. The z -averaged molecular weight of HASE is ~ 200000 Da. Alkali-swallowable HASE latex, also known as the cross-linked HASE latex, is shown in Figure 3.2, where the molar ratio of MAA/EA ($X:Y$) $\sim 50:50$ and the density of the di-allyl phthalate (DAP) crosslinker is ~ 4 wt%.

Figure 3.1 Chemical structure of alkali-soluble HASE latex, where $X:Y:Z = 49:50:1$ and $P = 35$, $n = 16$ (HASE-EO35C16).

Figure 3.2 Chemical structure of the alkali-swellable HASE latex or the cross-linked HASE latex.

HASE latexes were dialyzed using a cellulose membrane placed in Millipore de-ionized water for about 4 weeks, with a weekly change of water. The cellulose dialysis membrane removes molecules with M_w below 14,000 g/mol. After dialysis, 1 wt% HASE latex stock solutions were prepared using de-ionized water and kept in refrigerator at a temperature below 6 °C.

Anionic surfactant sodium dodecyl sulfate (SDS) was purchased from BDH Laboratory Supplies (Poole, UK). Cationic surfactant dodecyl trimethylammonium bromide (DoTab) and non-ionic surfactant polyoxyethylene dodecyl ether ($C_{12}E_9$) were purchased from Sigma (St. Louis, USA). All the surfactants are GR and used as received without further purification. Other reagents, such as ethylene glycol (EG), propylene glycol (PG) and glycerol (GR) were purchased from Merck (Darmstadt, Germany). The de-ionized water was from Alpha-Q Millipore (Millipore Corp.

Bedford, MA) water purifying system and a 0.22 μm filter was used to filter the water.

For PEG, PEO, Pluronic-R copolymer and HASE latex, different concentrations of polymer solutions were directly prepared by dissolving the polymer into water or the pre-prepared solvent mixtures at room temperature. For PPG, the polymer solutions were prepared at $\sim 5\text{ }^{\circ}\text{C}$ due to the low LCST of PPG. However, due to the strong thickening properties of HEUR polymer in solution, 2 wt% solutions were first prepared and used as stock solutions. The required HEUR solutions were prepared by diluting from those stock solutions. 0.2 M or 0.1 M surfactant solutions were prepared directly using fresh and filtered de-ionized water. All the sample solutions were sealed and kept away from light in refrigerator at $4\text{ }^{\circ}\text{C}$. For ITC experiments, both titrant and titrate solutions were degassed to remove dissolved gases. For laser light scattering, the 0.2 micron filter or the centrifuge were used to remove the dust.

3.2 Equipment

3.2.1 Isothermal Titration Calorimeter

Isothermal titration calorimeter (ITC) measures the differential enthalpy changes isothermally while titrating one component into another. From the analysis of the ITC thermogram, various thermodynamic parameters, such as enthalpy and heat capacity could be obtained. In this study, all calorimetric measurements were performed using a Microcal isothermal titration calorimeter (Microcal Inc., MA). The details of this power compensation, differential instrument were described elsewhere [Wiseman et al. 1989]. It has a reference cell and a sample cell of 1.35 ml, both insulated by an adiabatic shield. The schematic diagram of ITC is shown in Figure

3.3. The titration was carried out by a step-by-step injection of concentrated surfactant solutions from a 250 ml injection syringe into the sample cell filled with solvents or polymer solutions. The syringe is tailor-made so that the tip acts as a blade-type stirrer to ensure continuous mixing efficiency at 400 rpm. Using interactive software, an injection schedule was automatically carried out for a predefined number of injections, volume of each injection, and the time between each injection. The time interval between each injection is set at 4 min. The measurements were carried out at different temperatures controlled by a PolyScience water bath and the temperature fluctuation was within ± 0.02 °C. The reproducibility of the titration data was checked by repeating similar ITC experiments and it suggests that the thermodynamic parameters derived from ITC experiments are reliable and reproducible to within ± 5 % [Dai and Tam 2003].

Figure 3.3 The schematic diagram of isothermal titration calorimeter.

3.2.2 Laser Light Scattering

Both static and dynamic light scattering were carried out using a Brookhaven laser light scattering system (Brookhaven Instruments Corp., NY). The system consists of a BI200SM goniometer, BI-9000AT digital correlator and other supporting data acquisition and analysis software and accessories. A 488 nm power adjustable Argon-ion laser was used as the light sources. A BI-SFS sample filtration system was used to remove dust. An Atago 3T Abbe refractometer was used to measure the refractive index and a BI-DNDC differential refractometer was used to determine the refractive index increment. The measurement temperature was controlled by a PolyScience water bath. The schematic representation of the light scattering system is shown in Figure 3.4.

Figure 3.4 Schematic representation of BIC laser light scattering system.

For static light scattering (SLS), Zimm plot was used to analyze the experimental data. Toluene (Sigma, HPLC grade) was used as the reference in SLS. For dynamic light scattering (DLS), the inverse Laplace transform of regularized

positive exponential sum (REPES) was used to analyze the intensity-intensity autocorrelation functions (TCF) [Brown 1993]. The grid was set to 10 and the probability of reject was set to 0.5.

3.2.3 Rheometer

Viscosity measurements were carried out using a Contraves LS40 controlled rate rheometer (Contraves AG, Switzerland). The rheometer was fitted with the MS41S/1S concentric cylinder measuring system consisting of a cup with diameter of 12 mm and a bob with the diameter of 11 mm and the height of 8 mm.

3.2.4 UV-visible Spectrophotometer

To detect the LCST of PPG solutions, a HP UV-visible spectrophotometer (Agilent Technology, Germany) was used under the thermal denaturation mode at a fixed wavelength of 488 nm with path length of 1 cm. The HP-89090A temperature control system was used to control temperature. To detect the light transmittance of HASE latex, same UV-visible spectrophotometer was used under the standard mode at a fixed wavelength of 488 nm with path length of 1 cm.

3.2.5 Electrophoretic Mobility and ζ -potential

Brookhaven ZetaPlus ζ -potential analyzer was used to monitor the electrophoretic mobility and ζ -potential of the latex solutions with presenting different concentrations of surfactant, where the 671 nm He-Ne laser was used as the light source.

3.2.6 Surfactant Selective Electrode and Electromotive Force Technique

Surfactant membrane electrode selective to SDS monomers was kindly supplied by Professor Wyn-Jones and Dr. Bloor of University of Salford. The details on the construction of the SDS selective membrane electrode could be found elsewhere [Wan-Badhi et al. 1993; Xu 2001]. The electrode was used to monitor the monomeric SDS concentrations during SDS/polymer binding process by measuring the EMF values relative to a Metrohm bromide ion reference electrode. The set up and calibration of SDS membrane electrode, the solution preparation and the procedures to calculate the monomeric SDS concentration have been introduced in Chapter 2. A constant ionic strength solution of 10^{-4} M NaBr aqueous solution was used as the solvent for all the EMF measurements. Radiometer ABU93 tri-burette titrator with the modified Aliquot software was used to conduct the titration experiments and record the EMF values at 25.0 ± 0.1 °C, which was controlled by a PolyScience water-bath. The time interval between each injection is set to 5 min under continuous stirring to make sure the equilibrium was reached. A CDM83 conductivity meter was used to monitor the shift of conductivity during the binding process.

Chapter 4 Micellization Thermodynamics of Sodium Dodecyl Sulfate in Solvent Mixtures

4.1 Introduction

Surfactants are amphiphilic molecules. In solution, surfactant self-assembly leads to different structures, depending on the concentration. However, the most common microstructure is spherical micelle, where the onset concentration for formation of micelle is CMC. The CMC is the most important characteristic of a surfactant. When the surfactant monomers aggregate into micelles at CMC, many of the physicochemical properties of the surfactant solution will change [Jonsson et al. 1998; Rosen 1980]. Numerous methods have been used to measure the CMC of surfactant solution, such as surface tension, dye solubilization, steady-state fluorescence emission and excitation spectroscopy, conductivity, NMR, etc. The CMC are strongly dependent on the surfactant chemical structure, temperature and co-solvent.

Thermodynamically, enthalpy (ΔH_m), entropy (ΔS_m) and Gibbs free energy (ΔG_m) at CMC are the three basic thermodynamic parameters for describing the surfactant micellization process. Since ΔS_m cannot be measured directly from experiment, accurate measurement on ΔH_m is thus important. There are two ways to obtain ΔH_m experimentally; (i) direct measurement using a calorimeter and (ii) indirect measurement using the van't Hoff analysis [Jelesarov and Bosshard 1999]. In literature, a large proportion of the ΔH_m data for surfactant were obtained based on the van't Hoff analysis, through the temperature dependence of Gibbs free energies (ΔG_m) measured during the micellization process based on Gibbs-Helmholtz equation;

$$\Delta H_m = -T^2 \left(\frac{\partial \left(\frac{\Delta G_m}{T} \right)}{\partial T} \right)_p = -RT^2 \left(\frac{\partial (\ln CMC)}{\partial T} \right)_p \quad (4.1)$$

where ΔH_m is the surfactant micellization enthalpy at temperature T . However, the above method is not applicable for low aggregation number system or when the aggregation number is temperature dependent [Bijma et al. 1994; Holtzer and Holtzer 1974; Meguro et al. 1981]. ITC is a novel sensitive and powerful technique that can be used to quantify the surfactant micellization behavior. This microcalorimeter can provide more accurate and reliable thermodynamic information than other conventional calorimeters. ITC measures the differential enthalpy change when a surfactant solution with concentration greater than the CMC is continuously titrated into a pure solvent. Not only the micellization enthalpy but also the CMC can be determined from one ITC experiment [Dai and Tam 2003; Meagher et al. 1998; Wang 1997; van Os et al. 1991].

In this chapter, the micellization behaviors of a typical anionic surfactant, SDS, in different co-solvents at different temperatures were examined by ITC, where the CMC and corresponding thermodynamic parameters were determined from the thermograms.

4.2 ITC of SDS Micellization in Aqueous Solution

When a micellar surfactant solution is titrated into water, ITC records the differential enthalpy changes associated with the demicellization and the dilution of surfactant molecules. When the surfactant concentration in the titration cell is lower than CMC, the observed enthalpy contains the heats from surfactant demicellization and dilutions of both surfactant micelles and monomers, i.e.

$$\Delta H_{\text{obs}} = \Delta H_{\text{d},2} (\text{micelle dilution}) + \Delta H_{\text{d},1} (\text{monomer dilution}) \\ + \Delta H_{\text{dm}} (\text{micelle demicellization at CMC}) \quad (C \leq \text{CMC}) \quad (4.2)$$

However, when the surfactant concentration in the titration cell exceeds CMC, only the enthalpy of surfactant micelle dilution is measured, i.e.

$$\Delta H_{\text{obs}} = \Delta H_{\text{d},2} (\text{micelle dilution}) \quad (C > \text{CMC}) \quad (4.3)$$

where ΔH_{dm} corresponds to the enthalpy change when surfactant micelles cooperatively demicellize into surfactant monomers at CMC. If ΔH_{m} refers to the enthalpy change when surfactant monomers cooperatively aggregate into micelles at CMC, then $\Delta H_{\text{m}} = -\Delta H_{\text{dm}}$. Since the dilution enthalpies for both surfactant monomers and surfactant micelles are negligible for non-ionic surfactants compared to the enthalpy of surfactant demicellization process, a step transition for the enthalpy at CMC can be observed from the ITC thermograms. Hence, both CMC and ΔH_{m} can be directly obtained from one ITC thermogram [Dai and Tam 2003; Hait et al. 2002]. However, due to the counterion binding and the non-ideal properties of the ionic surfactants, the ITC thermogram for ionic surfactant is not as well-defined when compared to non-ionic surfactant.

Figure 4.1 shows the titration curve of 0.2 M SDS into water at 31 °C. The typical S-shape isothermal titration curve commonly observed for nonionic surfactant solution is not evident. The determination of ΔH_{m} from the SDS ITC thermogram is illustrated in the figure, where $\Delta H_{\text{d},1}$, $\Delta H_{\text{d},2}$ and ΔH_{m} represent the dilution enthalpies of surfactant monomers, surfactant micelles and the micellization enthalpy respectively [Dai and Tam 2004; Garidel et al. 2000; Paula et al. 1995]. The dilution enthalpies of both surfactant monomers and surfactant micelles $\Delta H_{\text{d},1}$ and $\Delta H_{\text{d},2}$ cannot be ignored for ionic surfactants, which is related to the non-ideal properties of ionic surfactant system.

Figure 4.1 ITC thermogram of 0.2 M SDS into water at 31 °C and 1 atm. (The dash lines were used for the determination of ΔH_m)

Figure 4.2 Differential curve of ITC thermogram in Figure 4.1.

The CMC of ~ 8.32 mM was determined from the first-order differential curve of the ITC thermogram as shown in Figure 4.2, which agrees with the value in literature [Jonsson et al. 1998; Rosen 1980]. The Gibbs free energy for SDS micellization is related to the CMC according to the expression [Evans and Wennerstrom 1999; Wang et al. 1997];

$$\Delta G_m = \left(1 + \frac{m}{n}\right) RT \ln(CMC) \quad (4.4)$$

where the CMC is in the unit of molar fraction, m is the number of counterions bound per micelle, n is the aggregation number, and β defined as m/n is called the effective micellar charge fraction. For SDS, β value ranges from 0.46 to 0.86, depending on the experimental techniques employed [Moroi 1992]. Hence, from ITC experiment, ΔS_m for the surfactant micellization can be obtained based on the second law of thermodynamics as shown in Eq. (4.5) [Rosen 1980];

$$\Delta S_m = \frac{\Delta H_m - \Delta G_m}{T} \quad (4.5)$$

As described previously, $\Delta H_{d,1}$ and $\Delta H_{d,2}$ cannot be neglected for SDS in aqueous solutions. At $C < CMC$, identical amounts of sodium (Na^+) and dodecyl sulfate (SD^-) ions are present in solution. $\Delta H_{d,1}$ is proportional to SDS concentration in solution and the slope $d\Delta H_{d,1}/dC$ (denoted by k_1) remains constant. As $C > CMC$, surfactant micelles with n anionic monomers and m counterions coexist with $(n-m)$ free counterions in solution. $\Delta H_{d,2}$ is proportional to SDS concentrations and the slope $d\Delta H_{d,2}/dC$ (denoted by k_2) is constant. Since the SD^- and SDS surfactant micelle are much larger than Na^+ , the absolute value of $(d\Delta H_{d,2}/dC)/(d\Delta H_{d,1}/dC)$, i.e. $(|k_2/k_1|)$, is approximately equal to $(1-\beta)$. The calculated β value from ITC is ~ 0.70. Similar approximation was adopted for studying the counterion binding effect from SDS

conductivity titration curves, where $(1-\beta)$ was determined by the ratio of linear slopes of data before and after the CMC [Chatterjee et al. 2001; Ruiz 1999]. The conductivity titration of SDS was carried out as shown in Figure 4.3 and the measured β value from conductivity was found to be ~ 0.65 . Both values from ITC and conductivity are in reasonable agreement and are closed to the literature value as discussed previously [Moroi 1992].

Figure 4.3 Conductivity titration curve of 0.2 M SDS into water at 25 °C and 1 atm.

In addition, to verify that the above method for determining β using the ITC data is valid, the ITC results of cationic surfactant, dodecyl trimethylammonium bromide (DoTab) was also conducted as shown in Figure 4.4 and the calculated β value is 0.68, which is in good agreement with the literature value of 0.77 [Wang et al. 1997].

Figure 4.4 ITC thermogram of 0.3 M DoTab into water at 25 °C and 1 atm.

4.3 Temperature Dependence of SDS Micellization in Aqueous Solution

The temperature dependence of SDS micellization was examined by titrating micellar SDS solution into water at temperatures ranging from 18 to 31 °C and the thermograms are shown in Figure 4.5. It is evident that the CMCs are independent of temperature within the experimental range. For the temperature dependence of the CMC of SDS, CMC varies in a non-monotonous way by ~ 10 - 20% over a wide temperature range with a constant shallow minimum from 15 to 40 °C have been reported [Jonsson et al. 1998]. The CMC decreases with temperature below 10 °C and increases with temperature above 40 °C. The above non-monotonous trend can be simply compared with a similar minimum in the solubility of hydrocarbon in water. However, the effects of temperature on surfactant micellization are often quite complex. Besides, the effect of the hydrophobic moieties on the solubility, an increase

in the temperature also affects the electrostatic repulsion of these charge groups and the hydration of these hydrophilic groups. The balance of these factors dominates the temperature dependence of the surfactant CMC.

Figure 4.5 Thermograms of 0.2 M SDS into water at different temperatures and 1 atm. From bottom, the temperatures are 18, 20, 21, 22, 23, 24, 25, 27, 29 and 31 °C respectively.

At SDS concentration lower than the CMC, surfactants are in the monomeric form. Temperatures significantly alter the thermograms, but the titration curves are parallel to each other. The linear and parallel titration thermograms for SDS concentrations lower than CMC indicate the weak temperature dependence of the SDS monomer dilution enthalpy. Beyond the CMC, the surfactant micelle dilutions are almost independent of temperature. Similar trends on the temperature dependence of other amphiphilic systems have been reported recently [Chatterjee et al. 2001; Garidel et al. 2000; Heerklotz and Epand 2001; Paula et al. 1995]. Since the

temperature effect on the dilutions of surfactant monomers and surfactant micelles is not significant, the difference in the titration thermograms by varying temperatures is mainly attributed to the temperature dependence of SDS micellization process. Based on the following relationship, the thermal heat capacity of micellization $\Delta C_{p,m}$ could be evaluated,

$$\Delta C_{p,m} = \left(\frac{\partial \Delta H_m}{\partial T} \right)_p \quad (4.6)$$

Figure 4.6 shows the temperature dependence of ΔH_m for SDS in aqueous solution and the slope corresponds to the, which was determined to be -0.527 kJ/molK. It is the negative $\Delta C_{p,m}$ that gives rise to the decrease of ΔH_m with increasing measurement temperatures as evident in Fig 4.5.

Figure 4.6 Temperature dependence of micellization enthalpies for SDS aqueous solution at 1 atm.

The CMC and related thermodynamic parameters of SDS aqueous solution determined from ITC at different temperatures are summarised in Table 4.1. The slopes for the linear fittings for both monomeric and the micellar SDS at different concentration ranges as well as the calculated β values at different temperatures are also tabulated. The constant CMC value and effective micellar charge fraction β within the narrow experimental temperature range as shown in Table 4.1 suggest that the association mechanism of the surfactant do not change significantly, but ΔG_m values become more negative with increasing temperature, indicating the more favorable micellization process. The micellization of SDS at different temperatures is an entropic driven process.

4.4 Solvent Polarity Effect on the SDS Micellization

Having understood the SDS micellization in aqueous solution, the micellization of SDS in less polar solvents will be discussed in this section since solvent polarity can affect either the head or tail groups of surfactant. The less polar solvents used here are the co-solvents of glycols (glycerol, ethylene glycol, propylene glycol) and water prepared by addition of different concentrations of glycols into water.

Figure 4.7 shows the dilution thermograms of 0.1 M SDS into glycerol-water mixtures at different weight ratios. It is evident that the ITC thermograms exhibit an “S”- shape and the enthalpy change for SDS micellization increases with increasing amounts of glycerol.

T (°C)	$\Delta H_{d,1}$ (kJ/mol) ¹	ΔH_m (kJ/mol)	$\Delta H_{d,2}$ (kJ/mol)	CMC (mM)	k_1^2	k_2^2	β^3	ΔG_m (kJ/mol)	ΔS_m (kJ/mol)	$\Delta C_{p,m}$ (kJ/molK)
18	-0.75	2.93	1.52	8.32	0.115	-0.034	0.70	-36.2	0.13	-0.527
20	-0.76	1.76	1.45	8.32	0.118	-0.035	0.70	-36.5	0.13	-0.527
21	-0.76	1.12	1.42	8.32	0.120	-0.036	0.70	-36.6	0.13	-0.527
22	-0.74	0.61	1.40	8.03	0.116	-0.037	0.68	-36.9	0.13	-0.527
23	-0.75	0.13	1.38	7.76	0.120	-0.037	0.69	-37.1	0.13	-0.527
24	-0.75	-0.33	1.37	7.76	0.121	-0.037	0.69	-37.3	0.12	-0.527
25	-0.77	-0.89	1.34	8.32	0.125	-0.037	0.70	-37.1	0.12	-0.527
27	-0.74	-1.91	1.29	8.32	0.126	-0.038	0.70	-37.3	0.12	-0.527
29	-0.70	-2.95	1.23	8.32	0.124	-0.038	0.70	-37.6	0.11	-0.527
31	-0.70	-4.06	1.16	8.32	0.127	-0.038	0.70	-37.8	0.11	-0.527

- 1
- Obtained from the intercept of the fitted monomeric SDS dilution curves.
- 2
- $k_1 = d(\Delta H_{d,1})/dC$ and $k_2 = d(\Delta H_{d,2})/dC$, obtained from the fitted monomeric and micellar dilution curves respectively
- 3
- $\beta = 1 - (k_2/k_1)$

Table 4.1 Temperature dependence of the SDS titration into water as observed from isothermal titration calorimetric studies at 1 atm.

Figure 4.7 ITC thermograms for 0.1 M SDS dilution in glycerol-water mixed solvents with different ratios of glycerol and water at 298 K and 1 atm.

Typically, for the micellization of ideal surfactant solutions, “S”- shape ITC curves should be observed. For example, non-ionic surfactants such as $C_{12}E_9$ or Triton display a well-defined “S”- shape dilution curve in water [Dai and Tam 2003; Tam et al. 2000]. However, due to non-ideality of SDS solution in water at 298K, an “S”- shape titration curve is not observed, instead a weak transition is evident at the CMC [Olofsson and Wang 1994; Wang 1997; Wang and Olofsson 1998]. By adding glycerol into water, the solvent polarity decreases, and this alters the SDS micellization as shown in the figure. The dielectric constants for water and glycerol are 78.5 and 40.1, while the dipole moments are 3.11 and 2.68 for water and glycerol respectively [Alexandridis et al. 2000; Alexandridis and Yang 2000; Ivanova et al. 2000, 2001]. Hence, mixtures of glycerol and water will result in the reduction in the polarity of the solvent mixtures as the proportion of glycerol increases. Since the non-

ideal properties for ionic surfactants are attributed to the changes in dielectric properties, a reduction in the polarity will minimize the non-ideality of SDS in the solvent mixtures, hence an “S”- shape titration curve is observed.

In addition, the effective micellar charge fraction β was calculated and summarized in Table 4.2. For glycerol concentrations greater than 20 wt%, k_2 cannot be accurately determined from the thermogram, thus the averaged of previous k_2 values was used in the calculation of β . From the data, it is evident that β remains almost constant until 20 wt% glycerol, where it then decreases sharply. In the limiting condition, both slopes are parallel and β is close to 0, which indicates there is no counterion binding during the micellization process and the micellization is similar to that for ideal non-ionic surfactant with an “S”- shape ITC thermogram.

The dependence of CMC and ΔH_m on glycerol concentration for SDS micellization is shown in Figure 4.8 and the thermodynamic parameters are also summarized in Table 4.2.

[Glycerol] (wt%)	CMC (mM)	ΔH_m (kJ/mol)	ΔG_m (kJ/mol)	$T\Delta S_m$ (kJ/mol)	k_1^2	$k_2^{1,2}$	β^3
0	8.28	-1.63	-37.2	35.6	0.125	-0.037	0.70
3	7.72	-2.74	-37.6	34.8	0.130	-0.038	0.71
5	7.45	-3.53	-37.1	33.5	0.121	-0.039	0.68
8	7.19	-4.85	-37.4	32.5	0.130	-0.041	0.68
10	7.09	-5.56	-37.3	31.8	0.135	-0.043	0.68
12	6.91	-6.43	-37.3	30.9	0.132	-0.043	0.67
15	6.91	-7.80	-36.6	28.8	0.124	-0.044	0.65
20	6.90	-9.54	-36.5	27.0	0.119	-0.043	0.64
30	7.44	-12.62	-34.9	22.3	0.095	-0.040	0.58
40	8.06	-14.96	-26.9	12.0	0.052	-0.040	0.23
50	8.29	-16.39	-21.8	5.4	0.033	-0.040	~ 0

1) k_2 for 30, 40 and 50 °C is obtained from the average of previous eight k_2 s

2) $k_1 = d(\Delta H_{a,1})/dC$ and $k_2 = d(\Delta H_{a,2})/dC$, obtained from the fitted monomeric and micellar dilution curves respectively

3) $\beta = 1 - (|k_2/k_1|)$

Table 4.2 Thermodynamics of SDS micellization in the glycerol-water solvent mixtures with different ratio of glycerol and water at 298 K and 1 atm.

Figure 4.8 The CMC (open circle) and ΔH_m (filled circle) for SDS in glycerol-water mixtures containing different ratios of glycerol at 298 K and 1atm.

It is evident that the CMC first decreases until 12 wt% and then remains essentially constant up to ~ 20 wt% of glycerol, and increases continuously up to ~ 50 wt% glycerol. On the other hand, the enthalpy of micellization increases proportionally to the glycerol content up to 20 wt%. Beyond that, the enthalpy continuously increases with glycol content but deviates from the linear relationship.

Based on the phase separation model as described by Eq. (4.4), the CMC can be related to the Gibbs free energy of micellization once the effective micellar charge fraction β is known. In addition, the entropy for the SDS micellization can be calculated based on the second law of thermodynamics as depicted by Eq. (4.5). The numerical values of thermodynamic parameters are tabulated in Table 4.2.

The thermodynamics revealed that the micellization is an entropy-driven process when the glycerol content is lower than 20 wt%, but an enthalpy-driven process when the glycerol exceeds 20 wt%. Surfactant micellization in water is an entropy-driven process due to the fact that micellization destroys the water structure, which gives rise to the increase in the solution entropy. The addition of large amounts of glycerol into water not only decreases the solvent polarity, but also significantly changes the water structure. Glycerol has three OH groups per molecule and it has similar properties as water. Glycerol could act as either donor or acceptor for hydrogen bond, thus glycerol molecules could form hydrogen bond by themselves or with water molecules in solution. Addition of small amounts of glycerol (up to 20 wt% glycerol or 4.7 mol%), the main contribution of glycerol in the solvent polarity is not significant. These glycerol molecules will be solubilized into the hydrophobic core of SDS micelles, which gives rise to the decrease in the CMC values, while keeping β constant. Within this concentration range, the water structure prevails and the micellization is driven by the increase in entropy. The ΔH_m of surfactant micellization increases linearly with glycerol concentration. Beyond 20 wt% glycerol content, the water structure is destroyed due to the formation of hydrogen bonds between glycerol molecules and water molecules. The solvent polarity is decreased dramatically and thus the solubility of the surfactant tails increases. At the same time, the electrostatic interactions are also shielded with further addition of glycerol as evident from the decrease in β and the decrease in the dielectric constant. Both effects lead to an increase in the CMC values. Similar behavior had also been observed by other researchers for nonionic surfactants or amphiphiles in glycol-water mixtures [Dai et al. 2003b; Penfold et al. 1997]. At this condition, the surfactant micellization

is driven by enthalpy instead of entropy, as depicted by the deviation from the linear relationship at glycerol content exceeding ~ 20 wt%.

To verify the above interpretation, SDS micellization behaviors in other glycol/water solvent mixtures, which have a lower solubility parameters and dielectric constants, were also studied. Figure 4.9 shows the ITC thermograms of SDS in the ethylene glycol/water solvent mixture at 298 K and 1 atm.

Figure 4.9 ITC thermograms for 0.1 M SDS dilution into ethylene glycol-water mixtures containing different ratios of ethylene glycol and water at 298 K and 1 atm.

Since ethylene glycol has similar chemical structure but possesses a lower polarity compared to glycerol [Ivanova et al. 2000], similar trends comparable to glycerol/water should be observed. “S”- shape titration curves were obtained with the addition of excess amounts of ethylene glycol into water. The micellization enthalpy increases with the content of ethylene glycol, where the CMC decreases until ethylene glycol concentration of ~ 15 wt%. After that, CMC increase with the ethylene glycol

concentration. The effective charge fraction β remains constant at ethylene glycol concentration lower than 10 wt%, and decreases with further increase in ethylene glycol concentration. The details on the SDS micellization in ethylene glycol and water mixtures are shown in Figure 4.10 and Table 4.3.

Figure 4.10 The CMC (open circle) and ΔH_m (filled circle) for SDS in ethylene glycol-water mixtures containing different ratios of ethylene glycol at 298 K and 1 atm.

Due to the fact that ethylene glycol and glycerol have similar structure, the SDS micellization mechanisms in ethylene glycol and water solvent mixture are similar to the glycerol/water solvent mixture. But the dramatic decrease in solubility give rise to the shift in the micellization properties. Next, the SDS micellization in propylene glycol/water solvent mixture was carried out and the observed phenomena are compared with other glycol/water solvent mixtures. The ITC details on the SDS in propylene glycol/water mixtures are summarized in Figures 4.11 and 4.12 as well as Table 4.4.

[Ethylene Glycol] (wt%)	CMC (mM)	ΔH_m (kJ/mol)	ΔG_m (kJ/mol)	$T\Delta S_m$ (kJ/mol)	k_1^2	$k_2^{1,2}$	β^3
0	8.28	-1.63	-37.2	35.6	0.125	-0.037	0.70
3	7.49	-3.19	-37.3	34.1	0.132	-0.041	0.69
5	7.37	-4.35	-37.1	32.8	0.131	-0.042	0.68
10	7.06	-7.39	-37.2	29.8	0.129	-0.042	0.67
20	7.07	-13.04	-35.7	22.6	0.114	-0.045	0.61
30	7.92	-17.21	-29.2	12.0	0.061	-0.041	0.33
40	9.27	-18.83	-21.5	2.7	~ 0	-0.41	~ 0

- 1) k_2 for 30 and 40 °C is obtained from the average of previous five k_2 s
- 2) $k_1 = d(\Delta H_{d,1})/dC$ and $k_2 = d(\Delta H_{d,2})/dC$, obtained from the fitted monomeric and micellar dilution curves respectively
- 3) $\beta = 1 - (|k_2/k_1|)$

Table 4.3 Thermodynamics of SDS micellization in the ethylene glycol -water mixed solvents with different ratios of ethylene glycol and water at 298 K and 1atm.

[Propylene Glycol] (wt%)	CMC (mM)	ΔH_m (kJ/mol)	ΔG_m (kJ/mol)	$T\Delta S_m$ (kJ/mol)	k_1^2	$k_2^{1,2}$	β^3
0	8.28	-1.63	-37.2	35.6	0.125	-0.037	0.70
2	6.85	-3.38	-37.8	34.4	0.154	-0.047	0.69
5	6.35	-5.73	-38.4	32.7	0.155	-0.045	0.71
10	5.94	-9.58	-38.3	28.7	0.158	-0.049	0.69
15	5.31	-15.04	-39.5	24.4	0.169	-0.047	0.72
20	5.09	-18.71	-15.1	-3.6	0.035	-0.047	-0.34
30	5.73	-24.58	-22.7	-1.8	~ 0	-0.47	~ 0

- 1) k_2 for 15, 20 and 30 °C is obtained from the average of previous three k_2 s
- 2) $k_1 = d(\Delta H_{d,1})/dC$ and $k_2 = d(\Delta H_{d,2})/dC$, obtained from the fitted monomeric and micellar dilution curves respectively
- 3) $\beta = 1 - (|k_2/k_1|)$

Table 4.4 Thermodynamics of SDS micellization in the propylene glycol –water mixtures containing different ratios of propylene glycol and water at 298 K and 1atm.

Figure 4.11 ITC thermograms for 0.1 M SDS dilution in propylene glycol-water mixtures containing different ratios of propylene glycol and water at 298 K and 1 atm.

Figure 4.12 The CMC (open circle) and ΔH_m (filled circle) for SDS in the propylene glycol-water mixtures containing different ratios of propylene glycol at 298 K and 1 atm.

Figure 4.13 The CMC for SDS in different glycol water mixtures at 298 K and 1 atm.

It is evident that the micellization of SDS in propylene glycol/water solvent mixtures are identical to other glycol/water mixtures. However, due to the further decrease in the solvent polarity by addition of propylene glycol, the effect of propylene glycol is more significant. Although the SDS micellization behaviors in the mixtures of water and different glycols are similar, there is some observable difference. The main reason for the difference is attributed to the different polarity or different solubility parameters. For the solubility parameter, water > glycerol > ethylene glycol > propylene glycol [Ivanova et al. 2000]. In addition, all of them can form strong hydrogen bond with water. The hydrophobicity of three glycols are, propylene glycol > ethylene glycol $\cong$ glycerol. The comparison of the CMC of SDS in different solvent mixtures is shown in Figure 4.13. The lowest CMC occurs at ~ 15 wt% glycerol or ethylene glycol, but that occurs at ~ 20 wt% for propylene glycol. In

addition, it is also evident that solvent composition dependence of CMC are identical for ethylene glycol and glycerol, but the solvent mixture of water and propylene glycol is more significant. This can be attributed to the more hydrophobic character of propylene glycol, which is easy to be solubilized to form mixed micelles at CMC. In addition, from the co-solvent composition dependence of CMC at higher co-solvent concentration, it seems that the capability to destroy water structure obeys the following trends; ethylene glycol > glycerol > propylene glycol. The effect of different glycols on the micellization enthalpy is shown in Figure 4.14. The micellization enthalpy increases with the content of glycol, but the dependence of glycol concentration on the micellization enthalpy is, propylene glycol > ethylene glycol > glycerol.

Figure 4.14 The micellization enthalpies for SDS in different glycol water mixtures at 298 K and 1atm.

4.5 Summary

In addition to the CMC, the micellization enthalpy can also be determined from the ITC thermogram. For ionic surfactant, we propose for the first time the determination of the effective micellar charge fraction β from ITC experiment. Hence, the Gibbs free energy and the entropy change during the micellization process can be calculated. Temperature plays an important role in surfactant micellization, where it not only affects the solubility of the hydrophobic segments, but also the hydration of the hydrophilic heads. For SDS micellization at temperature ranging from 18 to 31 °C, SDS monomer dilution enthalpy and SDS micelle dilution enthalpy remain constant, but the micellization enthalpies increase linearly with temperature, where the heat capacity can be calculated. Co-solvent is another important factor that affects the surfactant behaviour. The addition different glycol gives rise to the shift in the solvent polarity and the solvent structure. With increasing content of glycol, the non-ideal properties of SDS decrease as evident by the decrease in the effective micellar charge fraction β . The CMC decreases with glycol concentration until 15 ~ 20 wt% and then increases, which is attributed to the solubilization for the former and the shift in solvent polarity for the latter. In addition, the micellization enthalpy increases with the glycol concentration. However, the glycols exhibit the following trends in altering the solvent polarity and water structure; namely propylene glycol > ethylene glycol > glycerol, which is related to their different solubility parameters.

Chapter 5 Interactions Between Sodium Dodecyl Sulfate and Poly(ethylene glycol) in Aqueous Solution

5.1 Introduction

The system of PEG or PEO and SDS has been well studied in the past two decades by many different techniques, such as surface tension [Schwuger 1973], ITC [Olofsson and Wang 1994; Wang and Olofsson 1995], neutron scattering [Cabane and Duplessix 1982, 1987], laser light scattering [Brown et al. 1992], viscosity [Brackman 1991; Francois et al. 1985], conductivity [Francois et al. 1985; Minatti and Zanette 1996], dialysis equilibrium [Shirahama 1974; Shirahama and Ide 1976], NMR [Gao et al. 1990, 1991; Gjerdde and Hoiland 1996] and size exclusion chromatography [Rodenhiser and Kwak 1999]. Two good reviews on this subject can be found in the monographs by Goddard and Kwak [Goddard and Anaathapadmanaban 1993; Kwak 1998]. When the molecular weight of PEO is lower than 1500, the interaction is either negligible or non-existence. However, when the molecular weight exceeds 4000, significant interaction between SDS and PEO chains occurs. Beyond this molecular weight, the SDS/PEO interaction becomes independent of molecular weight, but the binding of SDS to PEO is affected by PEO concentration. The CAC decreases slightly, and is only weakly dependent on the polymer concentration. However, C_2 and C_m are directly proportional to the polymer concentration and increase linearly with increasing polymer concentration. The PEO could be solubilized into the hydrophobic core of SDS micelles [Gao et al. 1991], or located close to the surface of the SDS micelles and interact with the surfactant head groups to form a necklace-like structure [Cabane and Duplessix 1987]. For PEO/SDS saturation complexes, there are approximately three monomer units of PEO for per SDS molecule. SDS micelles

formed on PEO chains are smaller than SDS free micelles in water with a size of about 2 nm in radius. At CAC, the aggregation number is low and found to be about 1/3 that of the aggregation number of free SDS micelle in aqueous solution [Brown et al. 1992; van Stam et al. 1991; Zana et al. 1985]. The average aggregation number of SDS/PEO complexes increases with SDS concentration and reaches about 60 at saturation, which is slightly smaller than the aggregation number of free SDS micelle in aqueous solution. The complex increases in size as SDS concentration increases. The saturated SDS/PEO aggregation complex has the properties resembling those of polyelectrolytes with similar charge density.

From ITC thermogram of polymer and surfactant system, the CAC, C_2 and C_m can be determined, and the thermodynamic parameters as well as the association mechanisms can be derived. However, the interpretation of the ITC thermogram is still not very developed and there is significant scope for further research. Although many studies on the SDS-PEO system have been conducted, the main investigation is focused on the molecular weight more than 8000 Da. In addition, the effect of PEO's polydispersity on the binding interaction is still not clear. In this chapter, the binding interactions between SDS and PEG of different molecular weights were systematically investigated by ITC. In addition, the effect of polydispersity on the binding interaction is also discussed. From the ITC thermograms, various binding mechanisms were analyzed and proposed.

5.2 Effect of Polymer Molecular Weight on the Interaction between SDS and PEO in Aqueous Solution

5.2.1 Interaction between SDS and PEGs with low molecular weights

The titration curve of 0.2 M SDS into 0.1 wt% PEG-0.4K and that into water is shown in Figure 5.1 as filled and open circles respectively. It is evident that the titration curve of 0.2 M SDS into 0.1 wt% PEG-0.4K aqueous solution is almost identical to that of SDS into water. The small difference in the two curves is attributed to the slight change in the solvent environment due to the presence of PEG molecules. If the molecular weight of PEG is too low, such as PEG-0.4K with the molecular weight of less than 400 Da, the hydrophilic nature of the polymer chain dominates and no interaction with SDS is present. Gao et al. also observed similar experimental results from their NMR paramagnetic relaxation study [Gao et al. 1990].

Figure 5.1 The ITC curves of 0.2M SDS titrating into water and 0.2 M SDS titrating into 0.1 wt% PEG-0.4K at 298K and 1 atm.

5.2.2 Interaction between SDS and PEGs with moderate molecular weights

For PEG with molecular weight of 900 Da, the interactions between SDS and PEG were detected by the ITC technique. Figure 5.2 reveals the ITC curve of titrating

0.2 M SDS into 0.1 wt% PEG-0.9K ($M_n = 900$ Da) aqueous solution. The dilution curve of 0.2 M SDS in water is also included (shown by the open circle) in the figure. A pronounced endothermic peak for the titration of SDS into PEG-0.9K is observed. Due to the fact that ITC detects the isothermal enthalpy changes after titrating surfactant solution into water or aqueous polymer solution, the difference between the ITC curves of titrating into polymer solution and that into water is attributed to the polymer/surfactant interaction [Olofsson and Wang 1994; Persson et al. 1994]. The insert reveals the difference thermograms of 0.2 M SDS into 0.1 wt% PEG aqueous solution and water.

Figure 5.2 The ITC curve of 0.2 M SDS titrating into 0.1 wt% PEG-0.9K and 0.1 wt% PEG-1.5K at 298 K and 1 atm. The open circle is the SDS dilution curve in water. The insert is a plot on the difference curve of 0.2 M SDS into PEGs and water.

At SDS concentration lower than 5.9 mM, both titration curves are paralleled to each other. The small difference may be due to the change in the solvent quality

between water and 0.1 wt% PEG-0.9K aqueous solution. However, this also includes the small enthalpy contribution from the non-cooperative binding between SDS monomers and PEO. Beyond 5.9 mM SDS, a large deviation between the thermograms is observed. After exceeding the maximum value, the titration curve of SDS into PEG solution begins to decrease and then merges with the SDS dilution curve at SDS concentration greater than 30 mM.

Johnson and Olofsson studied the interactions of SDS and 1-pentanol by isothermal titration calorimetry and they observed an endothermic peak at low SDS concentrations [Johnson et al. 1989]. The peak was attributed to the dehydration of 1-pentanol molecules from water phase into the hydrophobic core of SDS micelles. Since the EO segment contains two methylene groups and one ether group that can act as the proton acceptor, the PEO is not strongly hydrophilic but possesses some amphiphilic properties. Thus, the endothermic peak in the thermogram of SDS/PEG system is also due to the dehydration of PEG segments from the water phase to the hydrophobic core in SDS mixed micelles [Olofsson and Wang 1994]. The enthalpy changes for the transfer one mole of EO groups from water to the dehydrated core is about 7 kJ/mol of EO at 25°C [Andersson and Olofsson 1989]. In the presence of hydrophobic polymer segments such as ether groups of PEG, SDS micelles of lower aggregation number (~ 30) can be induced at the hydrophobic segments of the polymer chain at concentration lower than its CMC. Such an effect is referred to as the polymer-induced micellization process, where SDS monomers are adsorbed on the PEG backbones in the form of micelles and PEG segments are dehydrated and solubilized in the hydrophobic core of SDS micelles. Hence, we first observed co-operative binding of SDS with PEG at molecular weight of about 900 Da, which is

significantly lower than 4000 Da previously described in the monograph by Goddard [Goddard and Anaathapadmanaban 1993].

The onset point for the formation of SDS/PEG mixed micelles or aggregates is defined as CAC. With increasing SDS concentration after CAC, the binding interaction becomes more significant and the aggregation number of SDS increases. As the aggregation number of SDS in the mixed micelles increases, the electrostatic repulsion between the anionic head groups of SDS becomes more significant and this retards the SDS/PEG interaction. After the maximum, ΔH begins to decrease. Further increase in SDS concentration results in merging of SDS/PEG with the SDS/water curves. Beyond this, free SDS micelles begin to form in the polymer solution at C_m .

With further increasing PEG molecular weight to 1450 Da, the thermogram exhibits similar trends, except for the significant endothermic peak as shown in Figure 5.2. The value of CAC decreases slightly which is due to the fact that the hydrophilicity of the PEG decreases with increasing length of PEG chains and thus the polymer-induced interactions become more significant. It is also evident of the small exothermic peak at higher SDS concentrations and C_m greater than 30 mM.

Figure 5.3 shows the polymer concentration dependence of the enthalpy changes for SDS/PEG-1.5K system. It is evident that the endothermic peak increases with increasing polymer concentration, while the values of CAC remain almost constant. With increasing polymer concentration, larger enthalpy changes are observed as reflected by the peak area. The weak exothermic peak also increases with increasing polymer concentration and C_m and C_2 also shift to higher SDS concentration. By comparing the trends observed in Figures 5.2 and 5.3, it is concluded that the binding interactions between SDS and PEG-0.9K and PEG-1.5K

are identical. For the PEG with moderate molecular weight from 900 to 1450 Da, SDS and PEG interact only through the polymer-induced micellization mechanism.

Figure 5.3 ITC thermograms of 0.2 M SDS titrating into different concentrations of PEG-1.5K solutions at 298 K and 1 atm. The open circle is the SDS dilution curve in water.

5.2.3 Interaction between SDS and higher molecular weight PEGs

As the molecular weight of PEG increases to 3350 Da, the titration curve of SDS into polymer solution differs significantly from that of SDS titration into water and moderate molecular weights of PEG solutions respectively. Figure 5.4 shows the ITC thermogram of 0.2 M SDS into 0.1 wt% PEG-3.5K. In addition to the significant endothermic peak, a large exothermic peak is also observed in the thermogram. The insert of Figure 5.4 reveals the difference curve of 0.2 M SDS into 0.1 wt% PEG-3.5K and that into water. For SDS concentration lower than 4.6 mM, the deviation between the titration curves is still attributed to changes in the solvent quality and the

non-cooperative binding. Beyond CAC of 4.6 mM, the SDS/PEG aggregates begin to form and the value of CAC is smaller than the values observed for lower molecular weights PEG. The exothermic peak is attributed to the rehydration of PEG segments from the hydrophobic core of SDS micelles to the water phase and these rehydrated PEG segments then wrap around the circumference of the SDS micelles to form another type of SDS/PEG aggregation complex.

Figure 5.4 The ITC curve of 0.2 M SDS titrating into 0.1 wt% PEG-3.5K (●) at 298K and 1 atm. The open circle is SDS dilution curve into water. The insert is a plot representing the difference curve of 0.2 M SDS into PEG and water. The dotted lines in the insert figure indicate the two binding processes at different SDS concentrations: (A) for polymer-induced micellization and (B) for the ion-dipole association.

The driving force for the re-hydration process of the PEG segments is the ion-dipole association between SDS head groups and EO segments. The stabilization of this SDS/PEG aggregation complex is brought about by two phenomena, i.e.;

- (i) The electrostatic repulsion between the SDS charged groups are reduced when the PEG chains are wrapped around the SDS micelles.
- (ii) The wrapping of PEG segments around the SDS micelles also minimizes the contact between the SDS hydrophobic segments and the water phase.

Beyond the minimum of the exothermic peak, the titration curve passes through C_2 , and then merges with the SDS dilution curve at C_m . The determination of CAC, C_2 , and C_m are marked in Figure 5.4.

The existence of endothermic and exothermic peaks in the ITC curves suggests that the interaction between surfactant and polymer is controlled by the balance of two binding mechanisms: the polymer-induced micellization at low SDS concentrations (endothermic process) and the re-hydration of PEG chains to form the ion-dipole aggregation at high SDS concentrations (exothermic process). At low surfactant concentrations, the endothermic process corresponds to the cooperative binding of SDS to the dehydrated PEG segments, where the amphiphilic PEG segments are dehydrated and solubilized by SDS monomers and formed mixed micelles in solution. With increasing surfactant concentrations, the formation of surfactant micelles on the polymer chains diminishes. The dominant interaction at high SDS concentration is the binding interaction between ionic charged surfaces of SDS micelles and PEG segments, which is driven by PEG/SDS ion-dipole interaction. In this process, previously dehydrated PEG segments re-hydrate from the core of SDS mixed micelles to water phase and form ion-dipole complex with SDS micelles, hence the enthalpy changes is direct opposite to the enthalpy change for de-hydration of PEG from water phase to SDS hydrophobic core [Wang 1997]. The de-hydration of PEG segments from water phase to the SDS hydrophobic core (an endothermic process shown by dotted line marked “A”), and the re-hydration of PEG segments

from the SDS hydrophobic core to the outer-part of the SDS hydrophilic head groups (an exothermic process shown by dotted line marked “B”) is illustrated in the inset in Figure 5.4 [Dai and Tam 2001]. This binding interaction between SDS and PEG is clearly evident for PEG of high molecular weight, where the energetics is controlled by the equilibrium of the two processes as shown by the dotted lines in Figure 5.4.

It is evident that the re-hydration process of PEG chains with moderate molecular weights is weak because no significant exothermic peak is observed. The contour length is 6 nm for PEG-0.9K, 10 nm for PEG-1.5K and 23 nm for PEG-3.5K. From previous studies on the SDS micelles, the hydrodynamic radius of SDS is ~ 1.5 nm [Brown et al. 1992]. Hence the circumference of SDS micelle is approximately 10 nm. By comparing with the above data, it is clear that the total contour length larger than the circumference of SDS micelle is critical for the onset of the re-hydration process of PEG chain in the presence of SDS. From the present study, we conclude for the first time that the minimum molecular weight for the formation of the re-hydrated PEG aggregation complex is about 3350 Da.

The effect of polymer concentration of PEG-3.5K was examined and shown in Figure 5.5. The CAC is independent of polymer concentration, while C_2 or C_m shifts to a higher value with increasing polymer concentration. Since CAC represents the onset for cooperative binding of SDS and PEG chains, it is only sensitive to the hydrophobicity of the polymer, temperature and ionic strength. Whilst C_2 is the saturation concentration for the binding of SDS micelles onto the polymer chains, it is proportional to the number of polymer chains present in solution. With increasing polymer concentration, more surfactants are required to saturate the increasing number of polymer chains.

Figure 5.5 ITC thermograms of 0.2 M SDS titrating into different concentrations of PEG-3.5K solutions at 298 K and 1 atm. The open circle is the SDS dilution curve in water.

The phase diagram for the interaction of SDS and PEG-3.5K is derived from the experiments and summarized in Figure 5.6. The phase diagram provides a useful tool for describing the dependence of CAC, C_2 and C_m on polymer concentration. Included in the figure is the possible microstructure describing the types of interactions for each of the concentration regime applicable to the SDS/PEG-3.5K system. In region 1, there is no interaction between SDS monomers and polymer chains or very weak non-cooperative binding. Region 2 describes the regime where cooperative binding between SDS micelles and PEG chains is operative. This region is divided into two parts, i.e. region 2a and 2b. In region 2a, the aggregates comprise of SDS micelles adsorbed onto the polymer backbone, while in region 2b, PEG chains are wrapped around free SDS micelles. The dividing line for regions 2a and 2b indicated by open square symbols represent the transition between the de-hydration

and re-hydration of PEG chains in SDS solution. With further increase in SDS concentration, the C_2 asymptote is reached, and beyond this limit all the PEG chains are saturated with SDS micelles. In region 3, defined between the C_2 and C_m lines, the microstructure is similar to region 2 and no further interaction between SDS monomers and PEG occurs and SDS molecules are in the form of monomers. At the C_m line and beyond (region 4), free SDS micelles exist together with the re-hydrated PEG aggregation complexes.

Figure 5.6 The phase diagram for the SDS/PEG-3.5K system at 298K and 1 atm. The square line between CAC and C_2 was determined from the crossover in the titration curves of SDS into water and into different concentrations of PEG aqueous solutions.

With increasing polymer molecular weight to 4600 Da (PEG-4.6K), the titration curve exhibits similar trend as PEG-3.5K with the CAC value of 4.4 mM, which is identical to that of PEG-3.5K. With a further increase in the molecular weight to 8000 Da (PEG-8.0K), the shape of the titration curve becomes different,

where two exothermic peaks are evident, instead of previous one broad peak at high SDS concentrations. Figure 5.7 shows the thermogram of the titration of 0.2 M SDS into 0.1 wt% PEG-8.0K (filled circle). For this system, the CAC is about 4.2 mM, which is fairly close to the literature value of 4.3 mM [Olofsson and Wang 1994]. C_m and C_2 were determined from the second exothermic peak at high SDS concentration.

Figure 5.7 The ITC curve of 0.2 M SDS titrating into 0.1 wt% PEG-8.0K (●) at 298K and 1 atm. The open circle is SDS dilution curve in water. The insert figure is the difference curve of 0.2 M SDS into PEG and water.

The origin of two exothermic peaks observed from the titration curves for PEG-8.0K is still unclear. Wang et al. examined the isothermal titration of 10 wt% SDS into 0.1 wt% PEO with molecular weight of 8000 Da and they also observed two exothermic peaks. When the molecular weight of PEO increases, the two exothermic peaks disappear and are replaced by one exothermic peak. They attributed this behaviour to the phenomenon where only one SDS aggregate per PEG chain is

formed [Olofsson and Wang 1994; Persson et al. 1994]. Based on our previous results for low molecular weights PEG, it seems that this behaviour is unique for the interaction between SDS and PEG-8.0K. In addition, our previously discussion clearly shows that the minimum molecular weight requirement for one SDS micelle is 3500, not 8000 Da. Hence, our results contradict the interpretation by Olofsson and co-workers as reported by Wang et al. It is believed that the observed trend is probably attributed to the reorganization of the structure of PEG/SDS complex and the phenomenon only occurs at a prescribed molecular weight regime.

The ratio of $(C_2 - CAC)/C_{PEG}$ can be approximately used to evaluate how much SDS monomers are bound onto one PEG chain. From Table 5.1, it is found that the number is 120 for PEG-8.0K, 63 for PEG-3.5K and 70 for PEG-4.6K at saturation. It was reported in the literature that the SDS aggregation number for PEO/SDS complex is about 60 [Zana et al. 1985; van Stam et al. 1991]. Thus, we believe that our current experimental results suggest that one PEG-8.0K chain can wrap around two SDS micelles, while PEG-3.5K or PEG-4.6K can only wrap around one SDS micelle.

Nomenclature	MW	CAC* (mM)	C_2^* (mM)	C_m^* (mM)
PEG-0.4K	400	-	-	-
PEG-0.9K	900	5.9	27.0 ^a	35.0 ^b
PEG-1.5K	1450	5.3	25.0 ^a	33.0 ^b
PEG-3.5K	3350	4.6	23.5	29.9
PEG-4.6K	4600	4.4	19.8	24.6
PEG-8.0K	8000	4.2	19.1	22.5

*: PEG concentration is 0.1 wt%.

a: Calculated using $C_2 = C_m - CMC$, where the CMC is 8 mM for SDS.

b: Obtained from extrapolation of the data in the titration curves.

Table 5.1 The values of CAC, C_2 and C_m for the interaction between PEGs with different molecular weight (M_n) and SDS determined from ITC at 298 K and 1 atm.

From Figure 5.7, the concentration at the maximum of the exothermic peak is 12.5 mM and the ratio of $(C - CAC)/C_{PEG}$ at this concentration is 66, which indicates

that only one SDS micelle associates with one PEG-8.0K chain. With further increase in SDS concentration, more and more SDS monomers are bound to PEG chain, which results in the reorganization of the structure of SDS/PEG complex. This reorganization and rearrangement of the necklace-like PEG structure from one to two SDS micelles corresponds to the transition from the first to the second exothermic peak as depicted in Figure 5.8.

Figure 5.8 The schematic plot of the ion-dipole associations between PEG-8.0K and SDS at moderate and high SDS concentrations.

To verify the above hypothesis, four more mono-dispersed PEG samples from different sources were examined and the ITC thermograms are shown in Figure 5.9. It is clear that there is only one exothermic peak for PEG molecular weight of 4000 and two exothermic peaks for PEG molecular weight of 7000 Da. However, the two exothermic peaks disappeared at molecular weight of 11000 Da. With further

increasing molecular weight to 20000 Da, the two peaks appeared again. When the polymer molecular weight is n times 4000 Da, the isotherms exhibit two exothermic peaks, and otherwise, only one exothermic peak is evident. From earlier discussion, we observed that the minimum molecular weight requirement for one SDS micelle to bind to PEG is 3500 ~ 4000 Da. Hence, there is a high possibility for the structural reorganization due to the limited segment chain length. Further studies should be carried out using different anionic surfactants such as sodium dodecyl phenyl sulphate (SDPS). If this hypothesis is true, the shift of the two peaks with molecular weight should be observed due to the different aggregation number and micellar size.

Figure 5.9 Thermograms for 0.2 M SDS titrating into 0.1 wt% PEGs of different molecular weight (from SP²) at 298 K and 1 atm. The open circle is the SDS dilution curve in water.

5.2.4 Dependence of CAC, C₂ and C_m on molecular weight

The above three critical concentrations are important for interpreting the binding interactions between surfactant and polymer chains in solution. Figure 5.10 reveals the isothermal titration curves of 0.2 M SDS into 0.1 wt% PEG solutions of different molecular weights. It is evident that the CAC is not sensitive to the molecular weight of PEG. With increasing molecular weight, CAC decreases slightly and the decrease is more evident for PEG of lower molecular weights. For PEG molecular weight greater than 4000 Da, CAC is independent of the polymer molecular weight. The decrease in the CAC is attributed to the decreasing hydrophilicity of PEG chains.

Figure 5.10 Effect of PEG molecular weights: The ITC thermograms for 0.2 M SDS titrating into 0.1 wt% PEGs of different molecular weight at 298 K and 1 atm. The open circle is the SDS dilution curve in water.

However, C_2 and C_m decrease with increasing PEG molecular weight until the molecular weight of 11000 Da and they become independent of molecular weight

thereafter. After normalizing the polymer molecular weight ranging from 4000 to 8000 Da, the values of C_m and C_2 are not identical. That indicates that the number of bound SDS micelles is not proportional to the length of PEG chain, i.e., the ratio of EO/SDS increases with increasing polymer molecular weight.

5.3 Effect of Polydispersity on the Interaction between SDS and PEG in Aqueous Solution

Besides varying molecular weights, the molecular weight distribution as described by the polydispersity index (PDI) may have an impact on the binding interactions between SDS and PEG since the physical properties of many polymeric systems are dependent on PDI [Flory 1953]. In this section, the effect of polydispersity index on the interaction of SDS and PEG was examined. Polydispersed PEGs were prepared by mixing different proportions of narrow MW PEGs.

As discussed previously, two exothermic peaks were observed in the titration thermogram for SDS and PEG with molecular weight of 8000 Da. We postulate that this may be attributed to the structural reorganization of the PEG/SDS complex at a predefined PEG segment length. To verify this, a PEG mixture containing 1:1 weight ratio of PEG-4K and PEG-11K, with a weighted-average molecular weight of ~ 8055 Da, was prepared. Comparison on the titration of 0.2 M SDS into 0.1 wt% PEG 8.0K and 0.1 wt% containing 1:1 weight ratio of PEG-4K and PEG-11K mixture was conducted and the results are shown in Figure 5.11. Only one exothermic peak was observed for the PEG mixture with molecular weight of ~ 8055 Da, which differs from the titration curve of SDS into the mono-dispersed PEG 8.0K. However, the values of CAC and C_2 are identical for the two samples of fairly similar molecular weight. The observed trends shown in Figure 5.11 reinforce that the two exothermic

peaks in the ITC thermogram is not due to the polydispersity of PEG chains, but is potentially related to the contour chain length or the molecular weight of the PEG chain. From Figure 5.9, it is evident that only one exothermic peak is evident for both PEG-4K and PEG-11K systems. Hence, we can conclude that the titration curve is strongly dependent on the polymeric chain length or the molecular weight of PEG, and not on the averaged molecular weight and polydispersity. Although CAC and C_2 remain constant, the binding isotherms during CAC and C_2 are only sensitive to molecular weights of each PEG chains prior to mixing.

Figure 5.11 Thermograms for titrating 0.2 M SDS into 0.1 wt% PEG8.0K and PEG4K/11K mixtures of similar averaged molecular weight at 298 K and 1 atm. The open circle is the SDS dilution curve in water.

To verify that the polydispersity has negligible effects on the ITC thermogram and the binding isotherm, several PEG mixtures were prepared in different weight ratios, where the details of the PEG mixtures are summarized in Table 5.2. For PEG

mixtures, the polydispersity index PDI was not calculated from M_w/M_n for polymer with discrete molecular weights.

Name	Mixture Details (wt%)	Mn (Ave)	Mw (Ave)
PEG 4-7	4K+7K (50%+50%)	5045	5750
PEG 4-11	4K+11K (50%+50%)	5930	8055
PEG 4-11-a	4K+11K (32%+68%)	7154	9439
PEG 4-7-11	4K+7K+11K (16%+50%+34%)	6956	7870
PEG 4-20	4K+20K (50%+50%)	6716	12905
PEG 7-11	7K+11K (50%+50%)	8467	9595
PEG 7-20	7K+20K (50%+50%)	10166	14445
PEG 11-20	11K+20K (50%+50%)	14544	16750
PEG4K	4K (100%)	4020	4210
PEG7K	7K (100%)	6770	7290
PEG11K	11K (100%)	11300	11900
PEG20K	20K (100%)	20400	21600

Table 5.2 Specifications of PEG mixtures used in the study. The mixed PEGs were prepared based on the weight ratio shown in the parenthesis.

Figure 5.12 Thermograms for 0.2 M SDS titrating into 0.1 wt% PEG mixtures with different proportion of PEG4K, PEG7K and PEG11K at 298 K and 1 atm.

Figure 5.12 reveals the ITC thermograms of 0.2 M SDS into 0.1 wt% PEG mixtures with different mixing ratios. The CAC is almost independent of the mixing ratio, but C_2 shifts to lower concentration with increasing averaged molecular weight of PEG mixture up to 8000 Da and it then remains constant. For the titration of SDS into pure PEG4K and PEG11K solutions, only one exothermic peak appears in the thermogram, and similar trend was observed for the titration curves of PEG4K and PEG11K mixtures. When PEG7K was added into the PEG4K/PEG11K mixture, no change in the CAC and C_2 was observed, but the shape of the titration curve becomes different. Instead of one exothermic peak, two exothermic peaks were observed after the addition of PEG7K. One probable reason can be attributed to the presence of PEG7K polymer chains that produce the two exothermic peaks in the titration thermogram. It seems that the shape of the overall titration curve is strongly dependent on the characteristic behaviour of each component. To further verify this, titrations of SDS into other PEG mixtures were carried out.

Figure 5.13 show the ITC thermograms of 0.2 M SDS into different mixtures of PEG 4K and other PEGs. It is evident that the CAC is independent of composition of the PEG mixture, but C_2 shifts to the left until the averaged molecular weight is closed to 8000 Da. In addition, mixtures of PEG4K containing PEG7K and PEG20K exhibit two exothermic peaks and one broad exothermic peak respectively. The titration of SDS into PEG mixtures of PEG7K, PEG11K and PEG 20K are shown in Figure 5.14 to Figure 5.16 respectively.

Figure 5.13 Thermograms for 0.2 M SDS titrating into 0.1 wt% PEG4K and into the different mixtures of PEG4K and other PEGs at 298 K and 1 atm. The open circle is the SDS dilution curve in water.

Figure 5.14 Thermograms for 0.2 M SDS titrating into 0.1 wt% PEG7K and into the different mixtures of PEG7K and other PEGs at 298 K and 1 atm. The open circle is the SDS dilution curve in water.

Figure 5.15 Thermograms for 0.2 M SDS titrating into 0.1 wt% PEG11K and into the different mixtures of PEG11K and other PEGs at 298 K and 1 atm.

Figure 5.16 Thermograms for 0.2 M SDS titrating into 0.1 wt% PEG20K and into the different mixtures of PEG11K and other PEGs at 298 K and 1 atm.

From the four figures, it can be concluded that PEG mixtures containing PEG7K or PEG20K always show two exothermic peaks. For others, only one exothermic peak was observed in the thermogram. The CAC is independent of the PEG mixtures, and C₂ decreases with the averaged molecular weight and reach a minimum at around molecular weight of 8000 Da.

5.4 Summary

In this chapter, the binding interaction between SDS and PEG with different molecular weights was first examined by isothermal titration calorimetry (ITC) technique. When the molecular weight of PEG is lower than 400 Da, no interaction is present. Increasing the molecular weight from 900 to 1450 Da, an endothermic peak is observed in the thermogram and this is attributed to the binding interactions between SDS and PEG through the polymer-induced micellization process. The SDS/PEG aggregates consist of SDS micelles bound on PEG chains and the PEO segments are dehydrated and solubilized in the SDS hydrophobic core. With increasing PEG molecular weight to greater than 3350 Da, a significant exothermic peak (in addition to the endothermic peak) appears in the thermogram at high SDS concentration. This exothermic peak is attributed to the re-hydration of PEG segments from the SDS hydrophobic core to water, which then binds to the outer surface of SDS hydrophilic head groups. The binding process is controlled by the balance of two different mechanisms, i.e. polymer induced micellization at low SDS concentrations and polymer re-hydration binding at high SDS concentrations. For the PEG with the molar mass of 8000 Da, two exothermic peaks are observed and this unusual behaviour may be attributed to the structural re-organization of the aggregates. The CAC is almost independent of both polymer molecular weight and concentration.

However, C_2 and C_m increase with polymer concentration and decrease with polymer molecular weight for a fixed polymer concentration. The ratio of EO/SDS increases with polymer molecular weight. Beyond molecular weight of 8000, C_2 and C_m are independent of the polymer's molecular weight.

The effect of polydispersity of PEG on the interaction of SDS and PEG were carried out by titrating SDS into PEG mixtures containing different mono-dispersed PEGs. The polydispersity of PEG did not affect the CAC and C_2 values at a fixed averaged molecular weight, where the CAC is almost independent of PEG's molecular weight, but C_2 decreases and reaches a minimum at molecular weight of ~ 8000 Da. However, the binding isotherm between CAC and C_2 are strongly dependent on the composition of PEG mixtures. When the PEG mixture contains PEG7K or PEG20K, the thermogram is more or less identical to the titration of SDS into their pure solutions. The observation proves that the interaction between SDS and polydispersed PEG complex is controlled by the interaction between SDS micelles and PEG of a given molecular weights.

Chapter 6 Interaction Between Sodium Dodecyl Sulfate and Poly(propylene glycol) in Aqueous Solution

6.1 Introduction

Surfactant molecules can self-assemble into aggregates of different morphologies when the concentration exceeds the CMC [Evans and Wennerstrom 1999]. In the presence of polymer, the micellization behaviour alters, depending on the characteristics of polymer, surfactant, temperature, and solvent environment [Goddard and Ananthapadmanaban 1993]. In industrial applications and theoretical importance, interaction of water-soluble polymers and surfactants is a rich field for both fundamental and applied research [Kwak 1998]. In the system of charged polymers and oppositely-charged surfactants, electrostatic attraction dominates the interactions at low surfactant concentrations. Once all the charged groups on the polymer backbone are neutralized, hydrophobic interaction begins to control the binding, which induces the restructuring of polymer chains to produce necklace-like aggregates. On the other hand, interactions between uncharged polymers and surfactants are mainly due to the hydrophobic interaction [Bloor et al. 1995a; Couderc et al. 2001; Dai and Tam 2001, 2004; Dai et al. 2001b, 2001c, 2001d, 2004a; Ghoreishi et al. 1999a, 1999b; Li et al. 1999, 2000b, 2001; Olofsson and Wang 1994; Persson et al. 1994; Tam 1996; Wang and Olofsson 1995, 1998]. The binding isotherms and the resulting mechanisms for uncharged polymer-surfactant systems are dependent on surfactant type, polymer molecular weight, chemical structures of polymer and surfactant, hydrophobic content of polymer, electrolyte, temperature and solvent quality. Anionic surfactants exhibited strong cooperative binding interaction with uncharged water-soluble polymers, such as PEG or PVP, while cationic

surfactant, such as DoTab only binds to very hydrophobic polymers, such as hydrophobically modified water-soluble polymers [Goddard 1993; Ghoreishi et al. 1999b]. For PEG-SDS system, the binding isotherms are independent of molecular weight when the molecular weight is greater than 8000 [Dai and Tam 2001; Gao et al. 1991]. The binding process is controlled by the equilibrium of polymer-induced micellization at low SDS concentrations and ion-dipole association at high SDS concentrations [Dai and Tam 2001; Wang and Olofsson 1998]. Since the binding interaction between surfactant and polymer is a cooperative process and the driving force for the binding is to minimize the contact area of the hydrophobic segments and water, enhanced hydrophobicity of the polymers favours the binding process [Dai et al. 2001b; Person et al. 1994; Thuresson et al. 1995; Wang and Olofsson 1995]. Currently, although CAC and C_2 can be accurately determined by combining ITC and EMF techniques [Bloor et al. 1995a; Dai et al. 2004a; Li et al. 2000b, 2001], the polymer-surfactant binding mechanisms between the CAC and C_2 concentration regime are still not well understood.

For uncharged water-soluble polymers, temperature plays an important role in controlling the solubility of polymer in aqueous solution. At temperature exceeding the LCST, the polymer precipitates from solution. The polymer-surfactant binding interactions at temperatures greater than the LCST should be different from those lower than the LCST. PEG is one of the widely used water-soluble polymers with LCST at greater than $\sim 80^\circ\text{C}$. As a result of the methyl group, the LCST of PPG in aqueous solution is significantly lower than PEG. Although polymer-surfactant interactions between SDS and PEG at room temperatures have been extensively studied and the binding mechanisms are better understood, there are only few reported studies on the interactions between SDS and PPG [Olofsson and Wang 1994; Wang

and Olofsson 1998]. In previous studies, only PPG with molecular weight of 1000 was reported and these studies were conducted at temperatures lower than the LCST of PPG. From our knowledge, there is currently no study on the polymer-surfactant interactions at temperatures near or greater than the LCST of PPG. In this study, the interactions between SDS and various molecular weights of PPG were systematically studied over the temperature range of lower and greater than the LCST. The findings, which provide a detailed explanation for the nature of surfactant-polymer interactions near the LCST, are described in this chapter.

6.2 Temperature Dependence of PPG Aqueous Solutions

The micellization of surfactants and the phase behaviours of polymers with LCST properties are extremely sensitive to changes in temperature. Before detecting the temperature dependence on the SDS-PPG binding interaction in aqueous solution, the temperature effect on the SDS micellization and the phase behaviours of PPG must be studied. In Chapter 4, the temperature effect on the SDS micellization has been discussed. In this section, the temperature dependence on the phase behaviour of different molecular weight of PPG in aqueous solution was examined.

Solvent quality and polarity alter the polymer solubility and chain conformation, where hydrogen bonds play an important role in the behaviour of uncharged water-soluble polymer solutions. Polymers whose solubility is controlled by the strength of hydrogen bonding normally possess a LCST. The occurrence of LCST is related to the fact that hydrogen bonds are destroyed at higher temperatures, resulting in the phase separation of the polymer solutions. The second virial coefficient, A_2 changes from positive to 0 and then to negative at the LCST [Teraoka 2002]. It can be determined by either naked eye or photo-detectors, such as UV-vis

spectrophotometer or light scattering [Cai et al. 2001; Gan et al. 2001]. For example, poly(N-isopropyl acrylamide) possesses a LCST of $\sim 30\text{ }^{\circ}\text{C}$ and the LCST decreases with increasing molecular weights [Teraoka 2002]. As the solvent quality changes from good to poor, the random coil conformation changes to a globular shape in order to minimize polymer-solvent contact. For long chain water-soluble uncharged polymers, an abrupt coil-globular transition has been observed [Wu and Zhou 1995, 1996].

Since the solubility of polyoxyalkylene in water is due to hydrogen bond, the LCST of PEG varies from 80 to 100 $^{\circ}\text{C}$, depending on the molecular weight. However, the LCST for PPG is much lower due to the methyl group, and is usually within the room temperature range. Hence, PPG is a good model system for studying the temperature effect on the surfactant-polymer interaction near the phase separation temperatures. The phase behavior of different molecular weights of PPG in aqueous solution was examined. For PPG1K, PPG2K and PPG3K, the phase behaviors were measured using the UV-visible spectrophotometer at fixed wavelength of 480 nm over the temperature range of 20 to 60 $^{\circ}\text{C}$ as shown in Figure 6.1. For PPG3K, naked eye was also used to assist in the determination of the LCST since the temperature is too low to be measured accurately using our UV-visible spectrophotometer due to condensation of water vapor on the cuvette. The LCSTs for PPG1K, PPG2K and PPG3K in aqueous solution are found to be approximately 42.0, 23.0 and 15.5 $^{\circ}\text{C}$ respectively.

Figure 6.1 The temperature dependence of the UV-vis. transmittance at wavelength 480 nm for PPG1K, PPG2K and PPG3K in aqueous solution.

6.3 The Binding Interaction of PPG and SDS at Different Temperatures

The ITC curves for the titration of 0.2 M SDS into different concentrations of PPG1K at 25 °C and 1 atm are shown in Figure 6.2, where the dilution curve of SDS in aqueous solution is depicted by the open circle. The difference between the titration and dilution curves is attributed to the polymer-surfactant interaction. Only one endothermic peak is present, and the peak area increases with polymer concentration, similar to that reported by Olofsson and co-workers [Wang and Olofsson 1998]. Since the experimental temperature is lower than the LCST of PPG1K, the curves possess identical shapes to that observed for the titration of SDS into moderate molecular weights PEGs (molecular weight ranges from 900 to 3350 Da), suggesting that similar binding mechanism must be present [Dai and Tam 2001]. The endothermic peak is

attributed to the dehydration of PPG segments, which induces the cooperative binding of SDS monomers onto the dehydrated PPG segments and form mixed micelles at SDS concentrations lower than the CMC. This process is commonly referred to as the polymer-induced micellization. The occurrence of mixed micelles is characterized by CAC, determined to be ~ 1.2 mM from ITC thermogram, which is much smaller than that for PEG-SDS system (~ 4.2 mM) [Wang and Olofsson 1998]. The lower CAC corresponding to the earlier onset of polymer-induced micellization is attributed to the more hydrophobic of PPG chains, where the Gibbs free energy ΔG_{agg} , can be described by Eq. (6.1) [Wang et al. 1997];

$$\Delta G_{agg} = \left(1 + \frac{m}{n}\right) RT \ln(CAC) \quad (6.1)$$

where the CAC is in the unit of molar fraction, m is the number of counterions bound per micelle, n is the aggregation number, and β defined as m/n is called the effective micellar charge fraction. In addition, the CAC decreases marginally with polymer concentration, but the saturation concentration C_2 increases with polymer concentration. These values are summarized in Table 6.1, where CAC and C_2 are determined from the SDS concentration where the titration curve begins to divert or merge with the dilution curve respectively.

Polymer	M _w	M _w /M _n	T (°C)	PPG conc (wt%)	CAC (mM)	C ₂ (mM)	ΔG _{agg} (kJ/mol)
PPG1K	1040	1.06	25	0.1	1.35	22.52	-44.8
			25	0.15	1.20	29.68	-45.3
			25	0.2	1.09	> 30	-45.7
PPG2K	2040	1.05	18	0.1	0.75	21.47	-46.1
			20	0.1	0.70	21.47	-46.7
			21	0.1	0.70	21.47	-46.9
			22	0.1	0.70	21.47	-47.1
			23	0.1	0.60	21.47	-47.8
			23	0.1	0.60	21.47	-47.8
			23	0.1	0.60	21.47	-47.9
			24	0.1	0.60	21.47	-48.0
			25	0.1	0.60	21.47	-48.2
			27	0.1	0.70	21.47	-47.8
			29	0.1	0.75	21.47	-47.9
			31	0.1	0.90	21.47	-47.4
			25	0.1	0.60	21.47	-48.2
			25	0.15	0.60	23.60	-48.2
			25	0.2	0.60	28.43	-48.2
PPG3K	2870	1.08	25	0.1	0.75	25.80	-47.2
			25	0.15	0.75	28.40	-47.2
			25	0.2	0.75	29.90	-51.4

Table 6.1 Physical properties of polypropylene glycols and the binding parameters for PPG/SDS determined at 1 atm and different temperatures.

Figure 6.2 ITC curves for titrating 0.2 M SDS into different concentrations of PPG1K aqueous solutions at 25 °C and 1 atm.

Figure 6.3 ITC curves of 0.2 M SDS into 0.1 wt% of different molecular weights PPG aqueous solutions at 25 °C and 1 atm.

The ITC thermograms for titrating 0.2 M SDS into 0.1 wt% of PPG1K, PPG2K and PPG3K aqueous solutions at 25 °C are shown in Figure 6.3. The molecular weight dependence of the titration curves exhibit trends that were not observed for PEG-SDS system. For the PEG system, the endothermic peak is essentially constant, but the exothermic peak is only evident for higher molecular weights (MW > 3500 Da) at higher SDS concentrations [Dai and Tam 2001]. For the three PPG systems, PPG3K displays only one exothermic peak. For PPG2K, one exothermic peak and one endothermic peak are present at low and high SDS concentrations respectively. In the case of PPG1K, only one endothermic peak is evident. From the UV-vis transmittance study, it becomes clear that the trend in the ITC thermograms can be correlated to the LCST of the PPG system. In addition, the CAC decreases with increasing molecular weight, which is consistent to the trend

observed for PEG-SDS system when the PEG molecular weight is lower than 8000 Da.

Figure 6.4 ITC curves for titrating 0.2 M SDS into 0.1 wt% of PPG2K aqueous solution at different temperatures and 1 atm.

The titrations of 0.2 M SDS into 0.1 wt% PPG2K aqueous solution at temperatures ranging from 18 to 31 °C were carried out and the ITC thermograms are shown in Figure 6.4. Only one endothermic peak was observed at temperature below 22 °C, which is similar to the results obtained for SDS-PPG1K and SDS-PEG with moderate molecular weights (MW < 3500) at 25 °C. However, when the temperature exceeds 29 °C, the endothermic peak disappears and only one exothermic peak is present. Similar trends have been observed for SDS-PPG3K at 25 °C. In the temperature range of 22 to 29 °C, the transformation from the endothermic to the exothermic peak is clearly evident. With increasing temperature, the magnitude of the endothermic peak decreases, while the magnitude of exothermic peak becomes more

dominant. Since the LCST for PPG2K was determined to be ~ 23 °C, this phenomenon is directly related to the LCST of PPG2K in aqueous solution where different binding mechanisms must be in operation at temperatures below and above the LCST.

At temperature lower than the LCST, homogeneous PPG2K aqueous solution similar to the solution property of PPG1K or moderate molecular weights PEG is present. Thus, similar binding mechanism as depicted by identical trends in the titration curves are observed. In this temperature range, PPG segments dehydrate and form SDS/PPG mixed micelles. The CAC and C_2 were determined and summarized in Table 6.1, and it is evident that both values are independent of temperature.

At temperature beyond 29 °C (above the LCST), all the PPG2K chains become insoluble due to the poor solvent quality and they phase separate from the solution. Addition of SDS induces the binding of SDS molecules directly onto the insoluble PPG particles since this minimizes the surface energies between insoluble PPG particles and water. The absence of an endothermic peak suggests that the dehydration process of PPG backbone is absent. The observed exothermic peak is related to the direct solubilization of PPG particles in SDS mixed micellar cores. Similar solubilization behavior and the exothermic peak were also observed for SDS and poly(methacrylic acid-ethyl acrylate) copolymer emulsion latex or poly(acrylate acid) at low pH. For the binding interaction between SDS and poly(methacrylic acid-ethyl acrylate) copolymer emulsion latex at low pHs will be discussed in Chapter 10, where the similar exothermic peak were observed in the ITC thermogram. This is also observed by our colleagues during their study on the binding between SDS and poly(acrylic acid) or poly(methacrylic acid) at low pHs [Wang 2004; Wang and Tam

2004]. The CAC and C_2 values as summarized in Table 6.1 are evident that they are not sensitive to temperature.

Figure 6.5 ITC curves for titrating 0.2 M SDS into 0.1 wt% of PPG3K aqueous solution at different temperatures and 1 atm.

In the temperature range of 22 to 29 °C, mixture of soluble PPG2K chains and insoluble PPG2K particles are present. Hence, in this temperature regime, the polymer surfactant interactions are dominated by the equilibrium of two different processes: (I) dehydration of soluble PPG segments and formation of SDS/PPG mixed micelles in solution; (II) solubilization of insoluble PPG particles directly and formation the SDS/PPG mixed micelles in solution. Because of the presence of the hydrophobic insoluble PPG particles, they are first solublized by SDS molecules and the solubilization of these particles gives rise to an exothermic peak at low SDS concentrations. With further increase in SDS concentration, the solvated PPG chains are dehydrated and they form mixed micelles with SDS, which gives rise to the

observed endothermic peak at high SDS concentrations. The combination of these two effects leads to the observed ITC thermograms, where CAC and C_2 are independent of temperature as shown in Table 6.1. Similar binding behaviors were also observed for SDS-PPG3K system at the phase transition temperatures as shown in Figure 6.5.

The titration curves of 0.2 M SDS into different concentrations of PPG2K aqueous solutions at 25 °C are shown in Figure 6.6. The CACs are independent of polymer concentrations, while C_2 increases with polymer concentration as summarized in Table 6.1. With increasing polymer concentration, the exothermic peak dominates while the endothermic peak becomes less evident. By comparing Figures 6.2 and 6.6, it is evident that the dependence of C_2 on polymer concentration for PPG2K at 25 °C is not as significant as that for PPG1K.

Figure 6.6 ITC curves for titrating 0.2 M SDS into different concentrations of PPG2K aqueous solution at 25 °C and 1atm.

The concentration dependence of SDS and PPG3K system at 25 °C was also examined and shown in Figure 6.7, where only exothermic peak is present and the CAC is independent of polymer concentration. In addition, the peak areas as well as the C_2 are not significantly altered by increasing polymer concentration, which suggests that the solubilization of PPG particles is not sensitive to polymer concentration. This correlates with the finding that the polymer concentration dependence of PPG2K-SDS system is not as significant as that of PPG1K-SDS system.

Figure 6.7 ITC curves for titrating 0.2 M SDS into different concentrations of PPG3K aqueous solution at 25 °C and 1atm.

For polymers that possess LCST are dissolved in water, the solvent quality changes from a good to a poor solvent as the temperature is increased. The nature of the solvent quality controls the polymer-solvent interaction and the chain conformation as well as the molecular parameters, such as the second virial

coefficient A_2 and the Flory interaction parameter χ [Flory 1953]. Such changes also alter the binding interactions between polymer chains and surfactant molecules. At temperature lower than the LCST, the solvent quality is good, thus the binding interaction between SDS and PPG is similar to SDS-PEG system at room temperature. However, at temperature greater than the LCST, the polymer chains are insoluble, and only hydrophobic binding interactions are observed, resulting in an exothermic peak after the CAC. At temperature in the vicinity of LCST, the balance of these two effects dominates the binding processes. The proposed binding mechanisms for PPG and SDS at temperatures below and above the LCST are shown in Figure 6.8.

Figure 6.8 Schematic diagrams describing the binding interactions for SDS and different molecular weights of PPG at different temperatures. (a) $T < LCST$ and (b) $T > LCST$.

6.4 Summary

ITC is an important research tool for studying surfactant micellization and surfactant-polymer interaction where the CAC, C_2 and the thermodynamics associated with the binding interaction can be determined. We propose for the first time the possible binding mechanisms between SDS and uncharged polymer close to their LCSTs. At temperatures below the LCST, the binding interactions between SDS and PPG are identical to those between SDS and moderate molecular weights PEG at room temperature. However, at temperatures exceeding the LCST, no dehydration process occurs and insoluble PPG particles are directly solubilized into the core of mixed micelles via hydrophobic interaction. At temperatures close to the LCST, the binding is controlled by the equilibrium of two competing processes, i.e. the solubilization of insoluble PPGs at low SDS concentrations and the dehydration of soluble PPGs at higher SDS concentrations. Both the CAC and C_2 values are independent of temperature. Although C_2 values are strongly dependent on polymer concentration for the dehydration process, they are not sensitive to polymer concentration for the solubilization process.

Chapter 7 Interactions Between Sodium Dodecyl Sulfate and Poly(ethylene oxide) in Less Polar Solvents

7.1 Introduction

Surfactant micellization, polymer conformation and surfactant-polymer interaction are strongly dependent on the characteristics of the solvent. There are two possible ways of altering the solvent property: (a) changing temperature; and (b) addition of organic/inorganic additives. The temperature dependence on the surfactant-polymer interaction was discussed in Chapter 6. In this chapter, the effect of co-solvents on the surfactant-polymer interaction will be discussed.

Glycol, such as ethylene glycol (EG), propylene glycol (PG), and glycerol (GR), constitutes a series of environmental friendly non-aqueous polar solvent with wide applications in personal home care and pharmaceutical product formulations [Invanova et al. 2001]. It has many characteristics similar to those of water and it can form hydrogen-bonded network in aqueous solutions, and thus is miscible with water. In addition, it also possesses a higher cohesive energy and has a fairly high dielectric constant [Ruiz 1999; Ruiz et al. 2001]. Hence, addition of glycol into water decreases the polarity of the solvent. The physical properties of three common types of glycols are listed in Table 7.1 [Brundrup and Immergut 1989; Invanova et al. 2001].

Solvent	Molar Mass	Density (g/ml)	Dielectric Constant	Solubility Parameter (MPa ^{1/2})
Water	18	1.000	78.5	47.8
Glycerol	92	1.257	40.1	36.2
Ethylene glycol	62	1.110	37.7	33.0
Propylene glycol	76	1.033	32.0	30.2

Table 7.1 Physicochemical parameters of water and three common types of glycols at 298K.

Studies on the aggregation behaviors of amphiphilic molecules in glycol-water mixtures have attracted significant interests from various research groups [Alexanderdis and Yang 2000; Dai et al. 2003b; Penfold et al. 1997; Ruiz 1999; Ruiz et al. 2001]. Such studies provided a better understanding on the effect of structure of liquids on the micellization and aggregation process. Several studies on the micellization behavior of surfactants in glycol-water mixtures have been reported [Bakshi 1997; Callagham et al. 1993; Palepu et al. 1993; Penfold et al. 1997; Ray 1971; Ruiz 1999]. The CMC shifted to a higher value by adding glycols to nonionic surfactant solutions, while the aggregation number and the size of the micelles decreased. The nonionic surfactant micellization in the glycol-water mixtures is controlled by the structure breaking ability of glycols and the interaction of co-solvents with the surfactant head-groups. Alexandridis et al. conducted a comprehensive investigation on aggregation of Pluronic PEO-PPO-PEO block copolymers in mixtures of water and glycols [Alexanderdis et al. 2000; Alexanderdis and Yang 2000; Ivanova et al. 2000, 2001]. The total micellar and core radii, micelle aggregation number and polymer volume fraction in the micellar core and corona decreased with increasing ethanol-water ratio. Addition of glycerol to water led to a larger aggregation number and higher volume fraction of the micelle corona. Based on the glycol relative polarity, the hypothesis on the phase behavior was proposed. From a polar to a less polar solvent, the structure transformed from a micellar cubic to hexagonal, to bicontinuous cubic and then to lamellar structures.

Since the solubility of PEG (or PEO) in water is due to the formation of hydrogen bonding with water, the solution behaviour of PEO in glycol solution should be very interesting. Glycols are not only less polar solvents than water, but also they are strong hydrogen-bonding agents like water. Both glycols and water can

work as hydrogen-donor in the H-bond, while PEO, glycols and water can act as the hydrogen-acceptor in the H-bond [Dai et al. 2003b]. Competition for the establishment of hydrogen bonds with PEO occurs when glycols are added to water. Although PEO can dissolve into water at room temperature, it does not dissolve in glycol. Only a few studies on the effects of glycol on the polymer solution properties of water-soluble polymers have been reported, and there is a lack of the fundamental understanding on the interaction of surfactants and polymers in the glycol-water mixed solvents. In this chapter, the effect of co-solvent on the PEO chain conformation and the effect of different glycols on the binding interaction of SDS and PEO in the glycol-water mixed solvents were examined using isothermal titration ITC and DLS techniques. The former provides the enthalpy changes associated with the interaction, while the latter offers information on the resulting microstructure.

7.2 Dynamic Light Scattering of PEO in SDS Solutions

From the discussion in Chapter 5, it is evident that the molecular weight and the molecular weight distribution do not alter the ITC thermogram when the PEG molecular weight is greater than 8000 Da. In order to carry out dynamic light scattering experiments, higher molecular weight of PEG, known as poly(ethylene oxide) (PEO), was used instead of the low molecular weight PEG used in the previous study.

7.2.1 DLS of PEO in water

Due to the formation of hydrogen bond with water, PEO is soluble in water, however, aggregation of PEO is commonly observed in aqueous solution. Dynamic light scattering experiments of PEO750 in aqueous solution were carried out and

Figure 7.1 shows the angular dependence of the decay time distributions of PEO750 in water. Two decay modes are evident from the decay time distribution functions. The light scattering vector $\mathbf{q}$ is defined as the difference of the incident and scattered wave vectors with the value described in Eq. (7.1);

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (7.1)$$

where n is the refractive index of the solvent, λ the wavelength of light and θ the scattering angle. The decay rate Γ is the inverse of the decay time τ , while the scattering vector q dependence on the decay rate, Γ can be used to determine the physics of the decay mode in the decay time distribution function [Dai 1999; Brown 1993]. It was found that both decay rates for PEO750 aqueous solution are q^2 dependent, which suggests that both decay modes are attributed to the translational diffusion of two types of particles in solution. The slopes of Γ versus q^2 are related to the translational diffusion coefficients D of particles in solution;

$$D = \frac{\Gamma}{q^2} \quad (7.2)$$

Based on Stokes-Einstein relationship, the apparent hydrodynamic radius R_h can be obtained from DLS measurement;

$$R_h = \frac{kT}{6\pi\eta D} \quad (7.3)$$

where k is the Boltzmann constant, T the absolute temperature, and η is the solvent viscosity. It was found that R_h values for both decay modes are 26 nm and 275 nm respectively [D (fast) = $9.4 \times 10^{-12} \text{ m}^2/\text{s}$ and D (slow) = $8.9 \times 10^{-13} \text{ m}^2/\text{s}$].

Figure 7.1 Measurements on angular dependence of the decay time distribution functions of 0.1 wt% PEO750 in aqueous solution.

Since water is a good solvent for PEO, the hydrodynamic radius R_h of the PEO chain can be approximately calculated based on following scaling relationship [Alami et al. 1996];

$$R_h = 0.0145M^{0.571} \quad (7.4)$$

The calculated R_h is ~ 20 nm. Hence, it can be concluded that the fast decay mode is attributed to the translational diffusion of the PEO750 unimers in solution. The second diffusional mode should be related to the PEO aggregates in solution, which are formed through hydrogen bonds in water. To verify the formation of PEO aggregates in water, $0.2 \mu\text{m}$ filter was used to filter the PEO750 solution and carried out dynamic light scattering experiments immediately. Figure 7.2 shows the decay time distribution functions of 0.1 wt% PEO750 before and after filtration.

Figure 7.2 Decay time distribution functions of 0.1 wt% PEO750 in aqueous solution. The filled circle is the unfiltered sample and the open circle is the filtered sample (0.2 μm filter).

There is only one decay mode available in the decay time distribution of the filtered sample solutions and the second decay mode was successfully removed by the 0.2 μm filter. The R_h was found to be ~ 26 nm for the filtered PEO750 aqueous solution. However, when the filtered PEO solution was left at room temperature for one day, the second slow decay mode reappeared in the decay time distribution. This confirmed the slow decay mode in the decay time distribution function is attributed to the PEO aggregates. We have reported similar properties on the hydrophobically modified polyelectrolyte solutions [Dai et al. 2000a]. Although the amount of PEO aggregates is small, their contribution to the scattered light intensity is significant due to their relatively large size. Thus, the presence of the large aggregates complicates

the study of binding interaction between SDS and PEO using the light scattering technique.

7.2.2 DLS of PEO in salt solutions

Salt seriously affect the solution behaviours of polyelectrolyte. Addition of salt into polyelectrolyte solution gives rise to a reduction in the particle size [Dai et al. 2001a; Hara 1993; Wang 2004]. Although PEO is not a polyelectrolyte, the addition of salt could also alter the solution properties of PEO solution by destroying the water structure and hydrogen bond [Bailey and Callard 1959; Xu et al. 2004]. It seems that mono-valent salt has small effects on the solution properties, but di- and tri-valent salt could significantly decrease the solution behaviour. The effect of mono-valent salt on the solution behaviour of PEO was examined before studying the interaction of PEO and SDS using light scattering technique. Figure 7.3 shows the decay time distribution functions of 0.1 wt% PEO750 in aqueous solution in different concentrations of salt. It is evident that salt has negligible effect on the hydrodynamic radius for PEO750 solution in filtered and unfiltered samples.

Figure 7.3 Decay time distribution functions of 0.1 wt% PEO750 in different concentrations of NaCl aqueous solution. The filled circles are unfiltered samples and the open circles are the filtered samples (0.2 μm filter).

7.2.3 DLS of PEO in SDS solution

Dynamic light scattering of PEO in different SDS solutions was examined. Since the salt effect in light scattering can be eliminated, the difference observed in the distribution functions for PEO in water and in SDS solution is attributed to polymer-surfactant interactions. Figures 7.4 and 7.5 revealed the decay time distribution functions of PEO750 in 10 mM and 25 mM SDS respectively, carried out at different scattering angles. From Figure 7.4, it was observed that two decay modes are present in the distribution functions. Both decay rates are q^2 dependence, which indicates the translational decay modes of two types of particles. By comparing with the decay time distribution functions for 0.1 wt% PEO750 in water, both modes are attributed to the SDS/PEO unimer mixed micelle and SDS/PEO aggregates

respectively. However, from Figure 7.5, another translational decay mode appears at lowest decay time with an averaged R_h of 1 nm, which should correspond to the free SDS micelles in solution.

Figure 7.4 Decay time distribution functions of 0.1 wt% PEO750 in 10 mM SDS aqueous solution. (45, 60, 75 and 90 in the figure are the scattering angles)

Figure 7.5 Decay time distribution functions of 0.1 wt% PEO750 in 25 mM SDS aqueous solution. (45, 60, 75 and 90 in the figure are the scattering angles)

Figure 7.6 Decay time distribution functions of 0.1 wt% PEO750 in different concentrations of SDS aqueous solution at scattering angle of 90.

The decay time distribution of PEO750 in different concentrations of SDS aqueous solution is shown in Figure 7.6. When no SDS was added, there are two modes corresponding to the diffusions of PEO unimers and PEO aggregates respectively. Addition of small amounts of SDS up to a concentration of 4 mM, the decay times of both modes remained almost unchanged. With further increase of SDS concentration to 10 mM, the decay time of the fast mode decreases, and the decay time for the slow mode increases. Beyond 10 mM of SDS, both decay times increase with SDS concentration. At SDS concentrations of 20 mM or 25 mM, a significant fastest translational decay mode is observed. Based on Einstein-Stokes equation (Eq.(7.3)), the apparent hydrodynamic radius R_h of PEO in different SDS aqueous solutions can be obtained and they are shown in Figure 7.7.

Figure 7.7 SDS concentration dependence of R_h s of both slow and fast modes of 0.1 wt% PEO750 in SDS aqueous solution.

For PEO unimer, it is clear that R_h remains constant first and then decreases to a minimum at 10 mM SDS, and it then increases to ~ 17 nm at 20 mM SDS. The R_h for the slow mode remains almost constant up to 4 mM SDS, where it increases with SDS concentration and reaches a maximum at 20 mM SDS.

Figure 7.8 Comparison of SDS concentration dependence of the ITC thermogram and $R_h(f)$ for 0.1 wt% PEO750 and SDS in aqueous solution.

To further understand this phenomena, Figure 7.8 compares the ITC thermogram for titrating SDS into 0.1 wt% PEO750 with the dependence of $R_h(f)$ on the SDS concentration. At SDS concentration lower than the CAC (~ 4.2 mM), only weak SDS/PEO interaction is present, and the $R_h(f)$ is independent of SDS concentration. Beyond CAC, PEO segments will be dehydrated and solubilized into the hydrophobic core of SDS/PEO mixed micelles. The decrease in R_h is the result of the folding of several units ethylene-oxide segment into the micellar core of the SDS micelles. Beyond 10 mM of SDS, these dehydrated PEO segments are gradually rehydrated into water phase, which then bind to the surface of SDS micelles. During

this process, the increase in SDS aggregation number and the solvation of PEO segments gives rise to the increase in the hydrodynamic radius. At the saturation concentration C_2 , free SDS micelles appear in the distribution function as evident from the fastest mode, where the R_h remained unchanged. However, the R_h of the SDS bound PEO is smaller than individual PEO chain in water. For PEO aggregates, R_h is independent of SDS concentration for SDS concentration below CAC and above C_2 , but it increases with SDS concentration between CAC and C_2 due to the fact that larger proportions of SDS molecules are bound to the PEO backbones.

We have also tried to detect the binding interaction between SDS and PEO750 in solvent mixtures of glycerol and water. However, well-defined time autocorrelation functions (TCF) cannot be obtained. The reason may be due to the weak scattering of individual PEO chains in the glycol/water mixed solvents, i.e. the refractive indexes of the solute and solvent are quite similar.

7.3 Interaction of SDS and PEO in Water/Glycerol Mixed Solvent

The binding interaction between SDS and PEO in various glycerol/water mixtures was examined by ITC. The ITC thermograms for the binding interaction between SDS and PEO750 in the solvent mixtures are shown in Figure 7.9. It is obvious that the titration curves are different when the glycerol contents were varied where the observed enthalpy increases with increasing amounts of glycerol, especially for glycerol concentration greater than 20 wt%. However, from Chapter 4, addition of glycerol in water also alters the SDS micellization behaviours in water.

Figure 7.9 The ITC thermograms of titrating 0.1 M SDS into 0.1 wt% PEO750 solution in glycerol-water solvent mixtures at 298 K and 1 atm.

Figure 7.10 The difference curves for titrating 0.1 M SDS into 0.1 wt% PEO750 solution in glycerol-water solvent mixtures at 298 K and 1 atm.

Since ITC measures the total enthalpy changes during the titration process, the difference in the enthalpy between titrating SDS into PEO solutions and that into the mixed solvent is attributed to the SDS/PEO interaction. The difference curves of SDS into PEO750 and SDS dilution in the solvent mixtures is shown in Figure 7.10. All the curves display similar trends for glycerol content lower than 8 wt%, exhibiting an endothermic peak at low SDS concentrations followed by an exothermic peak at high SDS concentrations. However, the areas of both peaks decrease when the glycerol was increased from 0 to 8 wt%. The two peaks are attributed to the polymer induced SDS micellization at low SDS concentrations and ion-dipole association at high SDS concentrations. The CAC values increase and C_2 and C_m decrease with glycerol concentration, which suggest a decrease in the PEO binding affinity. Addition of small amounts of glycerol decreases the cooperative micellization of SDS mixed micelles. In addition, it also leads to the reduction in the proportion of the dehydrated/de-solvated PEO segments. As the positive enthalpy corresponds to the formation of SDS mixed micelles at low SDS concentrations and the negative enthalpy at high SDS concentrations resulted mainly from the enthalpy associated with the rehydration/resolution of PEO chains. The lower proportion of PEO dehydration/desolvation gives rise to an overall reduction in the total enthalpy changes indicated by the peak areas of the titration curves.

At glycerol concentration greater than 15 wt%, the titration curves exhibit different trends from those at lower amounts of glycerol. There is a significant exothermic and endothermic peak at low and high SDS concentrations respectively, and the area of both peaks increases with glycerol concentration. The different titration curves suggest the presence of different binding mechanisms. As the amounts of glycerol is in excess, the solvent quality will be further affected, i.e. the solvent

polarity decreases, where the solvent for the PEO changes from a good solvent to Θ solvent due to the disruption of hydrogen bonds between PEO and water by glycerol [Dai et al. 2003b]. Hence, the solubility and the flexibility of PEO chains in the solvent mixtures decrease, and the HLB for SDS in the mixed solvents shifts accordingly.

Compared with the temperature dependence of the binding interaction between SDS and PPG as discussed in Chapter 6, similar trends were observed at temperature close to the LCST of PPG. For the formation of SDS/PEO mixed micelles at CAC, the observed enthalpy change is the result of the dehydration/desolvation (positive enthalpy) of PEO segments and hydrophobic attraction (negative enthalpy). In aqueous solution, the dehydration enthalpy dominates, however in the present concentration ranges, only weak or negligible dehydration/desolvation process is present, and the hydrophobic attraction dominates the binding process, which produces an exothermic peak at low SDS concentrations. With increasing SDS concentrations, the aggregation number of SDS increases, which causes a structural re-organization, where the previously solubilized PEO segments are expelled from the micellar core and then these segments bind to the external surface of SDS micelles. For the formation of ion-dipole SDS/PEO aggregates, the total enthalpy originates from two possible sources, i.e. the enthalpy for the rehydration/resolution of PEO segments (negative enthalpy) and the enthalpy for ion-dipole attraction (positive enthalpy). In water, the rehydration of PEO chains dominates, resulting in an exothermic peak. In the present condition, there is very weak or negligible rehydration/resolution process, and thus the ion-dipole association dominates the binding process, which leads to an endothermic peak at high SDS concentrations.

At glycerol concentrations ranging from 8 to 12 wt%, the binding interaction lies within the transition of the two processes described earlier, and the combination of these two effects gives rise to a weak binding enthalpy as shown in Figure 7.10. We noted that the solvent quality plays an important role in surfactant micellization process and the surfactant/polymers interaction. Small amounts of glycerol could be solubilized by surfactant molecules. However, larger amounts of the glycerol will alter the solvent polarity and polymer solubility, where the polymer desolvation and resolution processes in the binding interaction are minimized. Hence, the polymer-surfactant interaction is controlled by the equilibrium of hydrophobic attraction at low SDS concentrations and ion-dipole interaction at high SDS concentrations, which results in the structural reorganization.

7.4 Interaction of SDS and PEO in the Solvent Mixtures of Water and Other Glycol Systems

In this section, the SDS/PEO binding interactions in the solvent mixture containing other types of glycols and water will be discussed. From Table 7.1, propylene glycol and ethylene glycol are less polar solvents than glycerol, and hence they should have a significant effect on the binding interaction between SDS and PEO in solution. Figures 7.11 and 12 revealed the ITC and the difference ITC thermograms for titrating SDS into PEO750 in ethylene glycol/water mixed solvents. The titration curves are identical to those in glycerol/water mixtures, which indicate that similar binding characteristics must be in operation. However, the effect of the ethylene glycol content on the solvent quality is more significant. At the ethylene glycol concentration of 10 wt%, no endothermic peak or no PEO desolvation behaviour was

detected. Beyond ethylene glycol concentration of 40 wt%, no binding heat can be detected, which indicates that the binding interaction between SDS and PEO is absent.

Figure 7.11 The ITC thermograms for titrating 0.1 M SDS into 0.1 wt% PEO750 solution in different ethylene glycol-water solvent mixtures and water at 298 K and 1atm.

Figure 7.12 The difference curves for titrating 0.1 M SDS into 0.1 wt% PEO750 solution in different ethylene glycol-water solvent mixtures and water at 298 K and 1 atm.

Figures 7.13 and 7.14 revealed the ITC and the difference ITC thermograms of SDS into PEO750 in proylene glycol/water solvent mixtures. The titration thermograms are similar, but the decrease in the solvent quality for propylene glycol is more significant than for ethylene glycol. As propylene concentration exceeds 40 wt%, no more binding interaction between SDS and PEO is present. By comparison, glycerol is more polar and the effect on the PEO solvation and SDS micellization is lower than the other glycols, hence the above experimental phenomena were observed.

Figure 7.13 The ITC thermograms for titrating 0.1 M SDS into 0.1 wt% PEO750 solution in different propylene glycol-water solvent mixtures and water at 298 K and 1 atm.

Figure 7.14 The difference curves of titrating 0.1 M SDS into 0.1 wt% PEO750 solution in different propylene glycol-water solvent mixtures and water at 298 K and 1 atm.

7.5 Summary

The solvent quality significantly alters the surfactant micellization behaviour and polymer chain conformation. Addition of glycol into water not only destroys the water structure but also decrease the solvent's dielectric constant. The solubility of PEO decreases with the addition of glycols. Addition of small amount of glycols promotes the micellization of SDS, but excess amount of glycol has the negative effects. Consequently, the binding interaction between SDS and PEO depends on the nature of the solvent.

The interaction of SDS and PEO in aqueous solution was studied by ITC and DLS techniques. It was found that PEO aggregates each other in aqueous solution. With addition of SDS, PEO dehydrates and forms SDS/PEO aggregates in solution. After that, the aggregate rearranges itself through ion-dipole interaction.

The solvent quality was modified by the addition of glycols. For the binding interaction between SDS and PEO in the glycerol-water solvent mixtures, the endothermic peak in aqueous solution is progressively transformed to an exothermic peak, while the exothermic peak is progressively converted to an endothermic peak. At different amounts of glycerol, different binding mechanisms are in operation. By adding glycerol, the solvent quality decreases, and this reduces the polymer dehydration or desolvation process.

Mixed surfactant micelles are formed by the direct hydrophobic interaction at low SDS concentration. At high SDS concentration, the ion-dipole association dominates with less or no rehydration/resolvation process. From the study of SDS-PEO in the mixed solvents of ethylene glycol/water or propylene glycol/water, which are less polar than glycerol, the decrease in the PEO desolvation is more significant at low SDS concentration. In addition, only the solubilization process dominates when

the content of ethylene glycol or propylene glycol concentration is high. Beyond a certain critical concentration of the glycols, we observed no interaction between PEO and SDS in solutions, which is attributed to the reduction in polarity and dielectric constant of the solvents. This not only enhances the solubility of the surfactant tails, but also reduces the solubility of PEO.

Chapter 8 Interactions Between Sodium Dodecyl Sulfate and Hydrophobic Modified Poly(ethylene glycol) in Aqueous Solution

8.1 Introduction

Hydrophobic ethoxylated urethane (HEUR) is one common associative polymer used in many water-borne coating formulations [Schaller and Sperry 1993; Winnik and Yekta 1997]. In the mid-1980s, Glass and co-workers [Glass et al. 1984; Karunasena et al. 1989] and Sperry and Schaller [Schaller and Sperry 1993; Thibeault et al. 1986] were among the first to report on such telechelic associating polymers. Since then, research on telechelic associative polymers has been actively pursued, and numerous publications have appeared in the literature. Various techniques such as rheology [Annable et al. 1993; Jenkins 1991; Ng et al. 2000; Tam et al. 1998b], fluorescence spectroscopy [Wang and Winnik 1990; Yekta et al. 1993], pulse gradient NMR [Persson et al. 1992; Rao et al. 1995] as well as the laser light scattering [Alami et al. 1996; Chassenieux et al. 1997] were employed in these studies. As a result, the association mechanism and the network structure of these polymers are well understood. For HEUR with C_{16} hydrophobic end-caps and molecular weight greater than 10000 in dilute solution, HEUR polymer chains self associate into discrete micelles or rosettes consisting of a hydrophobic core that is surrounded by a corona of PEO chains looping back into the core. However, for the hydrophobe with alkyl chain smaller than $C_{12}H_{25}$ in dilute aqueous solution, open association dominates, where both hydrophobic end groups are located at different hydrophobic cores [Francois et al. 1996]. In this condition, the cluster-like aggregates are produced, and particle size increases with polymer concentration. With increasing HEUR concentration, the

micelles or aggregates are connected by bridging chains yielding a network structure that exhibits interesting rheological behavior [Zhang et al. 1996].

A detailed understanding on the interactions between HEUR and surfactant is necessary to enable formulators to develop superior water-borne coating formulations. Surfactant interacts strongly with HEUR and such interactions will influence the network structure of HEUR. The presence of small amounts of SDS enhances the viscosity of HEUR solution, but excessive amounts of SDS cause the viscosity to decrease. Annable and co-workers attributed the viscosity increase to the formation of larger number of bridging junctions formed by hydrophobic stickers displaced by SDS monomers [Annable et al. 1994a]. At high surfactant concentration, the hydrophobic micellar junctions are solubilized by surfactant micelles and the network structure disintegrates. Studies on the rheological behavior of HEUR/surfactant system have been conducted by several research groups [Binana-Limbele et al. 1993; Hulden 1994a, 1994b; Mast et al. 1993]. However, not many studies have investigated the thermodynamic and binding mechanism of this system in the dilute solution region [Dai et al. 2001c, 2004a]. Actually, the binding interactions between SDS and HEUR are more complicated than that between HEUR and other types of surfactant. In addition to the hydrophobic binding interaction, the attractive interaction between the charged head groups of SDS and PEO segments in the HEUR backbone are also present.

ITC not only determines CAC and C_2 , but also provides the thermodynamic parameters during the binding process. Several groups reported on the interactions between SDS and different water-soluble polymers, such as PEO [Dai and Tam 2001; Olofsson and Wang 1994; Persson et al. 1994; Wang and Olofsson 1998], PPO [Dai and Tam 2004], PVP [Thuresson et al. 1995], and EHEC [Wang and Olofsson 1995].

It was found that the CAC was dependent on the hydrophobicity of the polymer. In addition, EMF method is another versatile research tool to monitor the polymer/surfactant interaction. From the EMF curve, not only CAC and C_2 but also the free surfactant monomer concentration during the binding process could be determined. By combining ITC and EMF techniques, detailed binding isotherms and the binding mechanisms can be determined. In this chapter, the binding behavior between HEUR and SDS was examined systematically using the ITC, LLS and EMF techniques. By combining these three techniques, detailed information on the energetic and the structural changes could be determined. The polymer and SDS concentrations were varied to examine the concentration dependence of the CAC and the C_2 . Both the isothermal titration of SDS into HEUR and the isothermal titration of HEUR into SDS micellar solution were carried out and compared. From the static and dynamic light scattering results, the polymer chain conformation and the hydrodynamic properties were discussed with respect to the calorimetric data. From electromotive force, the SDS monomer concentration and the HEUR binding capacity were calculated.

8.2 HEUR Conformation from Static and Dynamic Light Scattering Methods

8.2.1 Static light scattering

For static light scattering, the weight-averaged molecular weight (M_w), the second virial coefficient (A_2) and the z-averaged radius of gyration (R_g) of polymers can be obtained from Equation 8.1 [Dai et al. 2000a; Flory 1953].

$$\frac{KC}{R_\theta} = \frac{1}{M_w} \left(1 + \frac{1}{3} q^2 R_g^2 \right) + 2A_2C \quad (8.1)$$

where $K (= 4\pi^2 n^2 (dn/dC)^2 / N_A \lambda^4)$ is an optical constant with N_A , n , and λ being the Avogadro's number, the solvent refractive index, and the wavelength of the light, respectively. C is the polymer concentration, R_θ is the excess Rayleigh ratio at scattering angle θ , and $\mathbf{q} (= 4\pi n \sin(\theta/2) / \lambda)$ is the scattering vector. The refractive index increment of HEUR polymer solution at 25°C, (dn/dC) , was determined from a BI-DNDC differential refractometer and found to be 0.160 ml/g for HEURC₁₆51K.

Figure 8.1 Zimm plot of dilute HEURC₁₆51K in aqueous solutions at 25 °C. (Concentrations: 2 mg/ml to 10 mg/ml; measurement angles: 45 to 135 °)

Figure 8.1 shows the Zimm-plot of dilute HEURC₁₆51K solution at 25°C. The apparent weight-averaged molecular weight and the radius of gyration of HEURC₁₆51K were found to be 930000 and 51 nm respectively. Winnik and co-workers had previously reported that the CMC for this polymer is about 0.01 wt% [Zhang et al. 1996]. The molecular weight obtained is much higher than that of HEUR unimers, reinforcing that the polymer chains are in the form of self-associated

micelles. The number of HEUR unimer chains per micelles can be calculated from the expression:

$$N_w = \frac{M_w(\text{micelles})}{M_w(\text{unimers})} \quad (8.2)$$

The calculated N_w is approximately 11. Since the averaged capping rate of the HEUR is 1.7 and there is only one association core in the micelle, the aggregation number of each micelle was determined from $N_{\text{agg}} = 1.7 \times N_w = \sim 19$. This value is identical to the aggregation number of 20 as reported by Winnik and co-workers using fluorescence spectroscopy [Xu et al. 1996; Yekta et al. 1996].

8.2.2 Dynamic light scattering

The relaxation time distribution functions of HEURC₁₆51K at different polymer concentrations are shown in Figure 8.2.

Figure 8.2 The relaxation time distributions of different concentrations of HEURC₁₆51K in aqueous solutions at 25 °C. (Measurement angle of 90°).

Only one peak is evident from the distribution functions. The linear dependence of the decay rates on q^2 suggests that the relaxation mode is a translational diffusion mode and the slope corresponds to the translational diffusion coefficient of HEUR micelles. The concentration dependence of the diffusion coefficients is shown in Figure 8.3.

Figure 8.3 The relationship between diffusion coefficients and concentrations of HEURC₁₆51K at 25°C.

The diffusion coefficients decrease with increasing polymer concentrations. The diffusion coefficients determined at finite concentration are characterized by the diffusion second virial coefficient, k_D , described by the equation below [Brown 1993];

$$D = D_0 (1 + k_D C + \dots) \quad (8.3)$$

where D_0 is the translational diffusion coefficient at infinitely dilute solution. It possesses a value of $7.1 \times 10^{-12} \text{ m}^2/\text{s}$, which is identical to the self-diffusion coefficient for HEURC₁₆51K micelles as determined from pulse-gradient NMR experiments

[Zhang et al. 1996]. From the Stokes-Einstein expression, the hydrodynamic radius, R_h , can be determined from,

$$R_h = \frac{kT}{6\pi\eta_0 D_0} \quad (8.4)$$

where k is the Boltzmann constant, T the absolute temperature in Kelvin, η_0 the solvent viscosity. The hydrodynamic radius of HEUR_{C₁₆51K} micelle was determined to be ~ 34.5 nm.

8.3 Interaction between SDS and HEUR

8.3.1 Titration of SDS into HEUR

The binding interaction between HEUR and SDS is more complicated than that between HEUR and other surfactant (such as cationic surfactants and nonionic surfactants) systems. SDS hydrophobic tails not only bind to the hydrophobic end groups of HEUR, but the head groups of SDS micelles could also bind to the PEO segments [Binana-Limbele et al. 1993; Cabane and Duplessix 1987; Zhang et al. 1996]. Previously rheological studies mainly focused on the hydrophobic interaction between SDS and semi-dilute HEUR solutions. It was found that SDS monomer could bind to the core of the HEUR end groups and strengthen the flower or rosette micelle of the HEUR at low SDS concentration. With increasing SDS concentrations, the SDS monomers would substitute some of the HEUR end groups in the HEUR micellar core. The substituted HEUR hydrophobic end groups are released to form bridges with other HEUR micelles, yielding larger proportion of hydrophobic junctions, which enhances the solution viscosity. Further increase in the SDS concentration saturates the HEUR hydrophobic end groups, resulting in the destruction of the flower-like structure thereby lowering the solution viscosity. When all the HEUR end-capped hydrophobes are fully saturated by SDS micelles, the interactions between

SDS and HEUR are identical to those between SDS and PEO of similar molecular weight. The detailed descriptions of HEUR and SDS interaction were summarized by Zhang et al. [Zhang et al. 1996] and Binana-Limbele et al. [Binana-Limbele et al. 1993].

Figure 8.4 Calorimetric titration curves for titration of 0.2 M SDS into water (open circle) and 0.1 wt% HEURC₁₆51K (filled circle) at 25°C and 1 atm. The insert figure is the difference curves.

Figure 8.4 (filled circle) shows the isothermal titration curve of 0.2 M SDS in 0.1 wt% HEURC₁₆51K solution together with the dilution curve of 0.2 M SDS in water shown by open circles. A large deviation between these two titration thermograms is evident. The difference is attributed to the interactions between SDS and HEUR. There is only one weak transition at 8.3 mM in the SDS dilution curve and this corresponds to the CMC of SDS, which is close to the literature value [Rosen 1980; Wang and Olofsson 1998]. At low SDS concentration, the titration curve for HEUR/SDS system begins to deviate from the SDS/water curve, but the enthalpy

change is not significant. The slight increase in enthalpy may be due to the non-cooperative hydrophobic interaction between HEUR end groups and monomeric SDS hydrophobic tails. However, the enthalpy changes also include those arising from the change in the solvent environment caused by the presence of HEUR chains. When the SDS concentration reaches 2.7 mM, ΔH increases sharply and reaches a maximum at 5.4 mM and then decreases. This endothermic peak correlates to the formation of SDS mixed micelles on the HEUR chains (or HEUR/SDS aggregation complex) and the solubilization of both the HEUR end groups and the dehydrated PEO segments from water phase into the hydrophobic core of mixed SDS micelles. The onset point for the sharp increase of ΔH is characterized by CAC. For the PEO/SDS system, the aggregation number of SDS inside the aggregation complex at CAC is much lower than that of free SDS micelles. With increasing SDS concentration, the aggregation number of SDS in the PEO/SDS complex continues to increase [van Satam et al. 1993]. However, as the aggregation number of the bound SDS micelles increases, the binding rate decreases due to electrostatic repulsions of these SDS head groups, which result in a decrease in ΔH beyond the maximum value. The titration curve then intersects with the SDS/water curve, and continues to decrease to a minimum. The minimum exothermic peak is attributed to the structural reorganization of the HEUR/SDS complex. With increasing SDS concentration, the aggregation number of SDS increases and the PEO segments in the SDS micellar core are expelled from the hydrophobic core into water due to their amphiphilic character. After dehydration, these PEO segments wrap around the charged surface of SDS micelles to form the necklace-like SDS/polymer complex. The driving force is the ion-dipole association between the dipoles of the hydrophilic PEO segments and the ionic head groups of the surfactant. The above structure results in the screening of the electrostatic interactions

between SDS hydrophilic heads. For the necklace-like complex, the wrapping of PEO segments of the HEUR chains also decreases the contact between the “exposed” hydrophobic segments of the SDS micelles and the water phase. With further addition of SDS, the degree of the rehydration becomes more rapid. It slows down after the minimum in the ΔH value and approaches another critical concentration designated as C_2 , where the HEUR chains become saturated by SDS molecules. Beyond C_2 , no further bindings between HEUR and SDS molecules can be detected and the titration curve merges with the dilution curve of SDS in water at C_m , where free SDS micelles are present and co-exist with HEUR/SDS complex. In this system, C_m is slightly larger than C_2 . However, Bloor and co-workers found that in some systems, C_m was smaller than C_2 [Li et al. 1999; Ghoreishi et al. 1999a, 1999b]. Detailed information on C_m and C_2 could be derived from the evaluation of the different binding constants [Goddard 1993].

From the literatures, it is evident that the definition and the determination of CAC and C_2 are ambiguous. Wang et al. [Wang and Olofsson 1998] determined these characteristic concentrations from a plot of the incremental enthalpy change, $[\Delta H(k) - \Delta H(k-1)]/\Delta m$, against SDS concentration, where $\Delta H(k)$ is the observed enthalpy change in the k th injection and Δm is the change in molarity. The CAC can be determined from the first peak in the difference enthalpy plot, whereas C_2 is defined when the difference curve becomes zero. The difference curve for titrating 0.2 M SDS into 0.2 wt% HEUR $C_{16}51K$ is shown by the insert in Figure 8.4. CAC and C_2 were determined to be 2.7 mM and 16.7 mM respectively. The CAC of HEUR $C_{16}51K$ /SDS system is smaller than that for PEO/SDS system (~ 4.2 mM), which indicates that the hydrophobic modification of PEO chains with a C_{16} alkyl chains enhances the polymer/SDS interaction. Based on the expressions below [Goddard 1993],

$$\Delta G = (1+\beta) RT \ln (CAC) \quad (8.5)$$

$$\Delta G = \Delta H - T\Delta S \quad (8.6)$$

The factor of $(1+\beta)$ accounts for the electrostatic interactions observed for ionic surfactants, where β (micellar charge fraction) equals to 0.85 for SDS in this chapter. The thermodynamic parameters for the binding of SDS to the HEURC₁₆51K polymer at CAC were determined and summarized in Table 8.1. By comparing the thermodynamic parameters, it is evident that the formation of HEURC₁₆51K/SDS complex at CAC is driven by a gain in the entropy.

	CAC ^a	ΔH^b	ΔG	$T\Delta S$	C at $\Delta H_{\max}^a$	ΔH at $\Delta H_{\max}^b$	C_2^a
	(mM)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(mM)	(kJ/mol)	(mM)
Different Concentrations' SDS into 0.1wt% HEUR							
0.20M	2.7	2.2	-45.5	47.7	5.4	4.2	16.7
0.15M	2.7	2.1	-45.5	47.6	5.4	3.8	16.7
0.10M	2.7	2.0	-45.5	47.5	5.4	3.3	16.7
0.08M	2.7	2.2	-45.5	47.7	5.4	3.3	-
0.05M	2.7	2.1	-45.5	47.6	5.4	3.3	-
0.2M SDS into Different Concentrations' HEUR							
0.20%	2.7	2.3	-45.5	47.8	5.4	5.2	23.9
0.15%	2.7	2.3	-45.5	47.8	5.4	4.8	20.6
0.10%	2.7	2.2	-45.5	47.7	5.4	4.2	16.7
0.08%	2.7	2.2	-45.5	47.7	5.4	3.8	15.2
0.05%	2.7	2.2	-45.5	47.7	5.4	3.4	12.5
0.03%	2.7	2.2	-45.5	47.7	5.4	3.1	10.4
0.01%	3.2	2.1	-44.7	46.8	5.4	2.3	9.1

a: estimated error ± 0.05 mM

b: estimated error ± 0.1 kJ/mol

Table 8.1 Thermodynamic parameters for SDS titration HEURC₁₆51K at 25 °C and 1 atm.

The titration curves of different concentrations of SDS into 0.1 wt% HEURC₁₆51K are shown in Figure 8.5. It is obvious that the CAC, C_2 and the titration curves are not affected by titrant (SDS) concentration. The slight fluctuations

observed in the titration curves maybe due to slight variations in the ΔH for different SDS concentrations. Since the CAC corresponds to the onset of HEUR/SDS complex formation, it should only be sensitive to the hydrophobicity of the solubilized polymer segments, the HLB of the surfactant, and the total free SDS monomer concentrations in the titration cell, but independent of the titrant (SDS) concentration. At a constant HEUR concentration, the total number of binding sites remains constant. The saturation concentration C_2 only depends on the concentration of SDS in the titration cell, but not the titrant (SDS) concentration. The thermodynamic properties for titrating different concentrations of SDS into 0.1 wt% HEURC₁₆51K solution are summarized in Table 8.1.

Figure 8.5 The isothermal titration curves for titrating different concentrations of SDS into 0.1 wt% HEURC₁₆51K at 25°C and 1atm.

The titration of 0.2 M SDS into different concentrations of HEURC₁₆51K was performed to examine the effects of HEUR concentration on the binding

characteristics between SDS and HEUR. From Figure 8.6, it is evident that the CAC, the ΔH at CAC and the SDS concentration at the maximum of the endothermic peak are independent of HEUR concentration, while the area for the endothermic peak increases with increasing HEUR concentration. The CAC is not sensitive to the total HEUR concentration. However, with increasing HEUR concentration, the binding reactions increase proportionately. This leads to an increase in the binding enthalpy changes as indicated by the increase in the area of the endothermic curve. The related thermodynamic parameters are summarized in Table 8.1.

Figure 8.6 The isothermal titration curves for titrating 0.2 M SDS into different concentrations of HEURC₁₆51K at 25°C and 1 atm.

It is evident from Figure 8.6 that the exothermic peak and C_2 shift to higher SDS concentration with increasing HEUR concentration. The difference between C_2 and CAC, i.e. (C_2 -CAC), approximately represents the amount of SDS needed to saturate the HEUR chains. The area under the endothermic and exothermic curves

becomes larger with increasing HEUR concentration. At higher HEUR concentrations, the total number of HEUR chains in the titration cell is high and larger amounts of SDS are needed to saturate the HEUR chains. A plot of C_2 vs. HEUR concentration revealed that C_2 increase linearly with HEUR concentration, i.e., $C_2 = 79.42[\text{HEUR}] + 8.45$. At HEUR concentration of 0, C_2 becomes 8.45 mM, which is closed to the CMC of SDS in water.

5.3.2 Dynamic light scattering

DLS of HEURC₁₆51K and SDS mixtures concentrations were examined with relaxation time distributions at different concentrations of SDS shown in Figure 8.7.

Figure 8.7 The relaxation time distribution functions of 0.1 wt% HEURC₁₆51K in different concentrations of SDS at 25°C.

Only one peak in the relaxation time distribution is evident when the SDS concentration is less than 2 mM. The peak corresponds to the translational diffusion of HEURC₁₆51K micelles. With increasing SDS concentration, the relaxation time distributions exhibit two distinct peaks. The relaxation times of the fast and the slow peak increase with SDS concentration until the SDS concentration reaches 20 mM. After that, a very fast mode appears. In this concentration range, the relaxation time of the fast and the slow peaks are independent of SDS concentration. The fast and the slow peaks in the relaxation time distributions are attributed to the translational diffusions of the SDS bound HEUR unimers and the HEUR/SDS micellar aggregation complexes respectively. The very fast peak at higher SDS concentration corresponds to the hydrodynamic radius of 1.5 nm, which is identical to the size of free SDS micelles.

The relationship of the apparent hydrodynamic radii of the slow modes, which represents the HEURC₁₆51K/SDS complex, and SDS concentration is shown in Figure 8.8. From the light scattering data, a microstructure for HEURC₁₆51K/SDS complex based on the aggregation mechanism as depicted in Figure 8.9 is proposed [Dai et al. 2001c, 2001d]. It is found that the apparent hydrodynamic radii (~ 40.7 nm) remain unchanged with increasing SDS concentration up to 2 mM. Beyond 2 mM, the hydrodynamic radii increase with SDS concentration, reaching an asymptote of ~ 220 nm at SDS concentration of ~20 mM.

Figure 8.8 The relationship between the apparent hydrodynamic radii and SDS concentration for 0.1 wt% HEURC₁₆51K and SDS (filled square). The open and filled circles are the thermograms for titrating 0.2 M SDS into water and 0.1 wt% HEURC₁₆51K at 25°C and 1 atm respectively.

Figure 8.9 The schematic diagram describing the binding interactions between SDS and HEUR at different concentrations of SDS.

In the absence of SDS, the 0.1 wt% HEUR_{C₁₆51K} are in the form of micelles as shown in Figure 8.9a. At SDS concentration lower than the CAC, SDS monomers un-cooperatively bind to the core of HEUR micelles (Figure 8.9b). The relaxation times and the hydrodynamic radii remain constant. With increasing SDS concentration, more and more SDS monomers are bound and the aggregation number of the synergism core increases. Since the aggregation number at 25 °C is 70 for SDS and lower than 70 for C₁₆H₃₃(OC₂H₄)_xOH (x is larger than 21), the aggregation number in the hydrophobic HEUR core cannot keep on increasing. Later, small amount of HEUR end C₁₆H₃₃ alkyl groups will be displaced by the tail groups of SDS monomers. Some HEUR chains are only replaced one end group and the other end group is still in the HEUR core, while small amount of HEUR chains are separated from the micelles with one ends exposed to the water phase (Figure 8.9c). When the SDS concentration exceeds the CAC of 2.7 mM, HEUR unimers are dehydrated from the water phase and solubilized into the SDS micellar core to form SDS bound HEUR unimers. This is represented by the fast relaxation mode with an apparent hydrodynamic radius of 9 nm which is fairly close to the hydrodynamic radius of ~ 9.5 nm for PEO chain of similar molecular weight. (The R_h of the PEO chain can be determined from $R_h = 0.0145M_w^{0.571}$.) [Alami et al. 1996] For the HEUR micelles, these exposed hydrophobic groups and the dehydrated PEO segments are solubilized by the polymer induced SDS mixed micelles, which form aggregates that grow in size yielding clusters of a few HEUR micelles as depicted in Figure 8.9d. The HEUR/SDS aggregation complex corresponds to the slow relaxation peak in the relaxation time distribution. Since the HEUR is in the dilute solution regime and the electrostatic repulsion from SDS micelles is strong, free HEUR end-groups are not able to form bridges with other HEUR micelles directly. Thus, the formation of the aggregation

complex must be driven by the solubilization of several “exposed” HEUR hydrophobic end groups by one SDS micelle. The CAC value determined from light scattering agrees with that determined from ITC technique. With increasing SDS concentrations, the SDS aggregation number will increase, giving rise to the increase in the relaxation times and the hydrodynamic radii for both fast and slow modes. When the SDS concentration exceeds 8 mM, the solubilized PEO segments re-hydrate and bind to the SDS micelles via ion-dipole association, and the structure re-organizes into a necklace-like conformation where the PEO chains wrap around the head groups of SDS micelles as indicated in Figure 8.9e. This re-organization results in the continuous increase in the SDS aggregation number. The cluster size increases from 150 to 220 nm when the SDS concentration is increased from 8 to 15 mM. At SDS concentration of 20 mM, all the HEURs are saturated by SDS micelles and free SDS micelles appear in the solution. This concentration is closed to the value of C_m as determined from ITC measurements. After that, both the hydrodynamic radii are independent of the SDS concentration.

8.3.3 Titration of HEUR_{C₁₆51K} into SDS Micellar Solution

As described above, the binding interactions between SDS and HEUR strongly depend on the SDS concentration. At low SDS concentrations, the aggregation complex is produced by the binding of SDS monomers to the polymer backbone. However, at high SDS concentrations, PEO segments on the HEUR backbones bind to the surface of SDS micelles through the ion-dipole associations to form the necklace-like aggregation complex. To verify this, the titration of HEUR into micellar SDS solution ($C_{SDS} \gg CMC$) was carried out. In the presence of excess SDS, hydrophobic end-groups of HEUR molecules are initially solubilized by SDS

micellar cores. The binding interactions between SDS and HEUR chains are similar to that reported for SDS and PEO molecules of similar molecular weight [Wang and Olofsson 1998; Goddard 1993; Brackman 1991; Brown et al. 1992; Dubin et al. 1992; Chari et al. 1994]. Before performing the titration of HEURC₁₆51K into SDS micellar solutions, the dilution behavior of 0.1 wt% HEURC₁₆51K in aqueous solution and the titration of 0.1 wt% HEURC₁₆51K into 7.5 mM SDS solution ($C_{\text{SDS}} < \text{CMC}$) were examined. Since the sensitivity of the Microcal ITC is 0.2 μCal , the measured heats for the above two titrations are lower than 0.2 μCal and thus reliable data cannot be obtained. The main factor for the extremely low heat is attributed to the high molecular weight of HEUR. However, based on the upper limit of 0.2 μCal , the maximum apparent ΔH of demicellization for 0.1 wt% HEURC₁₆51K in aqueous solution can be estimated, which are less than 5 kJ/mol.

Figure 8.10 The isothermal titration curves of titrating 0.1 wt% HEURC₁₆51K into different concentrations of SDS at 25°C and 1atm.

The thermograms for titrating 0.1 wt% HEUR_{C1651K} into different concentrations of SDS solutions are shown in Figure 8.10. The titration curves differ from those for the titration of SDS into HEUR. The apparent ΔH increases with increasing SDS concentration. The apparent binding enthalpy changes vary from 890 kJ/mol to 9405 kJ/mol, which is much larger than 5 kJ/mol for the maximum enthalpy changes of the demicellization of HEUR and the binding of SDS monomers to the HEUR hydrophobic end-groups. It is evident that the ΔH observed in the above titrations are related to the binding of SDS micelles to the PEO segments of HEUR through the ion-dipole association. The HEUR used in this study possesses a reasonably high molecular weight, and thus more than one SDS micelles can bind to one HEUR unimer chain. Supposing that one HEUR unimer chain contains n binding sites for SDS micelles, then the binding reaction between HEUR unimers and SDS micelles can be expressed by the equation below:

where $\{(1/n)\text{HEUR}\}$ represents one binding site in a HEUR unimer and the concentration of the binding site is n times of the HEUR concentration. The heat recorded by the ITC for HEUR titrating into SDS micellar solution is the apparent ΔH for one mole of HEUR injecting into the SDS micellar solution. If the fraction of binding sites bound to SDS micelles is assumed to be θ , then the apparent ΔH for per mole of HEUR injection is given by; $\Delta H = \frac{Q}{CV} = n\theta\Delta H_m$, where Q is the raw heat, C the titrant concentration and V the injection volume. For the binding reaction between SDS micelles and the binding sites, the binding constant, K and the molar binding enthalpy changes, ΔH_m , remained constant, but the fraction of binding sites bound to SDS micelles θ is strongly dependent on the concentrations of both SDS and HEUR.

At high SDS concentrations, larger amounts of SDS micelles are present in the titration cell. For a given HEUR concentration, the fraction of binding sites bound to SDS micelles θ increases with increasing SDS concentrations, which give rise to the larger ΔH .

Figure 8.11 The isothermal titration curves of titrating different concentrations of HEURC₁₆51K into 0.2 M SDS at 25°C and 1 atm.

Titration of eight different concentrations of HEURC₁₆51K into 0.2 M SDS were also performed and the titration thermograms are shown in Figure 8.11. The titration curves are similar to those for titrating 0.1 wt% HEURC₁₆51K into different concentrations of SDS, but the apparent binding ΔH decreases with increasing HEURC₁₆51K concentrations. The concentration of binding sites increases with increasing HEUR concentration, resulting in a corresponding reduction in the fraction

of sites bound to SDS micelles θ . The decrease in the fraction of binding sites gives rise to the decrease in the apparent binding enthalpy changes.

Combining the above two series of titration results, the relationship between the apparent enthalpy changes and the ratio of titrate and titrant concentrations, $[SDS]/[HEUR]$, is obtained and shown in Figure 8.12, where a simple relationship can be observed;

$$\Delta H = 0.94 \left(\frac{[SDS]}{[HEUR]} \right) - 503 \quad (8.7)$$

Figure 8.12 The relationship between the binding enthalpy changes and $[SDS]/[HEUR]$ for, (i) titration of different concentrations of HEURC₁₆51K into 0.2 M SDS (●), (ii) titrating 0.1 wt% HEURC₁₆51K into different concentrations of SDS (○) at 25°C and 1 atm.

Using equation 5.7, the apparent enthalpy changes per mole of HEUR injected into SDS micellar solution at any given ratio of $[SDS]/[HEUR]$ can be calculated. When $\Delta H \rightarrow 0$, the SDS concentration is estimated to be ~10.3 mM, which is slightly larger

than the CMC of SDS in aqueous solution. The critical concentration of 10.3 mM corresponds to onset point for the ion-dipole association between SDS micelles and the PEO segments of HEUR chains. This also reinforces that the binding interaction between SDS micelles and HEUR chains at high SDS concentration is different from that of SDS monomers and HEUR chains at low SDS concentration. In the former (high SDS concentrations), SDS micelles bind to the PEO backbone due to the ion-dipole association, while for the later (low SDS concentrations), SDS monomers cooperatively bind to the end groups and the dehydrated PEO segments of HEUR chains due to the hydrophobic association.

8.4 Effect of HEUR Specifications on the Binding Interaction

8.4.1 Electromotive force studies

The electromotive force (EMF) values of the surfactant membrane electrode as a function of total SDS concentration relative to the bromide electrode in the absence (open circle) and the presence of HEUR (filled circle) in solution were determined and shown in Figure 8.13. Figure 8.13a compares the dependence EMF on SDS concentration in the absence and presence of 0.1 wt% HEUR-C₁51K. At SDS concentration lower than 2.5 mM, the EMF values are identical, and beyond this concentration, they begin to deviate until the concentration of 17.5 mM, where they merge again. The onset for this deviation corresponds to the critical aggregation concentration (CAC) for the cooperative binding between HEUR chains and SDS, and the end point is related to the saturation concentration C_2 . Figures 8.13b and 8.13c show the dependence of EMF on SDS concentrations in the presence of 0.1 wt% HEUR-C₁₂51K and HEUR-C₁₆51K in aqueous solutions respectively. It is evident that the EMF curves of HEUR-C₁₂51K and HEUR-C₁₆51K are different from that of

HEUR-C₁51K. Besides the CAC for the cooperative binding between SDS and HEUR, the non-cooperative binding between SDS monomers and the hydrophobic domains of HEUR-C₁₂51K aggregates was detected, where the onset concentration for such binding (C_{UB} as shown in Figure 8.13b) was observed to be much lower than CAC, and possesses a value of ~ 0.4 mM. The C_{UB} for HEUR-C₁₆51K is significantly lower due to the more hydrophobic C₁₆H₃₃ alkyl chains and is not detectable within the SDS concentration measured. However, the saturation concentrations C_2 of the three HEUR solutions are identical.

Bloor and coworkers reported the temperature dependence of the binding interactions between SDS and Pluronic copolymer F127 or L64 [Li et al. 2000a; 2001; Xu 2001], and they found that the EMF curves in water and polymer solutions merged at low SDS concentrations for temperatures lower than the critical micelle temperatures (CMT) of F127 and L64. However, the two EMF curves no longer merged beyond the CMT and this was attributed to the fact that the onset of non-cooperative binding occurred at very low concentrations [Li et al. 2000b; Xu 2001]. At low temperatures where the hydrophobicity of PPO segments is not strong enough, Pluronic micelles are absent in solution, thus only cooperative binding between SDS molecules and Pluronic copolymer chains occurs. At high temperatures, where Pluronic micelles are present in solution, monomeric SDS molecules non-cooperatively bind to Pluronic micelle first, giving rise to the divergence in the EMF curves at SDS concentrations lower than CAC. The onset of non-cooperative binding leading to the deviation of the EMF curves at lower surfactant concentration is also evident for ionic surfactants and oppositely charged polyelectrolytes in solution [Wang 2004; Wang and Tam 2004]. For HEUR with only methyl group substitution such as HEUR-C₁51K, such aggregates are absent and the solution properties are

identical to PEO in water. Hence, cooperative binding of SDS to HEUR-C₁₅1K chains via the polymer-induced micellization process dominates at CAC. With increasing length of hydrophobic end-capped segments, the unimeric HEUR chains associate to produce aggregates or micelles in solution. The non-cooperative hydrophobic binding between SDS monomers and the hydrophobic core occurs at extremely low SDS concentration, which gives rise to the trends observed in Figures 18.3b and 18.3c at C_{UB}. The non-cooperative binding between monomeric SDS and the HEUR micellar core at lower concentration has been discussed in our earlier publications [Dai et al. 2001c]. The hydrophobicity of HEUR-C₁₆51K is stronger than that of HEUR-C₁₂51K, which gives rise to the closed association for the former and the open associate for the latter in dilute aqueous solution. Due to the fact that the micellar core of HEUR-C₁₆51K is more hydrophobic, the onset of non-cooperative hydrophobic binding for HEUR-C₁₆51K/SDS system is lower and not detectable over the concentration range investigated. At low SDS concentrations, HEUR micelles or aggregates are stable in solution and the non-cooperative bound SDS could not disrupt the formed structure [Annable et al. 1994b; Dai et al. 2001c]. As SDS concentration reaches the CAC, the cooperative binding between SDS and these HEURs commences, producing a sharp transition in the EMF curves. The EMF measurements of SDS in 0.1 and 0.2 wt% HEUR solutions were conducted, where the CAC is independent of HEUR concentration but C₂ increases with polymer concentration (Table 8.2).

Figure 8.13 The SDS concentration dependence of EMF values on total SDS concentrations at 298 K and 1 atm. The open circle is for SDS in water and the filled circles are for SDS in 0.1 wt% of (a) HEUR-C₁₂51K; (b) HEUR-C₁₂51K and (c) HEUR-C₁₆51K. The inserts are monomeric SDS concentrations versus total SDS concentration.

HEUR Name	Molecular Weight	Capped Hydrophobes	x	Length of PEO	[HEUR] (wt%)	[SDS] (M)	EMF Measurement				SDS Titration into HEUR				n	M* ^c	EO* ^d	ΔH^e (kJ/mol)
							CAC (mM)	C ₂ (mM)	C _{DS} ^a (mM)	CAC (mM)	C ₂ (mM)	CAC (mM)	ΔG_{ps}^b (kJ/mol)					
							HEUR Titration into SDS											
HEUR-C ₁₆ -18K	17500	C ₁₆ H ₃₃	2	360	0.2	0.2	3.1	26	2.6	2.7	29.6	-5.1	3.6	4815	99	1513		
HEUR-C ₁₆ -34K	34200	C ₁₆ H ₃₃	4	720	0.2	0.2	3.1	26	2.6	2.7	29.6	-5.1	7.1	4815	101	3206		
HEUR-C ₁₆ -51K	51000	C ₁₆ H ₃₃	6	1080	0.2	0.2	3.1	26	2.5	2.7	28.9	-5.1	10.4	4924	104	4659		
HEUR-C ₁₆ -68K	67600	C ₁₆ H ₃₃	8	1440	0.2	0.2	3.1	26	2.5	2.7	27.8	-5.1	13.2	5138	109	6306		
HEUR-C ₁₆ -84K	84300	C ₁₆ H ₃₃	10	1800	0.2	0.2	3.1	26	2.6	2.7	28.3	-5.1	16.7	5058	108	7817		
HEUR-C ₁₆ -100K	100400	C ₁₆ H ₃₃	12	2160	0.2	0.2	3.1	26	2.6	2.7	29.6	-5.1	20.9	4815	104	9246		
HEUR-C ₁ -51K	50200	CH ₃	6	1080	0.2	0.2	2.5	26	2.6	2.7	29.2	-5.1	10.3	4887	105	4651		
	50200	CH ₃	6	1080	0.1	0.2	2.5	17	2.9	2.7	17.9	-5.1	11.6	4333	93	9263		
HEUR-C ₁₂ -51K	50700	C ₁₂ H ₂₅	6	1080	0.2	0.2	3.1	26	2.7	2.7	28.9	-5.1	10.2	4962	106	4670		
	50700	C ₁₂ H ₂₅	6	1080	0.1	0.2	3.0	18	2.8	2.7	17.9	-5.1	11.8	4305	92	9263		
HEUR-C ₁₆ -51K	51000	C ₁₆ H ₃₃	6	1080	0.2	0.2	3.1	26	2.5	2.7	28.9	-5.1	10.4	4924	104	4659		
	51000	C ₁₆ H ₃₃	6	1080	0.1	0.2	3.0	17	2.7	2.7	17.9	-5.1	11.9	4276	91	9269		

a: Free monomeric SDS concentration at C₂.

b: $\Delta G_{ps} = 1.85RT \ln(CAC/CMC)$

c: M* = (molecular weight)/n

d: EO* = (total EO number)/n

e: ΔH obtained from the first several injections where enthalpies are independent of HEUR concentrations

Table 8.2 Characteristics of HEUR polymers and the binding parameters obtained from isothermal titration calorimetry and electromotive force measurements at 298 K and 1 atm.

The free monomeric surfactant concentration during the binding process could be obtained from EMF measurements. For the cell containing SDS selective electrode and bromide reference electrode, the potential can be described by the Nernst relationship,

$$E = E_0 - \frac{RT}{nF} \ln \left(\frac{a_{DS^-}}{a_{Br^-}} \right) = E_0 - \frac{RT}{nF} \ln \left(\frac{C_{DS^-} \gamma_{DS^-}}{C_{Br^-} \gamma_{Br^-}} \right) \quad (8.8)$$

where E_0 is the standard cell potential, R the gas constant, T the absolute temperature, F the Faraday constant, n the charge number of the ion ($n = 1$ in this case), a_i and γ_i are the activity and activity coefficient of ion in solution respectively. Since the activity coefficients of mono-valent ions with similar charge are approximately equal, Eq. (8.8) can be rewritten as,

$$E = E_0 - \frac{RT}{F} \ln \left(\frac{C_{DS^-}}{C_{Br^-}} \right) = E_0 + \frac{RT}{F} \ln(C_{Br^-}) - \frac{RT}{F} \ln(C_{DS^-}) = E_1 - \frac{RT}{F} \ln(C_{DS^-}) \quad (8.9)$$

Since the SDS selective electrode is only sensitive to the SDS monomer in solution, the monomeric surfactant concentration could be determined from Eq. (8.9). At low surfactant concentration where all surfactant molecules are in the monomeric form ($C < \text{CMC}$), E_1 and k ($= RT/F$) could be determined by fitting Eq. (8.9) to the linear region of the data. Therefore, the monomeric concentration of SDS during the binding or micellization process could be determined from Eq. (8.10),

$$C_{DS^-} = e^{\left[\frac{E_1 - E}{k} \right]} \quad (8.10)$$

The inserts in Figure 8.13 show the relationship between the SDS monomer concentration and total SDS concentration in solution. For SDS micellization process, it is evident that SDS monomer concentration increases and then decreases after CMC. However, for SDS/HEUR binding process, SDS monomer concentration

increases progressively and merges with the equilibrium value for SDS in water beyond C_2 .

The EMF measurements for SDS and different molecular weights HEUR solutions were conducted and the trends are shown in Figure 8.14a. The SDS monomer concentrations during the binding processes are shown in Figure 8.14b. It was observed that the polymer molecular weights have negligible effects on the binding isotherms as well as the SDS monomer concentrations, and this will be discussed later. The numerical data from EMF measurements are summarized in Table 8.2.

Figure 8.14 (a) The relationship between EMF values and SDS concentrations for 0.2 wt% HEURs with different molecular weights (end-capped with $C_{16}H_{33}$ alkyl chains) at 298 K and 1 atm. (b) The monomeric SDS concentrations for the binding interaction between SDS and 0.2 wt% HEURs with different molecular weights at 298 K and 1 atm.

8.4.2 Micellar SDS titrating into HEUR solutions

From our earlier studies using laser light scattering and ITC, the binding enthalpy thermograms and binding mechanisms for titrating SDS micellar solutions into HEUR and that of HEUR into SDS micellar solutions were found to be different [Dai et al. 2001c]. The titration of micellar SDS into HEUR solutions is discussed here, while the titration of HEUR into SDS micellar solutions will be discussed in next section. When micellar SDS was titrated into HEUR solutions, SDS micelles first

demicellize into SDS monomers and these SDS monomers bind to HEUR chains in a not cooperative manner at low SDS concentration. Beyond the critical aggregation concentration (CAC), the SDS/HEUR mixed micellar aggregates appear in solution, where the PEO segments in the HEUR backbones will be removed from the water phase, and these dehydrated PEO segments and hydrophobic groups of HEUR molecules are then solubilized into the hydrophobic core of SDS mixed micelles. With further increase in SDS concentration, the aggregation number of SDS in the mixed micelles increases and the SDS/HEUR aggregation complex re-organizes itself. The solubilized PEO segments are removed from the hydrophobic SDS micellar core into the water phase due to their amphiphilic properties. These rehydrated PEO segments then bind to the hydrophilic surface of SDS micelles via the ion-dipole interaction to produce necklace-like SDS/HEUR complexes. The aggregation number of SDS and the size of the SDS/HEUR complex continue to increase. At C_2 , the binding interactions between SDS and HEUR reach a saturation point and no further binding of SDS occurs. At C_m , free SDS micelles are formed in solution and they co-exist with SDS/HEUR aggregation complexes. For the SDS/HEUR system, free SDS micelles are formed after the saturation condition, i.e., C_m is larger than C_2 .

Figure 8.15 shows the ITC thermograms of titrating 0.2 M SDS into 0.2 wt% HEUR (end-capped with $C_{16}H_{33}$) polymer solutions with different molecular weights. The dilution curve of 0.2 M SDS in water is represented by the open circle. The transition point of the SDS dilution curve corresponds to the critical micelle concentration (CMC) of SDS in aqueous solution with a value of 8.3 mM. The difference between the titration curve and SDS dilution curve is attributed to the polymer/surfactant interaction. The ITC thermograms for titrating SDS into HEUR solutions show an endothermic peak at low SDS concentration and an exothermic

peak at high SDS concentration comparing to the SDS dilution curve, which are identical to that observed for SDS/PEO system. The endothermic and exothermic peaks are mainly related to the dehydration and the rehydration of PEO segments respectively, yielding different types of SDS/HEUR aggregation complexes at different SDS concentrations. The determination of CAC and C_2 was based on the approach described previously, where the CAC represents the concentration for the sharp increase in ΔH , and C_2 corresponds to the concentration where the titration curve merges with the SDS dilution curve. For all the HEUR polymers used in this study, the CAC was determined to be ~ 2.7 mM, which is independent of polymer molecular weight, while the C_2 values are also identical when the polymer molecular weight exceeds 17500 g/mol. The values of CAC and C_2 are summarized in Table 8.2. It is obvious that both critical values obtained from ITC agree well with those from EMF measurements. However, the heat of the non-cooperative binding is too low to be detected by ITC. In addition, introduction of polymers into aqueous solution also shifts the solvent quality. Hence, ITC could not provide further information on the non-cooperative binding process.

Figure 8.15 ITC thermograms for titrating 0.2 M SDS into 0.2 wt% HEURs (end-capped with $C_{16}H_{33}$ alkyl chains) with different molecular weights at 298 K at 1 atm. The open circle represents the dilution curve of 0.2 M SDS in water.

The CAC corresponds to the onset for the formation of SDS/HEUR mixed micelles cooperatively, where the PEO segments in the HEUR backbone are removed from water. The dehydrated PEO segments and the HEUR end-capped alkyl groups are solubilized into the core of SDS mixed micelles dominated by hydrophobic interaction. The Gibbs energies for the surfactant micellization and cooperative binding process could be described by the following equations [Attwood and Florence 1983; Lindman and Thalberg 1993],

$$\Delta G_{mic} = (1 + \beta)RT \ln(CMC) \quad (8.11)$$

$$\Delta G_{agg} = (1 + \beta)RT \ln(CAC) \quad (8.12)$$

where Eqs. (8.11) and (8.12) are for micellization and cooperative binding processes for ionic surfactant respectively, where β is the micellar charge fraction with the value

of 0.85 for SDS [Wang and Olofsson 1998]. Both the CMC and CAC are in the unit of mole fraction. The Gibbs energy required for driving one mole of free SDS micelles into the SDS/HEUR aggregation complex can be calculated from the expression:

$$\Delta G_{ps} = \Delta G_{agg} - \Delta G_{mic} = (1 + \beta)RT \ln \left(\frac{CAC}{CMC} \right) \quad (8.13)$$

From the values of ΔG_{ps} shown in Table 8.2, it is evident that the formation of SDS/HEUR aggregates at CAC is a thermodynamically favorable process since the ΔG_{ps} is negative. The entropy changes associated with the formation of SDS/HEUR aggregates can also be evaluated from the second law of thermodynamics, where;

$$\Delta S_{agg} = \frac{\Delta H_{agg} - \Delta G_{agg}}{T} \quad (8.14)$$

It is evident that the cooperative aggregation process at CAC is an entropic driven process, where ΔH_{agg} is positive and the contribution to the Gibbs energy is dictated by the magnitude of $T\Delta S$.

From previous studies on SDS/PEO systems, the interactions between SDS and PEO were independent of molecular weights for MW of PEO greater than 8000 [Gao et al. 1991; Goddard 1993; Wang and Olofsson 1998]. From Figure 8.15, the CAC for SDS/HEUR system is independent of molecular weights for M_n ranging from 17500 to 100400 g/mol. This suggests that the polymer-surfactant interaction is only dependent on the local concentration of dehydrated EO segments and the hydrophobicity of the HEUR chains, but not the total length of the polymer chains i.e. the molecular weight. However, the CAC value for SDS/HEUR system (2.7 mM) is lower than that for the PEO/SDS system (4.2 mM) [Wang and Olofsson 1998]. Since the CAC corresponds to the onset for the cooperative formation of SDS/HEUR mixed micelles through hydrophobic interactions, it is strongly dependent on the

hydrophobicity of the solubilized segments. Due to the fact that the HEUR chains are more hydrophobic than PEO chains, the HEUR polymers have an impact on the binding interactions and CAC values, which is also observed for SDS/(PPO-PEO-PPO) copolymers and SDS/(C₁₂EO₂₀₀C₁₂) system [Dai et al. 2001b; Persson et al. 1994].

Based on the EMF measurements, the SDS monomer concentration during the binding process could be determined. The value of (C₂ – C_{DS-}) represents the total amount of bound SDS molecules on the polymer chains, where C_{DS-} represents the monomeric SDS concentration at C₂. A smaller value of (C₂ – C_{DS-}) corresponds to a lower binding capacity of the polymer chains. We observed identical C₂ and C_{DS-} values for SDS and HEURs of different molecular weights as shown in Table 8.2, which suggests that the binding capabilities of these HEUR polymers are identical. If the aggregation number of SDS in the SDS/HEUR complexes at saturation concentration C₂ is N_{agg} and the molar concentration of HEUR is C_{HEUR}, the number of bound SDS micelles per HEUR chain, n, can be approximated by the expression [Cabane and Duplessix 1982]:

$$n = \frac{C_2 - C_{DS-}}{N_{agg} C_{HEUR}} \quad (8.15)$$

It was reported that the average aggregation number of SDS at saturation concentration C₂ for a SDS/PEO system is about 60 ~ 70 [van Stam et al. 1991; Zana et al. 1985]. Assuming that the aggregation number N_{agg} of each micelle for SDS/HEUR system is 65, the estimated number of micelles per HEUR chain can be determined using Eq. (8.15), where n increases from ~ 3 to ~ 20 when the MW of HEUR chain increases from 17500 to 100400 g/mol (see Table 8.2). The value of M* [= (MW)/n] corresponds to the averaged apparent molecular weight of HEUR

segment per SDS micelle in the SDS/HEUR complex. M^* also refers to the equivalent length of HEUR chain bound to one SDS micelle, which we referred to as the basic binding segment. The value of M^* was determined to be between 4000 to 5000 g/mol (see Table 8.2), which is close to the observed value of 3500 to 4000 (minimum MW required for SDS/PEO ion-dipole association) reported previously [Dai and Tam 2001]. We concluded that C_2 is only sensitive to the concentration of these basic binding segments, and not on the total HEUR concentration and chain length. At the fixed weight percentage of polymer, increasing polymer molecular weight produces long polymer backbone but lower HEUR chain number. However, the number or the concentration of the basic binding segments and C_2 remain constant.

Figure 8.16 shows the isothermal titration thermograms for titrating 0.2 M SDS into 0.2 wt% (open symbols) and 0.1 wt% (closed symbols) HEUR of similar molecular weights but different alkyl modified end-capped hydrophobes. The open circle represents the dilution of 0.2 M SDS into water. It is evident that the titration curves of SDS into HEUR solutions at a fixed concentration are not very much influenced by the size of end-capped hydrophobes. The values of CAC and C_2 are listed in Table 8.2.

Figure 8.16 ITC thermograms for titrating 0.2 M SDS into 0.1 wt% (closed symbols) and 0.2 wt% (open symbols) HEUR solutions containing different end-capped hydrophobic groups at 298 K and 1 atm. The open circle represents the dilution curve of 0.2 M SDS in water.

As discussed previously, the CAC decreases from 4.2 mM for SDS/PEO system to 2.7 mM for SDS/HEUR system, and this is attributed to the more hydrophobic HEUR chains. However, the values of CAC for the SDS/HEUR system with different hydrophobic modified groups are identical, and this means the length of the hydrophobic end groups (CH_3 to $\text{C}_{16}\text{H}_{33}$) does not alter the CAC. As the end groups are significantly hydrophobic, micelles or aggregates are produced in solution and SDS monomers bound non-cooperatively to the hydrophobic core at low SDS concentration as evident from EMF measurements. However, there is no aggregation and no non-cooperative binding for HEUR with CH_3 segments. Based on these experimental data, it is evident that the end-capped hydrophobes only induces non-cooperative binding, but the cooperative binding at CAC is influenced by the

hydrophobicity of the whole polymer chain. From the chemical structure, the hydrophobic segments of HEUR are comprised of several urethane groups on the PEO backbone and the alkyl chains at both ends of the HEUR chains. These hydrophobic segments make HEUR more hydrophobic than PEO chains, which contribute to the reduction in the CAC values. However, for HEURs with strong hydrophobic end groups, aggregates or micelles are formed in solution and SDS monomers could non-cooperatively bind to their hydrophobic core at low SDS concentrations. Both effects together with the long PEO segments decrease the effects of these end-capped segments on the cooperative binding process, and the urethane groups on the polymer backbones increase the polymers hydrophobicity and promote cooperative binding between SDS and HEUR. The value of (C_2-C_{DS-}) for SDS/HEUR system is larger than that for SDS/PEO system due to the smaller CAC, which implies that the binding capability of SDS/HEUR system is enhanced by the increased hydrophobic characteristics of the whole polymer chains.

From Figure 8.16, it is also evident that the CAC is independent of HEUR concentration, but C_2 increases with increasing HEUR concentrations. The concentration dependence of the binding interactions between SDS and HEUR can be described using a phase diagram. Figure 8.17 shows the phase diagram of SDS/HEUR- $C_{16}51K$ system as determined from ITC experiments. The non-cooperative binding between SDS and HEUR occurs in Region I. Region II corresponds to the SDS/HEUR complex generated by the polymer-induced micellization process. The CAC (represented by the open diamonds) is weakly dependent on polymer concentrations. Region III, with onset point determined from the cross point between SDS dilution SDS into HEUR solution, indicates the structural reorganization and formation the SDS/HEUR complex through the ion-

dipole association process. Region IV represents the saturated necklace-like SDS/HEUR complex co-existing with SDS monomers in solution. It is evident that C_2 is strongly dependent on the polymer concentration. Increasing the HEUR concentration also increases the concentrations of the basic binding segments and thus the saturation concentration shifts to higher SDS concentration. In Region V, SDS/HEUR aggregation complex co-exists with free SDS micelles. The value of ($C_m - C_2$) is smaller than the value of CMC of SDS in water (~ 8.3 mM) due to the presence of polymer chains in solution.

Figure 8.17 Phase diagram of SDS/HEUR- $C_{16}51K$ system in water at 298 K. Region I for non-cooperative binding between SDS monomer to HEUR; Region II for SDS/HEUR complex formed by polymer-induced micellization process and the delineating line represents the CAC; Region III for SDS/HEUR complex formed by ion-dipole association; Region IV for SDS unimers and the saturated SDS/HEUR complex and the delineating line represent C_2 ; Region V for SDS unimers co-existing with SDS/HEUR saturated complex, while the line indicates C_m .

8.4.3 Binding mechanisms.

From the EMF and ITC measurements, the binding mechanisms between SDS and different HEURs could be elucidated in Figure 8.18. HEUR-C₁51K is fairly similar to PEO except for the urethane linkage, which makes the backbone slightly more hydrophobic. The HEUR chains predominantly exist as unimers, and the binding interaction is identical to SDS/PEO system (Figure 8.18a). Since the hydrophobicity of linear HEUR chains is greater than PEO due to the urethane groups, the onset of cooperative binding (CAC) is lower. At $C \sim CAC$, polymer-induced SDS mixed micelles are formed first, followed by the formation of SDS/HEUR aggregation complexes through ion-dipole association, where the re-hydrated HEUR backbones are bound to the outer surface of the SDS hydrophilic head groups. For HEUR-C₁₂51K, polymer clusters are produced via the open association mechanism (Figure 8.18b). The hydrophobic domains consisting of several C₁₂H₂₅ segments induce the SDS monomers to bind non-cooperatively to these hydrophobic domains at C_{UB} . When the SDS concentration approaches CAC, cooperative binding between SDS and the HEUR backbones occurs, producing an obvious transition in the EMF curve. For HEUR-C₁₆51K, the -C₁₆H₃₃ segments are sufficiently hydrophobic to produce flower-like micelles in solution. The introduction of minute amounts of SDS monomers produces non-cooperative binding of SDS monomers to the hydrophobic core of flower micelles as shown in Figure 8.18c at $C_{UB} < c < CAC$. Compared to SDS/HEUR-C₁₂51K system, the onset of non-cooperative binding is significantly and is not detectable using the EMF measurements. The onset of cooperative binding at CAC could be determined from the transition point in the EMF figure. After CAC, the binding mechanisms of SDS/HEUR-C₁₂51K and SDS/HEUR-C₁₆51K are similar to that of SDS/HEUR-C₁51K.

Figure 8.18 The schematic plot for the binding interactions between SDS and HEURs with different hydrophobic end-capped groups.

The binding behaviors between SDS and HEUR can be divided into three concentration regimes, which can be identified using the combination of EMF and ITC techniques. The non-cooperative binding may occur at very low SDS concentrations, depending on character of hydrophobic substitutions. The non-cooperative binding process results in very small enthalpy change not detectable by the sensitive ITC technique, and is not evident from the ITC thermograms. When the SDS concentration reaches CAC, cooperative binding between SDS and HEUR occurs, and HEUR chains are dehydrated from the water phase to form mixed

micelles. This cooperative process is observable from both ITC and EMF measurements. With further increase in SDS concentration, the aggregation number of SDS in mixed micelles increases, which results in the rehydration of HEUR segments into water phase. These rehydrated HEUR segments are bound to the surface of SDS micelles through the ion-dipole interaction. Since EMF is only sensitive to the monomeric SDS concentration during the binding process and the monomeric SDS concentrations do not change much during this structural re-organization, such transition is only observable from ITC thermograms, and not from EMF measurements.

8.4.4 Titration of HEUR into micellar SDS solution

Previous sections focused on the titration of small amounts of micellar SDS solutions into various HEUR solutions, where ITC detects the differential enthalpy associated with the SDS/HEUR binding interactions in excess amounts of HEUR. Due to the fact that different binding processes for SDS/HEUR system is SDS concentration dependent, the interaction between excess amount of SDS and small amount of HEUR was investigated. In this section, titrations of HEUR into micellar SDS solutions were examined, where the amounts of SDS micelles are in excess and HEUR chains only bind to the surface of SDS micelles via the ion-dipole association to produce the necklace-like SDS/HEUR aggregation complexes [Cabane and Duplessix 1982; Goddard 1993; Kwak 1998]. Figure 8.19 shows the thermograms of titrating 0.2 wt% HEURs of different molecular weights into 0.2 M SDS solutions at 298 K. It is evident that the binding thermograms are different from that of titrating micellar SDS solution into dilute HEUR solutions. This reinforces the fact that

different binding mechanism must be in operation under each condition. In addition, the apparent binding enthalpies increase with increasing polymer molecular weights.

Figure 8.19 ITC thermograms for titrating 0.2 wt% HEURs with different molecular weights (end-capped with $C_{16}H_{33}$ alkyl chains) into 0.2 M SDS solutions at 298 K and 1 atm.

If one HEUR chain could bind to n SDS micelles (i.e. one HEUR chain contains n basic binding segments) and one basic binding segment only binds one SDS micelle, the binding interactions between SDS and HEUR molecules can be described by following equation:

The apparent enthalpy detected by ITC, ΔH_{obs} , is the enthalpy per mole of HEUR chain. If the binding fraction for the HEUR basic binding segments is θ and the binding heat detected by ITC is Q , then;

$$\Delta H_{obs} = \left(\frac{\partial Q}{\partial n_{HEUR}} \right)_{T,P,n_{SDS}} = n\theta \Delta H_m \quad (8.16)$$

Since the enthalpy for the binding of one SDS micelle to one basic binding segment, ΔH_m , is a constant, and the changes in the apparent enthalpy indicate that the binding capacity ($n\theta$) varies with polymer molecular weight. A linear relationship between the apparent enthalpies and HEUR molecular weight is shown in Figure 8.20, which indicates the binding enthalpies or the binding capacities ($n\theta$) increase linearly with polymer molecular weights.

Figure 8.20 The relationship between the apparent molar binding enthalpies and the molecular weights of HEURs (end-capped with $C_{16}H_{33}$ alkyl chains) for the titration of 0.2 wt% HEURs with different molecular weights into 0.2 M SDS solutions at 298 K and 1 atm.

The numbers of basic binding segment, n could be determined from the titration of SDS into HEUR solutions as discussed previously. If the numbers of the

basic binding segment, n as listed in Table 8.2 are used, it was found that the values of $\Delta H_{\text{obs}}/n$ ($= \theta \Delta H_{\text{m}}$) for 0.2 wt% HEUR are independent of polymer molecular weights, with an averaged value of 450 ± 30 kJ/mol, which indicates that θ does not change with HEUR molecular weights for a fixed SDS and HEUR concentrations (wt%) or the main contribution to the increase in the enthalpy with HEUR molecular weight is only correlated to the increase in the number of basic binding segments n .

It was observed that ΔH_{obs} decrease linearly with HEUR concentrations when titrating different concentrations of HEUR-C₁₆51K into 0.2 M SDS [Dai et al. 2001c]. Since the basic binding segment n remains constant, the values of $\Delta H_{\text{obs}}/n$ are inversely proportional to HEUR concentration, which suggests that the binding fraction θ decreases with increasing titrant polymer concentrations. From Figure 8.19, it is apparent that the ΔH_{obs} initially remains constant and begins to decrease when the amounts of HEUR in the SDS solution exceeds a critical value. The onset for the decrease in ΔH_{obs} is also attributed to the decrease in the binding capacity ($n\theta$) or binding fraction θ .

Figure 8.21 shows the thermograms for titrating 0.1 wt% (open symbols) and 0.2 wt% (closed symbols) HEUR with different hydrophobes into 0.2 M SDS solution. The apparent enthalpies for these titrations at a given polymer concentration are identical, which indicates that the size of the hydrophobes does not affect the binding interactions between HEUR and SDS micelles. This again confirmed that the interaction between HEUR chains and excess amount of SDS micelles is dominated by the PEO basic binding segments and not on the hydrophobic moieties.

Figure 8.21 ITC thermograms for titrating 0.1 wt% (closed symbols) and 0.2 wt% (open symbols) HEURs with different hydrophobic end capped alkyl groups into 0.2 M SDS aqueous solutions at 298 K and 1 atm.

Figure 8.22 Effects of SDS concentrations on the titration of 0.1 wt% HEUR-C₁₅₁K into different concentrations of SDS solutions at 298 K and 1 atm.

Figure 8.23 The relationship between the apparent molar binding enthalpies and the SDS concentrations for the titration of 0.1 wt% HEUR- $C_{151}K$ into SDS at 298 K and 1 atm.

To examine the effects of SDS concentrations on the above binding interaction, we titrated 0.1 wt% HEUR solution into different concentrations of SDS solutions. Figure 8.22 shows the ITC thermograms for the titration of 0.1 wt% HEUR- $C_{151}K$ solution into different SDS micellar solutions. The apparent binding enthalpies increase with SDS concentrations. Due to the higher molecular weights of HEUR and resolution of the macrocalorimeter, the dilution heat of HEUR- $C_{151}K$ and the binding heat between HEUR- $C_{151}K$ and monomeric SDS are too low to be accurately determined while titrating HEUR into SDS. The relationship between the apparent enthalpy and SDS concentration is shown in Figure 8.23. The linear relationship is evident, which is similar to that observed for HEUR- $C_{1651}K$ and SDS system. For a certain concentration of HEUR polymer chain, n and ΔH_m are constants. Hence, the

slope determined from Figure 8.23 is proportional to the dependence of the binding fraction on SDS concentrations, or $d\theta/d[\text{SDS}]$. The increase in the apparent binding enthalpies with increasing SDS concentrations is due to the increase in the binding fraction θ . The intercept at x -axis is 11.1 mM, which is larger than the CMC of SDS in aqueous solution. This reinforces that the present binding process only occurs when the SDS molecules are in the micellar form resulting in the formation of necklace like aggregation complex.

8.5 Summary

Static and dynamic light scattering data reinforced that the HEUR is in the form of rosette micelles. The enthalpy changes and the thermograms for SDS titrating into HEUR and HEUR titrating into SDS were measured. The difference in both types of titrations is attributed to the different binding mechanisms at different SDS concentrations.

For the former, from the EMF measurements, the non-cooperative and cooperative bindings between SDS and HEUR became evident at low SDS concentration. The onset of cooperative binding corresponds to the CAC. Besides CAC and the saturation concentration C_2 , the monomeric SDS concentrations during the binding process were determined from the EMF measurements. On the other hand, not only CAC and C_2 , but the thermodynamic parameters associated with the binding process were determined from ITC. Thermodynamic parameters revealed that the cooperative binding between SDS and HEUR at CAC is an entropy-driving process. Both critical values of CAC and C_2 as determined from EMF and ITC are in agreement. The CAC is independent of HEUR concentration, and C_2 is strongly dependent on the HEUR concentration. Dynamic light scattering data clearly show

that the HEUR/SDS complexes are present in the solutions after CAC. The hydrodynamic radii increase with SDS concentration between CAC and C_2 , but remained constant when $C > C_2$. By increasing the end-capped hydrophobic segments, aggregates or micelles are produced in solutions and monomeric SDS binds non-cooperatively to these hydrophobic cores at SDS concentration lower than the CAC. The presence of hydrophobic modified segments (alkyl chains) and urethane groups along the PEO backbones make HEUR more hydrophobic than PEO, which gives rise to a lower CAC. The value of C_2 is only dependent on the basic binding segment and not on the total polymer chains. The self-association of HEURs and the non-cooperative binding between SDS and HEUR at low SDS concentration decrease the effects of these end-capped segments on the cooperative binding process. HEUR molecular weight has small effect on the binding isotherms. The concept of the basic binding segment is proposed based on experimental observations.

For the latter, the SDS micelles bind to the hydrophilic PEO segments of the HEUR backbone. The apparent binding enthalpy decreases with decreasing HEUR molecular weight and SDS concentration as well as increasing HEUR concentration, but independent of the size of hydrophobes.

Chapter 9 Interactions Between Sodium Dodecyl Sulfate and Poly(oxypropylene)-Poly(oxyethylene)-Poly(oxypropylene) Tri-block Copolymers in Aqueous Solution

9.1 Introduction

Hydrophobically alkyl modified PEO shows interesting solution behaviours and strong binding interaction with SDS as depicted in the previous chapter. In this chapter, another category of amphiphilic polymer, amphiphilic block copolymer of PEO and PPO will be examined. Water-soluble tri-block copolymers of PEO and PPO are widely used in various industrial applications such as emulsifying, wetting, thickening, coating, solubilizing, stabilizing, dispersing, lubricating, and foaming agents [Chu and Zhou 1996]. These polymers exhibit interesting structural and phase behavior in solution [Alexandridis and Hatton 1995]. At present, two types of poly(oxypropylene) and poly(oxyethylene) tri-block copolymers are available for commercial applications, which are termed as the EPE-type [E and P represents poly(oxypropylene) and poly(oxyethylene), respectively] or Pluronic copolymers and the PEP-type or Pluronic-R copolymers. These polymers are commonly abbreviated as $(EO)_m(PO)_n(EO)_m$ and $(PO)_m(EO)_n(PO)_m$, where m and n represents the number of repeat units. In the past several years, the EPE-type copolymers were systematically studied by various techniques such as laser light scattering [Jorgensen et al. 1997; Mortensen et al. 1995; Schillen et al. 1993, 1994; Wu and Chu 1994; Wu et al. 1997], dye solubilization [Alexandridis et al. 1994], surface tension and gel filtration [Wanka et al. 1994]. The polymers associate into micellar aggregates in the forms of spherical to rod-like structure, depending on the temperature and concentration. However, relatively few studies were reported for the PEP-type copolymers [Liu et al. 1997;

Mortensen et al. 1994; Zhou and Chu 1994]. For these polymers in aqueous medium, random network or micelles could be formed by varying the chemical composition, concentration as well as temperature. For the PEP copolymers, hydrophobic PPO segments associate with each other, bridged by the hydrophilic PEO segments. The CMC is much higher and the aggregation number is much smaller than that of EPE system. For example, the CMC of 17R4 at 40 °C is approximately 10 wt% [Zhou and Chu 1994]. The details of the association behaviors of these polymers can be found in the monographs by Chu [Chu 1995; Chu and Zhou 1996].

Polymer/surfactant systems are commercially important in a number of applications [Goddard and Ananthapadmanaban 1993; Jonsson et al. 1998]. Numerous studies on the interaction between anionic surfactants and uncharged polymers have been reported and reviewed in the literature. [Brown et al. 1992; Goddard and Ananthapadmanaban 1993; Kwak 1998; Minatti and Zanette 1996; Olofsson and Wang 1994; Rodenas and Sierra 1996]. However, relatively few studies on the interaction between ionic surfactants and water-soluble tri-block copolymers of PEO and PPO have been reported in the literatures [Hecht and Hoffmann 1994; Hecht et al. 1995]. Just recently, Bloor and co-workers reported on the binding behaviour of EPE system (Pluronic F127) and SDS, where the aggregation process was examined by electromotive force, light scattering and microcalorimetry [Li et al. 2000a; Li et al. 2001]. However, the exact mechanism on how SDS binds to Pluronic-R copolymers is still unclear.

In this chapter, the interaction of Pluronic-R copolymers and SDS was investigated using the ITC technique at 25 °C. The effects of concentration, molecular weight, and copolymer composition were examined. The present system was also compared with the interaction between SDS and PEO at the similar molecular weight.

The driving force for the polymer/surfactant interaction was analyzed based on the thermodynamic parameters obtained from the ITC measurements.

9.2 Interactions between SDS and 25R4 in Aqueous Solution

9.2.1 Titration of micellar SDS into 25R4 solution

The enthalpy profile for the titration of 0.2 M SDS into 0.053 wt% 25R4 as a function of SDS concentration (C_{SDS}) is shown in Figure 9.1 (filled circles). For comparison, the 0.2 M SDS dilution curve in water is also included as evident by the open circle.

Figure 9.1 Calorimetric titration curves for the addition of 0.2 M SDS into water (○), and into 0.053wt% 25R4 aqueous solution (●) at 298 K and 1atm.

It is evident that the titration thermogram of SDS into 25R4 is different from titration into water. The curve comprises of an endothermic peak at low SDS concentration, followed by a broad exothermic peak at high SDS concentration, which

then merges with the SDS micelle dilution curve. The difference between the titration of SDS into 25R4 and into water is attributed to the interactions between SDS and 25R4. The CAC and C_2 are common nomenclatures used to describe the critical features of the polymer/surfactant interaction. In this chapter, the CAC was determined from the peak in the difference enthalpy plot i.e. $[\Delta H(k) - \Delta H(k-1)]/\Delta m$ vs. C_{SDS} , which corresponds to the concentration of the inflection point in the leading edge of the endothermic peak. C_2 is defined when the difference enthalpies becomes zero where C_m is analogue to C_2 for this system. The curve of the difference enthalpy changes and C_{SDS} for titrating 0.2M SDS into 0.053 wt% 25R4 is shown as the inset in Figure 9.1. The determination of CMC, CAC and C_2 are marked in the figure. It is found that the CAC is 1.36 mM and C_2 is 16.26 mM.

From thermodynamics consideration, the enthalpy change at CAC can be expressed by the equation below [Meagher et al. 1998]:

$$\begin{aligned} \Delta H_{obs} = & \Delta H_d \text{ (dilution of SDS micelles and monomers)} \\ & + \Delta H_{dm} \text{ (demellization of SDS micelles)} \\ & + \Delta H_{agg} \text{ (binding of SDS monomers to polymer chains)} \end{aligned} \quad (9.1)$$

Since the enthalpy changes for the SDS dilution and the demicellization of SDS micelles are small compared to the binding interaction between SDS monomers and polymer chains, the measured enthalpy change is mainly attributed to the enthalpy change for the formation of polymer/SDS aggregation complexes, ΔH_{agg} . Using the thermodynamic equations derived from the phase separation and the mass-action model [Attwood and Florence 1983; Lindman and Thalberg 1993], the Gibbs free energy for the formation of polymer/SDS aggregates (ΔG_{agg}) can be determined from Eq. (9.2);

$$\Delta G_{agg} = (1+\beta) RT \ln (CAC) \quad (9.2)$$

where β is the effective micellar charge fraction and a value of 0.85 for SDS is used in this chapter [Wang et al. 1997]. Combined the second law of thermodynamics as described by Eq. (9.3), the entropy change associated the aggregation process can be calculated.

$$\Delta G_{\text{agg}} = \Delta H_{\text{agg}} - T\Delta S_{\text{agg}} \quad (9.3)$$

The thermodynamic parameters are summarized in Table 9.1. Since ΔH_{agg} is positive, the contribution to the negative Gibbs free energy is dictated by the magnitude of $T\Delta S$. Hence, the aggregation process at CAC is an obvious entropic driven process.

Polymer Name	Polymer Concentration	SDS Concentration	CAC ^a (mM)	ΔH_{agg}^b (kJ/mol)	C@ ΔH_{max}^a (mM)	ΔH_{max}^b (kJ/mol)	C ₂ ^a (mM)	ΔG_{agg} (kJ/mol)	T ΔS_{agg} (kJ/mol)
25R4	0.49wt%	200mM	0.97	18.7	1.63	26.8		-50.2	68.9
25R4	0.49wt%	100mM	0.97	18.7	1.70	26.4		-50.2	68.9
25R4	0.49wt%	50mM	0.94	17.9	1.64	24.3		-50.4	68.3
25R4	0.49wt%	20mM	0.93	18.5	1.50	23.5		-50.4	68.9
25R4	0.49wt%	200mM	0.97	18.7	1.63	26.8		-50.2	68.9
25R4	0.40wt%	200mM	0.97	17.3	1.63	25.4		-50.2	67.5
25R4	0.30wt%	200mM	0.99	14.5	1.62	22.2		-50.1	64.6
25R4	0.20wt%	200mM	1.06	12.1	1.72	18.8	33.58	-49.8	61.9
25R4	0.10wt%	200mM	1.20	9.7	1.81	13.1	23.72	-49.3	59.0
25R4	0.053wt%	200mM	1.36	6.7	1.80	8.8	16.26	-48.7	55.4
25R4	0.15mM	200mM	1.36	6.7	1.80	8.8	16.26	-48.7	55.4
17R4	0.15mM	200mM	1.62	5.3	2.25	6.7	16.25	-47.9	53.2
10R5	0.15mM	200mM	2.55	2.1	4.02	3.6	16.25	-45.8	47.9
PEG75	0.29mM	200mM	4.81	2.2	6.90	4.1	23.57	-42.9	45.1

(a) estimated error ± 0.05 mM.(b) estimated error ± 0.1 kJ/mol.**Table 9.1** The critical aggregation concentrations (CAC), the saturation concentration (C₂), and the thermodynamic parameters for SDS in the presence of PEP-type copolymers at 298 K and 1atm.

With respect to the titration thermogram of SDS into 25R4 solution, similar ITC curves were observed for interactions between SDS and various water-soluble polymers [Bloor et al. 1995a, 1995b; Dai and Tam 2001; Dai et al. 2001c, 2001d, 2004a; Olofsson and Wang 1994; Persson et al. 1994; Thurssson et al. 1995; Wang and Olofsson 1995, 1998]. At $C_{\text{SDS}} < \text{CAC}$, the ΔH for the SDS/polymer system is slightly larger than the SDS/water system. The presence of 25R4 alters the solvent environment, which affects the demicellization behaviour of SDS micelles. In addition, there is also the enthalpy contribution from the non-cooperative binding between polymers and SDS monomers [Dai et al. 2004a]. At $C_{\text{SDS}} > \text{CAC}$, the ΔH becomes more endothermic, approaching a maximum at C_{SDS} of ~ 1.80 mM. Beyond this, ΔH decreases and crossover with the SDS dilution curve at ~ 4.71 mM. After that, it becomes exothermic and decreases to a minimum at $C_{\text{SDS}} \sim 11.16$ mM and further merges with the dilution curve of SDS in water at C_2 of 16.26 mM. Based on the interpretation of the ITC data for SDS/PEO system [Dai and Tam 2001; Olofsson and Wang 1994; Wang and Olofsson 1998], the endothermic and exothermic peaks observed for the SDS/25R4 system could be interpreted as follows. At $C_{\text{SDS}} = \text{CAC}$, SDS monomers cooperatively bind to the 25R4 segments to form aggregation complexes, which yield a sharp increase in the ΔH . Binding of SDS to PPO segments occurs first due to their relatively low solubility [Dai and Tam 2004], followed by binding to PEO segments. The interpretation for the endothermic peak was first proposed by Wang and Olofsson for SDS/EHEC system based on their previous studies on SDS/pentanol-1 system [Johnsson et al. 1989; Wang and Olofsson 1995]. It was subsequently extended to PEO/SDS system [Wang and Olofsson 1998]. The proportion of SDS molecules participating in the polymer/SDS complex increases with SDS concentration, as reflected by the increasing endothermic enthalpies. A

consequence of this is that the electrostatic repulsion between SDS head groups increases, and this impedes the binding of additional SDS molecules to the polymer/SDS complex. Beyond a C_{SDS} at maximum ΔH , the percentage of SDS participating in the polymer/SDS complex decreases, leading to the decrease in ΔH .

Further increase in C_{SDS} causes the polymer/SDS complex to reorganize where the solubilized 25R4 segments are expelled from the hydrophobic core into water phase due to their amphiphilic property [Wang and Olofsson 1998]. The exothermic ΔH is related to the rehydration and the subsequent binding of 25R4 segments to the hydrophilic surface of SDS micelles via ion-dipole association. Close to C_2 , the micellar core consists mainly of dodecyl SDS tail groups and the polymer chains reside on the outer region of the charged SDS head groups, which shield the electrostatic repulsions between these charged groups. This also minimizes the contacts between the hydrophobic segments of the surfactant molecules and water phase. Both effects give rise to the further increasing in the SDS aggregation number. It is reported that the aggregation number of the SDS aggregates is about 30 at CAC and increases to ~ 60 to 80 at C_2 for the SDS/PEO system from fluorescence decay measurements [Brown et al. 1992; van Satam et al. 1993]. At C_2 , the aggregation number is slightly smaller than the aggregation number of free SDS micelles in water [Goddard 1993]. The details of the association mechanism for SDS/PEP system will be discussed later.

SDS in the polymer/SDS mixed solutions can exist in three forms, i.e. free SDS monomers, free SDS micelles, and polymer/SDS aggregation complexes. The total concentration of SDS in the solution can be expressed by the following equation [Goddard and Ananthapadmanaban 1993].

$$X_t = X_u + N_f (K_f X_u)^{N_f} + N_b n X_p \left(\frac{(K_b X_u)^{N_b}}{1 + (K_b X_u)^{N_b}} \right) \quad (9.4)$$

where X_t is the total SDS concentration, X_u is the SDS monomer concentration, X_p is the total concentration of polymer in solution, N_f is the aggregation number of SDS in free micelles, N_b is the aggregation number of SDS in the polymer/SDS aggregation complex, K_f is the intrinsic equilibrium constant for the formation of free SDS micelles, K_b is the intrinsic equilibrium constant for the formation of polymer/SDS aggregation complex, and nX_p is the effective mass concentration, which is independent of polymer molecular weight. If $K_f > K_b$, and $N_f \cong N_b$, the formation of free micelles is preferred rather than the formation of the aggregation complexes. If $K_f < K_b$, and $N_f \cong N_b$, the formation of aggregation complexes occurs first and upon saturating the polymer chains by SDS molecules, free micelles begin to form. If $K_f < K_b$, and $N_f \gg N_b$, the formation of aggregation complexes occurs first, but free micelles begin to form in solution before the saturation of the polymer. For the SDS/PEO system, $K_f < K_b$ and N_f is slightly larger than N_b [Goddard 1993]. Because the thermogram of SDS/25R4 is similar to the thermogram of SDS/PEO system and the chemical structures of 25R4 and PEO are analogue, it can be concluded that the equilibrium constant (K_b) of SDS/25R4 aggregation complexes is larger than that of SDS micelles (K_f) and N_b is slightly smaller than N_f . Hence, the formation of SDS/25R4 aggregation complex is more favor than the formation of SDS free micelles.

9.2.2 Titration of 25R4 into SDS micelle solution

From previous discussions on the titration of micellar SDS solution into 25R4, it was observed that SDS concentration affects the binding characteristics. At low

C_{SDS} beyond CAC, SDS monomers cooperatively bind to the polymer backbone, producing aggregation complexes containing polymer segments that are dehydrated and solubilized in the hydrophobic core of SDS mixed micelles. At large C_{SDS} , the polymer chains bind to the surface of SDS micelles through the ion-dipole association. To verify this, we titrated 0.5 wt% (~ 1.4 mM) 25R4 solution into 0.1 M SDS solution (SDS micelles are in abundance) and the thermogram is shown in Figure 9.2 (filled circles). For comparison, the titration of 0.5 wt% (~ 1.4 mM) 25R4 into water is also included in Figure 9.2 (open circles). It is evident that negligible heat changes were detected for the dilution curve of 25R4, which implies that demicellization of micelles does not occur, confirming that 25R4 chains are in the form of unimers. This can be also verified from the published data for 17R4 (with very similar composition to 25R4), the CMC at 40°C was reported to be approximately 10 wt%.

The ΔH for titrating 25R4 into the micellar SDS solution (filled circles) is much larger than titrating 25R4 into water (open circles). This difference can be ascribed to the interaction of SDS micelles and 25R4. In addition, it is evident that the thermogram is different from the result of titrating micellar SDS solution into 25R4, thereby confirming that different binding mechanisms must be in operation in either case [Dai et al. 2001c, 2004a]. From Figure 9.2, ΔH for the 25R4/SDS system is $\sim 78 \pm 0.5$ kJ/mol, which corresponds to the apparent enthalpy change for the binding of 25R4 chains to the surface of SDS micelles via ion-dipole association since SDS micelles are present in abundance.

Figure 9.2 Calorimetric titration curves for the addition of 0.5 wt% 25R4 to water (○), and to 100 mM SDS solutions (●) at 298 K and 1 atm.

9.2.3 Effect of surfactant titrant concentration

Figure 9.3 shows the thermograms for titrating 20 to 200 mM SDS solutions into 0.5 wt% 25R4 solution. It is evident that CAC and ΔH_{agg} are independent of SDS titrant concentration. The related and the computed thermodynamic parameters are summarized in Table 9.1. The Gibbs free energies, enthalpy changes and entropy changes for the formation of polymer/SDS aggregation complexes are not sensitive to the initial concentration of SDS titrant solutions. Based on Eq. (9.1), we can conclude that SDS micelle structure during the experimental concentration range are identical. In addition, the binding interaction between SDS and 25R4 is only sensitive to the total SDS monomer concentration in the titration cell.

Figure 9.3 Calorimetric titration curves for titrating different concentrations of SDS into 0.5 wt% 25R4 at 298 K and 1 atm.

9.2.4 Effect of 25R4 titrate concentration

Figure 9.4 summarizes the thermograms for the titration of 0.2 M SDS into different concentrations of 25R4. The CAC (evident from the insert plot) is mildly dependent on polymer concentrations, where it decreases from 1.36 to 0.97 mM when the polymer concentration is increased from 0.053 to 0.49 wt%. From previous studies on the SDS/PEO binding interaction, it was found that CAC slightly decreases with PEO concentration if the molecular weight of PEO is not too high, but independent of concentration if the molecular weight is high [Dai and Tam 2001; Wang and Olofsson 1998]. The surfactant concentrations corresponding to the maximum value of the endothermic peak are also insensitive to the polymer concentration, but the enthalpies increase with increasing polymer concentration. However, the exothermic peak and C_2 shift to higher SDS concentrations when the

polymer concentration is increased. The strong dependence of C_2 on polymer concentrations is related to larger amounts of SDS molecules needed to saturate the more and more polymer chains in solution, which is in agreement with previous studies [Goddard 1993; Olofsson and Wang 1994; Seng et al. 2001a, 2001b; Wang and Olofsson 1998].

Figure 9.4 Calorimetric titration curves for titrating 0.2 M SDS into different concentrations of 25R4 at 298 K and 1 atm.

The concentration dependence of CAC and C_2 reveals that the span between CAC and C_2 increases with polymer concentrations. This can be described by the phase diagram for PEO/SDS system reported by Cabane and Duplessix [Cabane and Duplessix 1982]. The values of $C_2 - CAC$ can be approximately used to estimate the amount of bound SDS at a fixed polymer concentration. The values of CAC, C_2 and thermodynamic parameters are summarized in Table 9.1. By comparing the values of ΔG_{agg} , polymer concentration does not significantly affect the formation of

polymer/SDS aggregation complexes at CAC, but the contribution from the entropy changes increase with polymer concentrations due to the increase in ΔH .

Figure 9.5 shows the dependence of ΔH_{agg} on polymer concentration, where ΔH_{agg} increases linearly with polymer concentration. When extrapolated to zero concentration, the value of ΔH_{agg} is ~ 6.6 kJ/mol, which is two times larger than the ΔH_{mic} of SDS in water (~ 2.2 kJ/mol). This confirms that the formation of polymer/SDS aggregation complexes is a different cooperative process from the formation of free SDS micelles in aqueous solution, which may comes from the dehydration of the polymers. With increasing polymer concentration, larger proportions of the 25R4 segments are dehydrated and solubilized into the hydrophobic core of SDS micelles resulting in the corresponding increase in ΔH_{agg} .

Figure 9.5 The relationship of ΔH_{agg} and polymer concentrations for a SDS/25R4 system at 298 K and 1 atm.

9.3 Comparison of SDS into PEP Copolymer and That into PEO

In order to further understand the binding behaviour between SDS and PEP copolymer, the titration of SDS into PEO at similar molecular weight was compared. Figure 9.6 reveals the titration curves of 0.2 M SDS into 0.29 mM PEG75 and 0.28 mM 25R4. Since both polymers have similar molar mass and molar concentration, hence the number of polymer chains and the chain length are identical. Although the general trends of the thermograms are similar and both C_2 values are identical, the exothermic peak for SDS/PEP system is much broader than that for SDS/PEO system. In addition, the CAC of SDS/PEP system is much smaller than SDS/PEO system and the endothermic enthalpy is more than double that of PEO/SDS system.

Figure 9.6 Comparison of the titration curves for 0.2 M SDS into 0.28 mM 25R4 and 0.29 mM PEG75 at 298 K and 1 atm. The open circles represent the dilution curve of 0.2 M SDS in water at 298 K and 1 atm.

Due to the fact that PPO contains an additional methyl group, it is more hydrophobic than PEO [Dai and Tam 2004]. Thus, polymer/SDS aggregation complexes are produced at lower CAC. We conclude that binding of SDS onto PPO occurs first followed by binding to the PEO segments. The value of C_2 - CAC can be approximately used to estimate the amount of SDS bound to the polymer chains. For both PEG75 and 25R4 systems, the molar ratio of $[C_2 - CAC]/[\text{polymer}]$ is about 65 and 80 respectively. These numbers indicates that 25R4 can bind more SDS monomers at saturation concentration C_2 , but both are slightly lower than the aggregation number of free SDS micelles in water.

9.4 Effects of Polymer Molecular Weight and Length of PPO

For PEO/SDS system, cooperative binding of SDS monomers to PEO will occur when the molecular weight exceeds 900. However, the formation of ion-dipole associated complex (PEO chains wrapping SDS micelles) required a molecular weight greater than 3500 [Dai and Tam 2001]. At molecular weight less than 3500, where negligible or very weak exothermic peak is observed in the ITC thermogram. A weak exothermic peak was also observed for PPO/SDS system of molecular weight less than 1000 [Dai and Tam 2004; Wang 1997; Wang and Olofsson 1998]. For the PEP polymer with PPO and PEO segments, the exothermic peak is due to the re-hydration of these PEO and PPO segments into the water phase and these rehydrated segments could form ion-dipole association with the hydrophilic head groups of SDS micelles.

Figure 9.7 shows the thermograms for titrating 0.2 M SDS into 0.15 mM 17R4 and 25R4 aqueous solutions respectively. The 17R4 and 25R4 have similar molar ratio of PO/EO (~1.15), but the molecular weight of 25R4 is 3600 while that of 17R4 is 2650. Comparison of the titration curves between 17R4 and 25R4 provides

information on the effect of molecular weights on the interaction between SDS and the PEP copolymers. Both exhibit a distinct endothermic and an exothermic peak. The endothermic peak corresponds to the formation of polymer/SDS aggregation complex induced by hydrophobic interactions. The exothermic peak describes the formation of the polymer/SDS aggregation complex induced by ion-dipole association. From the figure, it is evident that molecular weights do not significantly affect CAC and C_2 , which is in agreement with published results for SDS/PEO system [Wang and Olofsson 1998]. Since CAC is a critical concentration for the onset of hydrophobic binding between SDS and dehydrated polymer segments, it is only sensitive to the character of the solubilized segments and SDS monomer concentrations but independent of the molecular weight.

Figure 9.7 Calorimetric titration curves of 0.2 M SDS into 0.15 mM of 25R4 and 0.15 mM 17R4 polymer at 298 K and 1 atm. The open circles represent the dilution curve of 0.2 M SDS in water at 298 K and 1 atm.

However, the ΔH_{agg} at CAC and the enthalpy of the endothermic peak for 17R4 are smaller compared to those of 25R4 system. Since both polymers have the same molar concentration, the number of polymer chains in the solution is identical. The higher molecular weight 25R4 system possesses a longer backbone, which gives rise to a larger ΔH_{agg} as the enthalpy change at CAC is directly proportional to the concentration of solubilized segments. When the values of $(\Delta H_{\text{agg}}/\text{MW})$ are compared, negligible difference is observed. Although the contribution to the negative Gibbs free energy for the formation of polymer/SDS aggregation complex is mainly dictated by ΔS , the entropy contribution for 17R4 is slightly smaller than 25R4 due to the different binding enthalpies.

At C_2 , the ion-dipole associated polymer/SDS complexes are present and we observed that the molecular weight does not affect C_2 . From Figure 9.7, two exothermic peaks for 17R4 and one broad exothermic peak for 25R4 are evident. The origin of these two peaks is still not clear, but it may be caused by the different re-hydration properties of PPO and PEO segments. It is expected that PEO segments re-hydrate first since it is less hydrophobic. The combination of these two processes yields the trends observed in the thermograms. When the PPO segments are longer, such as 25R4, re-hydration process is dominated by the re-hydration of PPO segments. The contribution from the re-hydration of PEO is smaller, hence only a broad exothermic peak dominated by the re-hydration of PPO segments is observed. For shorter PPO segments, such as 17R4, both the PEO and PPO segments have equal contribution to the re-hydration process, yielding two distinct exothermic peaks. When the length of PPO is shorter than PEO such as 10R5 (PO/EO = 0.72), the total re-hydration process will be dominated by the re-hydration process of PEO segments. This is reflected by a distinct exothermic peak caused by the re-hydration of PEO

segments, and a broad shallow second peak attributed to the re-hydration of PPO segments as shown in Figure 9.8.

Figure 9.8 Calorimetric titration curves of 0.2 M SDS into 0.15 mM of 10R5 and 0.15 mM 17R4 polymer at 298 K and 1 atm. The open circle is the dilution curve of 0.2 M SDS in water at 298K and 1 atm.

A schematic description of the binding interactions between SDS and PEP copolymers is shown in Figure 9.9 (Concentration regions A, B, C and D are marked in Figure 9.7). SDS micelles are formed on PEP backbones after CAC, PPO segments dehydrate from the water phase first (Region A) followed by the dehydration PEO segment to form a SDS/PEP complex (Region B). Due to the increase in the aggregation number of SDS, the PEO segments will first re-hydrate with the PEO segments binding to the SDS head groups (Region C). In region D, PPO segments re-hydrate into the water phase and bind to the head groups SDS micelle to optimize the aggregation number of SDS micelles and decrease the free energy.

Figure 9.9 A schematic diagram for the binding process of SDS and PEP copolymers. Regions A, B, C and D are marked in Figure 9.7. A and B represent the polymer-induced micellization binding process at low SDS concentration where PPO segments de-hydrate from water phase first followed by PEO segments. C and D indicate the SDS/PEP aggregation complex reorganization to form the ion-dipole associated complex, where PEO segments rehydrate into water phase first followed by PPO segments.

Next, the effect of the length of PPO on the binning interaction between SDS and PEP copolymer will be discussed. The PPO is more hydrophobic compared to PEO and changing the length of PPO should affect the binding behavior between SDS and PEP copolymers. The titration curves of 0.2 M SDS into 0.15 mM 17R4 and 10R5 shown in Figure 9.8 are compared to highlight the effects of length of PPO segment. The molar ratio of PO/EO is 0.72 and 1.15 for 10R5 and 17R4 respectively, and both copolymers have similar PEO length, but different PPO length. It is evident that 10R5 has a higher CAC, but smaller ΔH_{agg} . The Gibbs free energy of 17R4 is more negative than 10R5 (see Table 9.1), which suggests that the interactions between SDS and 17R4 are more favorable than between SDS and 10R5. Since 17R4

possesses longer and more hydrophobic PPO segments, the polymer interacts more strongly with SDS. The increase in the hydrophobicity of the polymer chains leads to the decrease in the critical aggregation concentration. The onset for binding is strongly dependent on the polymer composition, and the hydrophobicity of telechelic ends.

It is also evident from Figure 9.8 that the C_2 of the two polymers are fairly similar. This indicates that C_2 is not sensitive to the polymer composition for PEP copolymers but only dependent on the total polymer molar concentration. The ratio of $[CAC-C_2]/[PEP]$, corresponds to the number of SDS molecules absorbed on one PEP chain. It is estimated that about 94 SDS molecules are absorbed on each 17R4 and 10R5 polymer chain, which implies that either one 10R5 or one 17R4 chain can bind one SDS micelle at the saturation condition.

9.5 Summary

The binding interaction between three Pluronic-R tri-block copolymers and SDS was studied by isothermal titration calorimetry. The CAC and C_2 were determined from the titration thermograms. Beyond CAC, a significant endothermic peak is observed, followed by a broad exothermic peak, and the titration curve finally merges with the dilution curve of SDS micelles in water at C_2 . The Gibbs free energies at CAC confirmed that the onset for the formation of SDS/PEP aggregation complex is an entropic driven process. The lower value of CAC, compared to CMC, is due to the polymer-induced micellization. After CAC, SDS/PEP aggregation complex appears in solution. Binding of PPO and SDS occurs first followed by PEO and SDS. The CACs are independent of polymer molecular weight, weakly dependent on polymer concentration, but sensitive to polymer composition and the

hydrophobicity of the copolymer. With increasing SDS concentration, the polymer/SDS aggregation complex reorganizes and the dehydrated segments are re-hydrated into water phase and then bind to the surface of the SDS micelles through ion-dipole association, where PEO segments are dehydrated prior to PPO segments. An increase in the polymer concentration causes C_2 to shift to higher SDS concentration. The molecular weight of the polymer and the polymer composition do not significantly affect the values of C_2 .

Chapter 10 Interactions Between Surfactants and

Hydrophobically Modified Alkali-soluble Emulsion

(HASE) in Aqueous Solution

10.1 Introduction

Hydrophobically modified alkali soluble emulsion (HASE) is one type of associative thickener that is widely used in water-borne coating formulations [Winnik and Yekta 1997]. HASE is a comb-like polymer with the chemical structure described in Figure 3.1. On the methacrylic acid (MAA) and ethyl acrylate (EA) co-polymer backbone, small amounts of hydrophobic moieties are grafted through a dimethyl *m*-isopropenylbenzyl isocyanate and a short PEO linkage, where the grafted chains are referred to as the associative macromonomers (AM). At low pH, HASE is insoluble and possesses a compact structure. With the addition of a base, MAA segments are neutralized, which leads to the swelling and dissolution of HASE into water. After full neutralization, HASE backbone possesses a polyelectrolyte character and solubilizes in water, while the hydrophobic groups associate each other to form aggregates in solution. For semi-dilute HASE solution, these small aggregates become connected via bridging chains to form a gel-like cluster, which enhances the solution viscosity. The dissolution behaviours of dilute HASE solutions; the association behaviours of fully neutralized HASE dilute solutions, and the rheological properties of semi-dilute HASE solutions have been extensively studied by potentiometric titration, steady-state fluorescence spectroscopy, time-resolved fluorescence quenching, static and dynamic light scattering, pulsed-gradient NMR, and rheology (steady-flow and dynamic oscillation) techniques [Araujo et al. 2000; Dai et al. 2000a, 2000b, 2000c, 2001a, 2002; English et al. 1997; Guo et al. 1998; Horiuchi et al. 1998,

1999; Islam et al. 2000; Kumacheva et al. 1997; Nagashima et al. 2000; Ng et al. 1999; Siddiq et al. 1999; Tam et al. 1998a, 1999; Tan et al. 2000a, 2000c, 2001; Tirtaatmadja et al. 1997a, 1997b; Wang et al. 2000; Wang et al. 2002].

When HASE polymers are fully neutralized, the solution properties resemble that of polyelectrolyte solution. The binding interactions between fully neutralized HASE and all types of surfactant have been studied [Seng et al. 2000a, 2000b; Tam et al. 2000]. From the studies on HASE and non-ionic surfactants (alkyl ethoxylate, C_mEO_n) or HASE and anionic surfactants (SDS), it was observed that the hydrophobic binding between the hydrophobic tails of surfactant and the hydrophobic domains of the HASE aggregates dominates the binding interaction [Seng et al. 2000a, 2000b; Tam et al. 2000]. With further increase in surfactant concentration, the network-like cluster is destroyed as evident from the decrease in HASE solution viscosity [Seng et al. 1999, 2000c; Tan et al. 2000b; Tirtaatmadja et al. 1998; Tirtaatmadja et al. 1999]. However, the binding interaction between fully neutralized HASE and cationic surfactants (DoTab) shows different behaviors, which falls into the category of binding interactions between charged polymers and oppositely charged surfactants. Electrostatic interaction plays an important role during the binding process, which results in the phase separation of mixed solutions. However, the precipitates can be re-solubilized when excess amounts of surfactants were added. The electrostatic interaction can be minimized through the addition of excess amount of electrolytes. At higher surfactant concentrations, hydrophobic interactions dominate, which leads to the destruction of HASE network structure [Goddard and Ananthapadmanaban 1993; Wang and Tam 2002; Wang et al. 2003; Wang 2004].

We noted that the addition of surfactants to HASE could lead to the solubilization of HASE latexes at low pH in aqueous solution. Although the solution

behaviour of HASE in aqueous solution and the binding interaction between fully neutralized HASE and surfactants have been studied, the interactions between un-neutralized HASE latexes and surfactants have not been reported. In this chapter, the interaction between HASE latex and different types of surfactants, i.e. anionic (SDS), cationic (DoTab) and nonionic ($C_{12}E_9$), in dilute aqueous solution were studied by UV-vis spectroscopy, DLS, ζ -potential, and ITC techniques. The possible binding isotherms or binding mechanisms were elucidated.

10.2 Interaction of HASE Latex and Anionic Surfactant

The interaction between anionic surfactant (SDS) and HASE latexes was examined by light transmittance, DLS, ζ -potential and ITC in this section.

Figure 10.1 Light transmittance detected by UV-vis spectrophotometer for 0.1 wt% HASE-EO35C16 latex in different concentrations of SDS at 298K, 1atm and wavelength of 488 nm.

10.2.1 Interaction of HASE Latex and SDS

HASE latex at low pH is insoluble in aqueous solution, but it turns clear with the addition of SDS. The SDS concentration dependence of the turbidity of HASE latex was monitored by light transmittance. Figure 10.1 shows the light transmittance of 0.1 wt% HASE-EO35C16 with different concentrations of SDS at 298 K, 1 atm and wavelength of 488 nm. From the figure, it is evident that HASE latex turns clear after 5 mM SDS, which indicates that HASE latexes interact with anionic surfactants. Hydrophobic polymers can be solubilized into SDS micellar core to minimize the free energy of the latex/surfactant system.

Figure 10.2 Isothermal titration thermograms for titration of 0.2 M SDS into water and 0.1 wt% HASE-EO35C16 at 298K and 1 atm. The open square is the difference curve between SDS into HASE latex and that into water.

The thermodynamics of the interaction between SDS and HASE latex was studied by ITC. Figure 10.2 shows the ITC thermograms of 0.2 M SDS into water and into 0.1 wt% HASE-EO35C16 solution at 298 K and 1 atm respectively. The

interaction between SDS and HASE latex can be observed from the differential enthalpy curve for the titrations of SDS into HASE-EO35C16 and into water. In SDS dilution thermogram, the transition at SDS concentration of 8.3 mM corresponds to the CMC of SDS in aqueous solution. The titration curve of SDS into HASE latex solution is exothermic with a transition point at ~ 6 mM. It then merges with SDS dilution curve at ~ 15 mM. The difference curve between the SDS into HASE latex and water is attributed to the interaction between SDS and HASE latex. The obvious exothermic peak indicates the hydrophobic interaction between SDS and HASE latex [Dai and Tam 2004; Wang and Tam 2004]. In addition, it may also include the contribution from hydrogen-bonding. From the enthalpy difference curve, the sharp transition occurs at ~ 4 mM SDS, which corresponds to the CAC of the SDS/HASE latex system. Upon reaching ~ 15 mM SDS, the polymer-surfactant interaction ceases, and this critical point is related to the C_2 . The ITC results indicate that the interaction between SDS and HASE latex is dominated by the solubilization of HASE latex into the SDS mixed micellar core.

Since SDS is an anionic surfactant, the binding process will be accompanied by surface charge fluctuations. ζ -potential was utilized to monitor the surface charge fluctuation during the solubilization process as shown in Figure 10.3. The HASE latex possesses a slightly negative charge (-3.0 mV) at 0 mM SDS. When anionic surfactant SDS was added, the surface of the latex becomes more negative, and this is related to the non-cooperatively binding of SDS monomers onto the HASE latex. The ζ -potential exhibits a minimum of -18 mV at ~ 5 mM SDS. When the SDS concentration exceeds ~ 5 mM, the HASE containing SDS mixed micelles are cooperatively formed in solution, which solubilizes the HASE latex into the hydrophobic micellar core. During the latex-induced micellization process, the

accompanying counterion condensation could give rise to a reduction in the total surface charge and a corresponding increase in the ζ -potential. In addition, it is well known that increases in the salt concentration not only decreases the thickness of the double layer but also decreases the ζ -potential, which also contributes to the increase in ζ -potential at higher SDS concentration. Beyond SDS concentration of 8 mM, both the double-layer and latex structure HASE have been fully destroyed, and thus reliability of the ζ -potential value decreases and is closed to zero.

Figure 10.3 Zeta-potential of 0.1 wt% HASE-EO35C16 and different concentrations of SDS at 298K, 1 atm.

The HASE latex particle sizes during the binding process were monitored by DLS. Figure 10.4 shows the decay time distribution functions of 0.1 wt% HASE-EO35C16 in 1 mM SDS measured at different scattering angles. Two decay modes are evident and both decay times decrease with increasing scattering angle. The

relationship between the decay rates of slow mode Γ and q^2 is shown in Figure 10.5. It was evident that the decay rates are linearly proportional to the square of the scattering vector q , confirming that the slow decay mode is caused by the translational diffusion of HASE latex or latex containing micelles in solution. The translational diffusion coefficient could be obtained from the slope of the figure. Based on Stokes-Einstein relationship, the hydrodynamic radius of the particle was calculated.

$$R_h = \frac{kT}{6\pi\eta_0 D} \quad (10.1)$$

where k is the Boltzmann constant, T the absolute temperature in Kelvin, η_0 the solvent viscosity and R_h the hydrodynamic radius, D is the diffusion coefficient. R_h was found to be 83 nm.

Figure 10.4 Decay time distribution functions for 0.1 wt% HASE (HASE-EO35C16) and 1 mM SDS at 298K and different scattering angles.

Figure 10.5 The relationship of Γ and q^2 for 0.1 wt% HASE (HASE-EO35C16) and 1 mM SDS at 298K.

Figure 10.6 The relaxation time distributions of 0.1 wt% HASE-EO35C16 and different concentrations of SDS.

The linear relationship between the decay rates of the fast mode and q^2 was not observed, and this may be caused by two possible factors: The decay may be attributed to the internal mode of the slow translational decay mode, or may be attributed to the artefacts of the REPES software [Dai et al. 2000a].

Figure 10.7 The relationship between R_h and SDS concentrations for 0.1 wt% HASE (HASE-EO35C16).

The relaxation time distribution functions of 0.1 wt% HASE-EO35C16 with different concentrations of SDS (1, 2, 3, 5, 8, 10, 15 and 20 mM) are shown in Figure 10.6. From the figure, it is evident that the narrow distributed slow mode was detectable for SDS concentrations ranging from 1 to 5 mM, while a relatively broad distribution in the relaxation time distribution functions was observed for SDS concentration exceeding 8 mM. At low SDS concentrations, HASE latexes are in the form of compact coil, which exhibits strong scattering and narrow decay time distribution. At higher SDS concentrations, HASE latexes are solubilized by SDS to

produce mixed micelles in solution. After the HASE latexes are solubilized, the cloudy solution becomes clear. The scattering intensity decreases, accompanied by the broadening of the decay time distribution functions and an incremental increase in the decay time as the concentration of SDS increases. This increase corresponds to the increase in the hydrodynamic radius of the particles as shown in Figure 10.7.

In the absence of SDS, HASE latex is insoluble, and it possesses a hydrodynamic radius of ~ 80 nm. In the presence of small amounts of SDS (up to 3 mM SDS), the hydrodynamic radius increases slightly. Combining this trend with ITC results, we concluded that non-cooperative binding of SDS monomers onto the HASE latex occurs, where the surface charge is increased as evident from ζ -potential measurements. Further increase in SDS concentration results in an increase in the hydrodynamic radius, reaching a maximum of ~ 125 nm at 5 mM SDS. The sharp increase of the hydrodynamic radius in this concentration range may be attributed to the cooperative binding of SDS to the HASE latex, where the HASE latexes are solubilized into the core of SDS mixed micelles as evident from ITC thermograms. Thereafter, the hydrodynamic radius decreases to ~ 110 nm and exhibits a marginal increase over the range of 8 to 20 mM SDS. With further increasing in SDS concentration and aggregation number, the electrostatic repulsion is enhanced, and the balance between the hydrophobic and electrostatic forces is shifted, which leading to the reorganisation of the mixed micelles into smaller stable microstructures where the equilibrium of these two forces are attained again. In addition, the transition at ~ 8 mM SDS was also observed in the ITC thermogram, which may be related to the structural reorganization. The possible binding mechanism is included in Figure 10.7.

10.2.2 Interaction of Cross-linked HASE Latex and SDS

The interaction between SDS and cross-linked HASE latex was examined and discussed in this section. Due to the presence of cross-linkers, the insoluble particles do not disintegrate with the addition of SDS as observed in un-cross-linked system, it however will swell after SDS binds to the particles. The cross-linked HASE possesses a structure shown in Figure 3.2, where X:Y = 50:50 and the density of the di-allyl phthalate cross-linker is 4 wt%.

Figure 10.8 Decay time distribution functions for 0.1wt% cross-linked HASE latex and 1 mM SDS at 298K.

Figure 10.8 shows the relaxation time distribution functions of 0.1 wt% cross-linked HASE in 1 mM of SDS measured at different scattering angles. The decay times shift to left with increasing scattering angles. The linear relationship of decay rates Γ and q^2 indicates that the decay mode is caused by the translational diffusion of latex and the translational diffusion coefficients can be determined from the slope of

the straight line. For the translational mode, the decay time is proportional to the hydrodynamic radius of the diffusional particle in solution. The decay time distributions for 0.1 wt% cross-linked HASE and different concentrations of SDS (1, 2, 3, 5, 8, 10, 15 and 20 mM) are shown in Figure 10.9. In addition, it is also found that the cloudy sample solutions do not become clear in the presence of SDS, which is different from the SDS/uncross-linked HASE system.

Figure 10.9 The decay time distribution functions for 0.1 wt% cross-linked HASE and different concentrations of SDS at 298K.

From the decay time distribution functions, the obvious broadening in the distributions for the SDS and HASE latex is not evident, which suggests that the particle only swells but remains intact with the addition of SDS. SDS monomers bind non-cooperatively to the particle surface through hydrophobic interactions. The binding of anionic SDS monomers on the HASE particles imparts negative charges on the particle, which expands the cross-linked latex. The hydrodynamic radius was

determined from Stokes-Einstein equation (Eq.10.1) and was plotted as a function of SDS concentrations as shown in Figure 10.10. The hydrodynamic radius decreases slightly at low SDS concentrations ($< \sim 5$ mM), followed by a general increase in the hydrodynamic radius at higher SDS concentrations.

Figure 10.10 The relationship between R_h and SDS concentrations for 0.1 wt% cross-linked HASE at 298K.

The ζ -potential during the binding process was measured and shown in Figure 10.11. At 0 mM SDS, the ζ -potential value is ~ -17 mV, which is much higher than the ~ -3 mV for uncross-linked HASE latex. The cross-linked HASE latex has a higher charge due to the introduction of cross-linkers, because more chains are constituted into the particle. At very low SDS concentration, no interaction between SDS and cross-linked HASE occurs due to the stronger electrostatic repulsion. The slight decrease in the R_h may be due to the decrease in the latex double layer induced by the salt effect. Accompanying the slight decrease in the hydrodynamic radius and

decrease in the surface charge, $\text{Na}^{\oplus}$ ions in the solution will bind to the latex surface as shown by the decrease in the ζ -potential values. After partially neutralizing the latex surface charge at ~ 5 mM SDS, the hydrophobic tail of SDS monomers will bind non-cooperatively to the hydrophobic surface of the latex, which gives rise to the small increase in the hydrodynamic radius and the increase in negative ζ -potential.

Figure 10.11 ζ -potential of 0.1wt% cross-linked HASE and different concentrations of SDS at 298K.

10.3 Interaction of HASE Latexes and Cationic Surfactant

Since cationic surfactant possesses a larger hydrophilic head group, it has lower binding affinity compared to anionic surfactant, which possesses a smaller head group. In this section, the binding between un-neutralized HASE latex (HASE-EO35C16) and DoTab will be examined using UV-vis transmittance, ITC, ζ -potential and DLS techniques.

The DoTab concentration dependence of the HASE latex (HASE-EO35C16) was monitored by UV-vis transmittance as shown in Figure 10.12 for 0.1 wt% HASE latex in different DoTab concentrations.

Figure 10.12. UV-vis transmittance of 0.1 wt% HASE (HASE-EO35C16) in different concentrations of DoTab at 298K and wavelength of 488 nm.

At DoTab concentration lower than 2 mM, HASE latexes precipitate from solution. With further increasing surfactant concentration, the precipitation can be re-dispersed and a homogeneous cloudy solution was obtained. As DoTab concentration exceeds 5 mM, the solution becomes less turbid, and at DoTab concentration exceeding 10 mM, the HASE latex solution becomes clear. The precipitation of the HASE latex is caused by the electrostatic interaction. The surface of the latex is covered by the negative charge as evident from previous ζ -potential study. With the addition of DoTab, the positive head groups interact with the negatively charged particle surface, which gives rise to the coagulation and precipitation of the latex

system [Dai et al. 2003a]. Further addition of surfactant, induces the hydrophobic binding to the HASE latex, which solubilizes the particle.

The surface charge fluctuation during the binding process was monitored by ζ -potential measurement as shown in Figure 10.13 for the 0.1 wt% HASE latex (HASE-EO35C16) in different concentration of DoTab.

Figure 10.13 ζ -potential of 0.1 wt% HASE latex (HASE-EO35C16) and different concentration of DoTab at 298K.

In the absence of DoTab, the ζ -potential of the HASE latex is ~ -3 mV. Upon the addition of cationic surfactant (DoTab), electrostatic attraction dominates the binding interaction, which causes the coagulation and precipitation of HASE latex. At the isoelectric point (IEP) at ~ 1 mM DoTab, the surface charge shifts to positive values. Beyond 1 mM, DoTab non-cooperatively bind to the HASE latexes, which give rise to the continuous increase in ζ -potential until 8 mM DoTab. When DoTab concentration exceeds 8 mM, cooperative binding dominates the interaction between

DoTab and HASE latex, resulting in the formation of mixed micelles in solution. As a result, the HASE solution becomes clear. Accompanying the latex induced micellization, the counterion binding gives rise to the decrease in ζ -potential after CAC. However, it also includes the contribution from the salt effects that destroys the double layer. In this region, the ζ -potential value is not reliable due to the destruction of latex structure at higher SDS concentrations.

Figure 10.14 ITC thermograms for titration of 0.2 M DoTab into water and 0.1 wt% HASE latex (HASE-EO35C16) at 298K and 1atm. The open square is the difference curve.

The enthalpy changes associated with the binding process determined from the isothermal titration calorimetric study is shown in Figure 10.14. For the ITC curve of DoTab/water system (unfilled circle), the transition at DoTab concentration of 15 mM corresponds to the CMC of DoTab in water. For the ITC curve of DoTab/HASE, significantly large endothermic peak was observed at very low DoTab concentrations,

which is caused by the electrostatic binding as reported by Wang et al. in their earlier publications [Wang and Tam 2002; Wang et al. 2003]. Beyond this point, non-cooperative hydrophobic binding interaction occurs as evident from the weak enthalpy changes during the binding process. The CAC for the cooperative hydrophobic bindings was found to be ~ 10 mM DoTab, where DoTab/HASE mixed micelles are formed in solution. After saturation concentration C_2 at ~ 20 mM, all binding interactions cease.

Dynamic light scattering was used to monitor the shift in the particle size during the binding process. Figure 10.15 shows the angular dependence of the decay time distribution of 0.1 wt% HASE latex (HASE-EO35C16) and 1 mM DoTab.

Figure 10.15 Decay time distribution functions for 0.1 wt% HASE latex (HASE-EO35C16) and 1 mM DoTab at 298K.

The decrease in the decay time with increasing scattering angles signifies a translational diffusion motion of latex particles, which was confirmed from the linear

relationship of decay rate Γ and q^2 for 0.1 wt% HASE latex (HASE-EO35C16) in 1 mM DoTab. The DoTab concentration dependence of the decay time distribution is shown in Figure 10.16.

Figure 10.16 The decay time distribution functions for 0.1 wt% HASE latex (HASE-EO35C16) and different concentrations of DoTab at 298K.

From the light scattering data, three trends are evident; namely (1) The scattered light intensity for the 1 mM DoTab is higher than the other concentrations and phase separation occurs. (2) There is a general reduction in decay time for 1 to 8 mM DoTab. (3) For DoTab concentration exceeds 10 mM, the decay time increases and remained constant after 20 mM. The higher scattering intensity of 1 mM DoTab in 0.1 wt% HASE latex (HASE-EO35C16) solutions is associated with the phase separation and higher decay time indicated that the agglomeration of latexes. With the addition of oppositely charged surfactant, the negative charges on the latex surfaces will be neutralized and phase separation occurs, as confirmed by ζ -potential

measurements. The decrease in decay time from 1 to 10 mM DoTab indicates the non-cooperative binding and dissociation of latex agglomerates, while the increase in the decay time after 10 mM DoTab suggests DoTab/HASE mixed micelles or aggregates are produced in solution. Based on Stokes-Einstein relations, the decay time was converted into the hydrodynamic radius R_h and plotted in Figure 10.17.

Figure 10.17 The relationship between R_h and DoTab concentrations for 0.1 wt% HASE latex (HASE-EO35C16) at 298K.

In the absence of DoTab, the hydrodynamic radius is ~ 80 nm, and it phase separates at 1 mM DoTab due to the agglomeration of latex particles induced by the removal of the electrostatic barrier. At 2 mM DoTab, the hydrodynamic radius decreases dramatically to ~ 130 nm and approaches ~ 40 nm at 10 mM DoTab. The continuous reduction in particle size may be attributed to the agglomerate dissociation caused by the electrostatic repulsion from these non-cooperative bound DoTab head groups. Beyond 10 mM DoTab, cooperative hydrophobic binding dominates and

stable solubilized polymer chains with bound DoTab micelles are produced. Accompanying the formation of polymer bound micelles are bromide counterions, which bind to the surface of the polymer bound micelles. The balance between the hydrophobic forces and the electrostatic repulsion stabilizes the polymer bound micelles, which minimizes the free energy, and a stable particle of ~ 75 nm is produced. The possible mechanism is described in Figure 10.17.

10.4 Interaction of HASE Latexes and Nonionic Surfactant

The interaction between HASE latex and non-ionic surfactant was also examined using light transmittance, ITC and DLS techniques. The non-ionic surfactant corresponds to polyoxyethylene dodecyl ether, which possesses a $C_{12}H_{25}$ hydrophobe and 9 moles of hydrophilic ethoxylate (EO) segments, and the surfactant is denoted as $C_{12}E_9$.

Light transmittance was used to examine the dependence of turbidity of the HASE latex at various concentrations of $C_{12}E_9$. As seen from Figure 10.18, the solution becomes clear when the $C_{12}E_9$ concentration exceeds 4.5 mM, which is lower than the observed behaviour for HASE/SDS and HASE/DoTab systems. This is attributed to the lower CMC of the non-ionic surfactant. For ionic surfactants, the formation of micelle is controlled by balance of the hydrophobic attraction and electrostatic interactions. However, for non-ionic surfactant, the formation of micelle is dominated by the balance of the hydrophobic attraction and the excluded volume repulsion from these EO segments. For surfactants containing identical hydrophobic segments, the CMC of non-ionic system is always smaller [Rosen 1980].

Figure 10.18 UV-vis transmittance of 0.1 wt% HASE latex (HASE-EO35C16) with different concentration of C₁₂E₉ at 298K and wavelength of 488 nm.

Isothermal titration calorimetry was used to monitor the enthalpy change associated with the binding process. Figure 10.19 shows the ITC thermograms for titrating 0.2 M C₁₂E₉ into water and 0.1 wt% HASE latex dispersion. The observed difference is attributed to the surfactant/latex interactions. The CMC of C₁₂E₉ in water is extremely low (~ 0.1 mM), thus it cannot be accurately determined from the S-shape ITC curve. However, it is evident that the HASE/C₁₂E₉ deviates from the C₁₂E₉/water thermogram at very low surfactant concentration where it becomes exothermic, and merges at 6 mM C₁₂E₉. The onset of the cooperative binding (CAC) occurs at concentration less than 1.0 mM, where the solution is still cloudy as evident from the light transmittance results. Due to the low CMC value of C₁₂E₉, not all HASE latex can be solubilized by the surfactant at such low a concentration, which

leads to the partially cloudy solution at CAC. With increase in surfactant concentration, more and more HASE are solubilized and solution turns clear.

Figure 10.19 ITC thermograms of titration of 0.2 M $C_{12}E_9$ into water and 0.1 wt% HASE latex (HASE-EO35C16) at 298K and 1atm.

Light scattering was used to monitor the effect of surfactant concentration on the microstructure HASE latex during the binding process. The angular dependence of the decay time distribution functions for 0.1 wt% HASE latex (HASE-EO35C16) and 1 mM $C_{12}E_9$ is shown in Figure 10.20. Only one main peak in the decay time distribution function was evident and it shifts to shorter time with increasing scattering angles. The linear q^2 dependence of the decays rates is evident and the slope is related to the translational diffusion coefficients, which can be used to calculate the hydrodynamic radius of the latex particle in solution.

Figure 10.20 Decay time distribution functions for 0.1 wt% HASE latex (HASE-EO35C16) and 1 mM $C_{12}E_9$ at 298K.

Figure 10.21 The decay time distribution functions for 0.1 wt% HASE latex (HASE-EO35C16) and different concentrations of $C_{12}E_9$ at 298K.

The decay time distribution functions of 0.1 wt% HASE latex (HASE-EO35C16) with different concentrations of $C_{12}E_9$ is shown in Figure 10.21. From the figure, it is evident that the decay time distribution functions remain relatively constant until 2 mM of $C_{12}E_9$. From the Stokes-Einstein relationship, the decay time was converted into the hydrodynamic radius and the relationship between R_h and $C_{12}E_9$ concentrations for 0.1 wt% HASE latex (HASE-EO35C16) is shown in Figure 10.22. From the figure, no apparent change in the particle size was observed at 0.03 and 0.07 mM of $C_{12}E_9$. However, at 1 mM $C_{12}E_9$, which is greater than the CMC of $C_{12}E_9$ (CMC $\sim$ 0.1 mM), a slight increase in the hydrodynamic radius was evident, where the size increases from 80 to 100 nm at 2mM $C_{12}E_9$. Thereafter, the hydrodynamic radius decreases to $\sim$ 80 nm and becomes independent of $C_{12}E_9$ concentrations.

Figure 10.22 The relationship between R_h and $C_{12}E_9$ concentrations for 0.1 wt% HASE latex (HASE-EO35C16).

Due to the low CMC of nonionic surfactant, the binding mechanism may be slightly different from that of HASE latex and ionic surfactants. The probable mechanism of binding is that at low concentrations of $C_{12}E_9$, i.e. 0.03 and 0.07 mM, no or minimal non-cooperative interactions between the latex and surfactant occur. Beyond 0.1 mM, the surfactants form micelles in solution, and HASE latexes will be solubilized directly into the $C_{12}E_9$ surfactant micelles cores as evident from the increase in the particle size. After the maximum of 2 mM $C_{12}E_9$, the aggregation complexes reorganize themselves and reach an equilibrium states after 5 mM as described in Figure 10.22.

10.5 Summary

The interaction between water-insoluble HASE latex and different types of surfactants were studied using light transmittance, ITC, DLS and ζ -potential techniques. Due to the small amounts of negative charges on the surface of the HASE latex, the binding mechanism varies with the type of surfactant.

For the interaction between anionic surfactant (SDS) and HASE latex, it is found that the non-cooperative binding between SDS monomers and HASE latex through hydrophobic interaction dominates until the SDS concentration reaches ~ 4 mM. After that, cooperative hydrophobic binding occurs to produce SDS/HASE mixed micelles in solution at CAC, which is lower than the CMC of SDS in water. When the SDS concentration exceeds C_2 , interactions between SDS and HASE latex ceases. During the formation of mixed micelles, counterion condensations are observed as confirmed by the ζ -potential measurements. Light transmittance revealed that the latex solution becomes clear after formation of mixed micelles. Light scattering data suggested the formation of unstable large mixed micelles first and they

re-organize to form the smaller and more stable micelles in solution. For comparison, the system of cross-linked HASE latex and SDS was also studied. Due to the large particle size, no cooperative binding and structure reorganization was observed. The cloudy solution does not turn clear with the addition of SDS. The binding of SDS to the cross-linked HASE latex only causes the swelling of the colloidal particle.

For the interaction between cationic surfactant (DoTab) and HASE latex, it is found that the electrostatic interaction plays an important role during the binding process. Due to the negatively charged surface of the HASE latex, addition of small amounts of DoTab leads to the agglomeration at isoelectric point (IEP). With further increase in surfactant concentration, the cloudy solution becomes clear and the non-cooperative hydrophobic binding dominates until a concentration of ~ 10 mM DoTab. After that, the cooperative binding occurs until the polymer chains become saturated with bound DoTab at C_2 . Light transmittance revealed that the clear solution was obtained after the formation of DoTab/HASE mixed micelles at CAC. The CAC is lower than the CMC of DoTab in water, where the CAC and C_2 can be determined from ITC data. From light scattering, the particle size increases sharply at 1 mM DoTab due to the phase separation. It then decreases to ~ 40 nm during the non-cooperative binding and agglomerate dissociation process. After CAC, DoTab/HASE mixed micelles are formed in solution with R_h of ~ 130 nm and the counterion condensation can be observed from the ζ -potential data.

For nonionic surfactants ($C_{12}E_9$), the CMC is very low (0.1 mM). Surfactants form individual micelles first and the HASE latexes are directly solubilized into the core of nonionic micelles. After all the latexes are solubilized by $C_{12}E_9$ micelles, the solution becomes clear. When the surfactant concentration is low, large aggregates are

formed in solution. With further increase in surfactant concentration, small and stable mixed $C_{12}E_9$ /HASE micelles are formed in solution.

Chapter 11 Conclusions and Recommendations

11.1 Conclusions

In this thesis, the micellization behavior of anionic surfactant (SDS) under different solvent conditions and temperatures was examined by isothermal titration calorimetry (ITC). The interaction between various types of water-soluble polymers and SDS was investigated by ITC and laser light scattering (LLS) techniques in different solvent mixtures and temperatures. The aggregation behavior and conformation of amphiphilic polymers in aqueous solutions was studied by a combination of static light scattering (SLS) and dynamic light scattering (DLS) techniques. In addition, the binding behaviors of surfactants to various types of amphiphilic polymers were investigated by ITC, DLS and electromotive force (EMF) techniques. Lastly, the interaction between water-insoluble latex and different types of surfactant was investigated based on UV-vis spectroscopy, light scattering, ITC and ζ -potential methods. The results showed that ITC, EMF, and DLS are sensitive tools for studying the dynamic properties of polymer/surfactant systems. ITC and EMF provide information on the macroscopic changes induced by the binding interactions, while light scattering provides insights on the microscopic properties of the polymer/surfactant system.

For SDS micellization, the critical micelle concentration, the enthalpy change and the effective charge fraction were determined by ITC. Due to the non-ideality of SDS solutions, the titration curve deviates from the sigmodal shape. We proposed for the first time the determination of effective charge fraction β from ITC thermograms. The non-ideality of SDS solution decreased when the solvent non-polarity was enhanced.

The binding interactions between polyethylene glycol (PEG) and surfactants were systematically studied. Polymer molecular weights (MW) play an important role in the binding interactions. If the MW of PEG exceeds 900 Da, the binding interaction commences and an endothermic peak was detected in the ITC thermogram, which corresponds to the polymer-induced micellization process. Further increase in the MW to 3500 Da produces an exothermic peak, which is related to the structure re-organization of the SDS/PEG complex driven by ion-dipole association. The binding interactions are now dominated by the equilibrium of polymer-induced micellization process at low SDS concentrations and the ion-dipole association at high SDS concentrations. With increasing molecular weight to more than 11000 Da, the binding interactions become independent of polymer molecular weight. In addition, the molecular weight distribution does not affect the binding thermograms. The binding isotherm of SDS and the PEG mixtures is dominated by the binding isotherms of SDS and individual PEG chains of different molecular weights before mixing, and not by the averaged molecular weight PEG after mixing. From light scattering study, PEO forms aggregates in aqueous solution and the particles size is independent of monovalent salt. Addition of SDS into the PEO aqueous solution reduces the R_h to a minimum, and it then increases and becomes constant when the saturation concentration is reached. Due to the low scattering, the PEO in the glycol/water solvent mixture cannot be accurately determined.

Solvent quality strongly affects the binding interactions and the shifts in the solvent quality can be achieved by either varying temperature or by adding co-solvents. At temperatures lower than the LCST, PPG and SDS binding interactions are identical to the PEO/SDS system. At temperatures greater than the LCST, an exothermic peak was observed, which is related to the solubilization of PPG

dispersion. At temperature near the LCST, the binding process is dominated by the equilibrium between the solubilization at low SDS concentration and the polymer induced micellization processes at high SDS concentration. Addition of glycols to the PEO/SDS/water systems alters the solvent quality. Due to the low solubility parameter and dielectric constant of glycols, the polarity of glycol/water solvent mixtures decreases, which enhances the solubility of SDS hydrophobic segments and lowers the solubility of PEO. As a result, a reduction in the desolvation of PEO at low SDS concentration and the resolution process at high SDS concentration are observed as indicated by the shapes of the ITC thermograms. Beyond a certain glycol concentration, no interaction between SDS and PEO is observed. Propylene glycol has the largest effect in decreasing the solvent polarity compared to ethylene glycol and glycerol.

The HEUR conformation in aqueous solutions was investigated by SLS and DLS. The flower-like micelles are produced in aqueous solutions with an average aggregation number of ~ 20 , which agrees with the published data in the literature. For the binding interactions between SDS and the amphiphilic polymers in water, EMF revealed that the non-cooperative binding process occurs at low SDS concentration before the cooperative binding at CAC. The monomeric SDS concentration during the binding process can be determined from the EMF curves, where the CAC is smaller than for the PEO/SDS system. Both C_2 and C_m shift to higher concentration, but CAC is almost independent of polymer concentration. Varying the end-capped groups of HEUR only alter the non-cooperative binding process, while the molecular weight of HEUR does not affect the binding isotherms. The concept of the basic binding segments was proposed for the first time. For the titration of SDS into HEUR solutions, the SDS/HEUR aggregation complex is formed

in solution by the solubilization of several unassociated HEUR end-groups into one SDS micelle. ITC thermograms for titrating HEUR into SDS micellar solution exhibit different trends, where HEUR chains are directly bound to SDS micelles through the ion-dipole association. Due to the longer PEO segments on the HEUR backbone, the effects of end-capped hydrophobes and HEUR molecular weights on this binding mechanism are not significant.

For the SDS and amphiphilic tri-block copolymer, it was found that the CAC decreases with increasing hydrophobicity of the polymer chain. During the binding process, PPO dehydration is followed by PEO dehydration at low SDS concentration, while PEO rehydration is followed by the PPO rehydration at high SDS concentration. The equilibrium in the above binding interaction controls the binding isotherms of SDS and tri-block amphiphilic copolymer in aqueous solutions.

For the binding interaction between different surfactants and water-insoluble latex, the latex can be solubilized into the surfactant micellar cores, which turned the cloudy solution into clear. However, the size of the latex and the surfactant types affect the binding isotherms. When the latex is cross-linked, the solubilization cannot occur even at high concentration. Nonionic surfactant directly solubilizes latex into their micellar core, but ionic surfactants exhibit different behavior. For ionic surfactants, non-cooperative binding occurred first, followed by the cooperative binding at CAC resulting in the formation of mixed micelles with hydrophobic latexes and surfactants, when the CAC is lower than the CMC. For cationic surfactant, the electrostatic interaction occurred at low surfactant concentration, which leads to phase separation. With further increase in surfactant concentration, DoTab/HASE mixed micelles are formed in solution through hydrophobic interaction.

11.2 Recommendations

The present study constitutes an attempt to investigate the binding behavior and mechanisms between SDS and different types of uncharged polymers, such as water-soluble to amphiphilic polymers and water-insoluble latexes. Greater understanding on the binding mechanisms has been gained and this forms the basis for the future studies described below. The future research work on the polymer-surfactant interaction can be carried out in two possible directions:

(a) New Research Methodologies

Other research methods can be used to verify or improve our current understandings on the polymer-surfactant interactions. Steady fluorescence spectroscopy (SFS), surface tension (ST), ^1H and ^{13}C nuclear magnetic resonance (NMR), and time resolved fluorescence quenching (TRFQ) could provide further information on the critical aggregation concentration, the location of the interaction, and the averaged aggregation number. TEM and AFM can be used to verify the microstructures inferred from light scattering experiments.

(b) New Polymer-Surfactant Systems

The interaction between SDS and PEO can be carried out using multi-arms PEO system to investigate the effect of steric effect on the binding isotherm. At the same time, the interaction of other anionic surfactants, such as sodium dodecylbenzenesulfonate (SDBS), and PEO can be carried out to study the effect of surfactant structure on the binding process. In addition, the interaction between different anionic surfactants and other water-soluble nonionic polymers can be conducted at different temperatures, such as cellulose and their derivatives.

The interaction between SDS and oppositely charge polyelectrolytes can also be considered, such as poly[2-(N, N,-dimethylamino) ethyl methacrylate] (PDMAEMA) or poly[2-(N, N,-diethylamino) ethyl methacrylate] (PDEAEMA) at different pH values using different research tools.

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