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Isothermal Titration Calorimetric Studies on Interactions of Ionic Surfactant and Poly(oxypropylene)−Poly(oxyethylene)−Poly(oxypropylene) Triblock Copolymers in Aqueous Solutions

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ABSTRACT: Isothermal titration calorimetry was used to investigate the binding characteristics of sodium dodecyl sulfate (SDS) and PEP-type [P and E represent poly(oxypropylene) and poly(oxyethylene), respectively] triblock copolymers in aqueous solution. Beyond the critical aggregation concentration (CAC), PEP/SDS aggregation complexes are formed through the polymer-induced micellization process. SDS monomers first bind to the PPO segments followed by binding to the PEO segments. The polymer chains are dehydrated and solubilized in the hydrophobic core of SDS micelles containing an aggregation number smaller than that of free SDS micelles in water. From the contribution to the Gibbs energy, it is found that the formation of polymer/SDS aggregation complex is an entropic-driven process. The CAC is independent of the molecular weight of polymer, is weakly dependent on the polymer concentrations, and is strongly dependent on polymer composition. An increase in the length of PPO segments results in the reduction in the CAC. At the saturation concentration C_2, the polymer chains are saturated with SDS micelles, where the polymer chains are bound to the surface of SDS micelles through ion−dipole associations. C_2 is sensitive to polymer concentration and shifts to higher values with increasing polymer concentrations. A physical model describing the interactions between SDS and the copolymers is proposed.

Introduction

Water-soluble triblock copolymers of poly(oxypropylene) and poly(oxyethylene) are widely used in various industrial applications such as emulsifying, wetting, thickening, coating, solubilizing, stabilizing, dispersing, lubricating, and foaming agents.[1] These polymers exhibit interesting structural and phase behaviors in solution. Numerous studies have been carried out on aqueous solutions of these copolymers. At present, two types of poly(oxypropylene) (or PPO) and poly(oxyethylene) (or PEO) triblock copolymers are available for commercial applications, which are termed as the EPE-type [E and P represent 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 represent 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,[2−7] dye solubilization,[8] surface tension and gel filtration.[9] The polymers associate into micellar aggregates in the forms of spherical to rodlike structure, depending on the temperature and concentration. However, relatively few studies were reported for the PEP-type copolymers.[10−12] For these polymers in aqueous medium, random network or micelles could be formed by varying the chemical composition and concentration as well as temperature. For the PEP copolymers, PPO segments associate with each other, bridged by PEO segments. The aggregation number of PEP copolymers is much smaller than that for the EPE system. The details of the association behaviors of these polymers can be found in the monographs by Chu.[1,13]

Polymer/surfactant systems are commercially important in a number of applications. The interaction between surfactants and polymers can be described by two critical concentrations. The first concentration, critical aggregation concentration (CAC), corresponds to the surfactant concentration when binding interaction between surfactants and polymer molecules first occurs, which represents the onset for the formation of polymer/surfactant aggregation complex. In some literature, the notation of T_1 was used instead of CAC.[14] The second critical concentration, C_2 or T_2, is more obscure. It is commonly used to represent the surfactant concentration when the polymer becomes saturated with surfactant aggregates in polymer/surfactant aggregation complexes. In addition, another critical concentration C_m, representing the formation of free surfactant micelles in the polymer solution, was previously reported in the literature.[15−21] For some of polymer/surfactant systems, free surfactant micelles start to form after the saturation concentration, C_2. Under this condition, C_m is analogous to C_2. However, for other polymer/surfactant systems, the formation of free surfactant micelles precedes C_2 or C_m is less than C_2. In this case, there is a competition between the formation of free surfactant micelles and that of polymer/surfactants aggregation complexes at surfactant concentrations between C_m and C_2. Bloor and co-workers have made substantial contributions to the determination of CAC, C_m and C_2 using both surfactant ion selective electrodes and microcalorimetry techniques.[17−21]

Numerous studies on the interactions between surfactants and polymers have been reported in the literature.[22−25] A detailed review on this topic can be found in the monographs by Goddard[26] and Kwak.[27] However, relatively few studies on the interactions between ionic surfactants and water-soluble triblock copolymers of PEO and PPO have been reported in the literature.[28,29]

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Recently, Bloor and co-workers[30,31] reported on the binding behavior of the EPE system (Pluronic F127) and SDS, where the aggregation process was examined by electromotive force, light scattering and microcalorimetry. However, the exact mechanism on how SDS binds to Pluronic-R copolymers is still unclear.

In this study, the interaction of Pluronic-R copolymers and sodium dodecyl sulfate (SDS) was investigated using an isothermal titration calorimetry (ITC) technique. The effects of concentrations, polymer molecular weights, and copolymer compositions were examined. The present system was compared with the interactions between SDS and PEO at the similar molecular weight. The driving force for the polymer/surfactant interactions was analyzed based on the thermodynamic parameters obtained from the ITC measurements.

Experimental Section

Materials. Three triblock Pluronic-R copolymers of 10R5, 17R4, and 25R4 were donated by BASF (Mount Olive, NJ). 10R5 has a composition of $(PO)_8(EO)_{22}(PO)_8$ with a nominal molar mass of 1950 Da. 17R4 represents $(PO)_{14}(EO)_{24}(PO)_{14}$ with a nominal molar mass of 2650 Da, while 25R4 refers to $(PO)_{19}(EO)_{33}(PO)_{19}$ with a nominal molar mass of 3600 Da. The poly(ethylene glycol) or poly(ethylene oxide), PEG75, with the molar mass of 3350 Da was supplied by Union Carbide (Danbury, CT). Similar to the studies by Chu et al. and Brown et al.,[10,11] these polymers were used as received with no further purification. Sodium dodecyl sulfate (SDS) was purchased from BDH Laboratory Supplies (Poole, U.K.). The deionized water used was from a Millipore Alpha-Q water purifying system. Then 0.2 M SDS aqueous solution and 0.5 wt % tri-block copolymer solutions were prepared and used as stock solutions. Solutions with lower concentrations were prepared by diluting the stock solution with deionized water.

Isothermal Titration Calorimetry (ITC). The microcalorimeter used in this study is the Microcal ITC system (Northampton, MA). A detailed description of this power compensated system could be found in Wiseman et al.[32] The microcalorimeter consists of a reference cell and a sample cell of 1.35 mL, with both cells insulated by an adiabatic shield. The titration was carried out by step-by-step injections of a concentrated titrant solution from a 250 μL injection syringe into the sample cell filled with a dilute titrate solution. The syringe is tailor-made such that the tip acts as a blade-type stirrer to ensure continuous mixing efficiency at 400 rpm. Using the interactive software, an injection schedule was automatically carried out after setting up the number of injections, volume of each injection and time between each injection. In ITC experiments, one measures the enthalpy changes associated with the processes occurring at a constant temperature. The measurements of critical micelle concentration (cmc), CAC, the ΔH of micellization, and the ΔH associated with polymer−surfactant interactions were performed at a constant temperature of 25.0 ± 0.02 °C.

Results and Discussion

Dilution Behaviors of SDS and 25R4 in Water. By titrating a micellar surfactant solution into water, the demicellization behavior could be determined from the ITC experiment. Figure 1 shows the dilution curve of 0.2 M SDS into water (open circles), where ΔH_{mic} is -2.20 ± 0.04 kJ/mol and the cmc is 8.30 mM. These values are similar to those reported in the literature.[33,34] Using the expressions given by eqs 1 and 2, $\Delta G_{\mathrm{mic}} = -21.95 \pm 0.03$ kJ/mol and $T\Delta S_{\mathrm{mic}} = 19.75 \pm 0.04$ kJ/mol.

$$\Delta G_{\mathrm{mic}} = (1 + K)RT\ln(\mathrm{cmc}) \tag{1}$$

$$\Delta G_{\mathrm{mic}} = \Delta H_{\mathrm{mic}} - T\Delta S_{\mathrm{mic}} \tag{2}$$

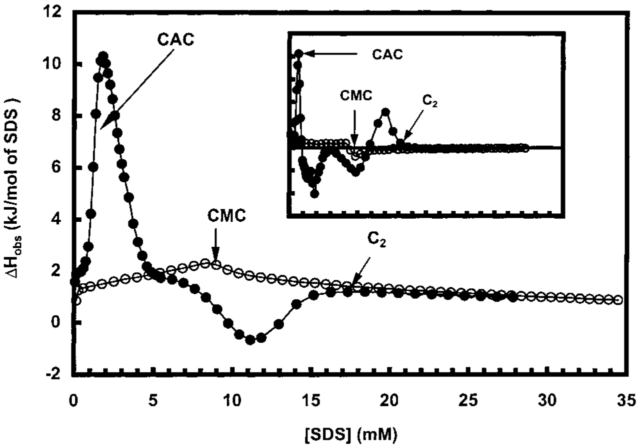

Figure 1. Calorimetric titration curves for the addition of 200 mM SDS into water (○) and into 0.053 wt % 25R4 aqueous solution (●) at 298 K. The inset is the difference curves of the ITC titration curves.

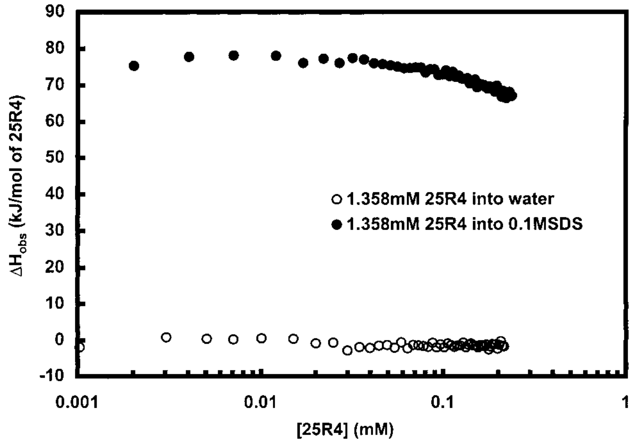

Figure 2. Calorimetric titration curves for the addition of 0.5 wt % 25R4 into water (○) and into 100 mM SDS solutions (●) at 298 K.

The factor of $(1 + K)$ accounts for the electrostatic interactions observed for ionic surfactants, where K (micellar charge fraction) equals 0.85 for SDS.[15,16]

The dilution curve of 0.5 wt % (~1.4 mM) 25R4 into water is shown in Figure 2 (open circles). Negligible heat changes were detected, which implies that demicellization of micelles does not occur, confirming that 25R4 chains are in the form of unimers. This agrees with the published data for 17R4 (with very similar composition to 25R4), where the cmc at 40 °C was reported to be approximately 10 wt %.[11]

Binding Behaviors of SDS and 25R4 in Aqueous Solutions. The ΔH 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 1 (filled circles). It is evident that the titration thermogram of SDS into 25R4 is different from that for titration into water. The curve comprises of an endothermic peak followed by a broad exothermic peak, which then merges with the pure 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 paper, 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

Table 1. The Critical Aggregation Concentrations (CAC), the Saturation Concentration (C_2), and the Thermodynamic Parameters for SDS in the Presence of PEP-Type Copolymer at 298 K

polymer name	polymer concn	SDS concn (mM)	CAC[a] (mM)	ΔH_{agg}[b] (kJ/mol)	C at ΔH_{max}[a] (mM)	ΔH_{max}[b] (kJ/mol)	C_2[a] (mM)	ΔG_{agg} (kJ/mol)	$T\Delta S_{agg}$ (kJ/mol)
25R4	0.49 wt %	200	0.97	18.7	1.63	26.8		−31.8	50.5
25R4	0.49 wt %	100	0.97	18.7	1.70	26.4		−31.8	50.5
25R4	0.49 wt %	50	0.94	17.9	1.64	24.3		−32.0	49.9
25R4	0.49 wt %	20	0.93	18.5	1.50	23.5		−32.0	50.5
25R4	0.49 wt %	200	0.97	18.7	1.63	26.8		−31.8	50.5
25R4	0.40 wt %	200	0.97	17.3	1.63	25.4		−31.8	49.1
25R4	0.30 wt %	200	0.99	14.5	1.62	22.2		−31.7	46.2
25R4	0.20 wt %	200	1.06	12.1	1.72	18.8	33.58	−31.4	43.5
25R4	0.10 wt %	200	1.20	9.7	1.81	13.1	23.72	−30.8	40.5
25R4	0.053 wt %	200	1.36	6.7	1.80	8.8	16.26	−30.3	37.0
25R4	0.15 mM	200	1.36	6.7	1.80	8.8	16.26	−30.3	37.0
17R4	0.15 mM	200	1.62	5.3	2.25	6.7	16.25	−29.5	34.8
10R5	0.15 mM	200	2.55	2.1	4.02	3.6	16.25	−27.4	29.5
PEG75	0.29 mM	200	4.81	2.2	6.90	4.1	23.57	−24.5	26.7

[a] Estimated error ± 0.05 mM. [b] Estimated error ± 0.1 kJ/mol.

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 0.2 M SDS into 0.053 wt % 25R4 is shown as the inset in Figure 1. It is found that the CAC is 1.36 mM and C_2 is 16.26 mM, which are marked in the figure.

From thermodynamics consideration, the enthalpy change at CAC can be expressed by the equation below:[35]

$$\begin{aligned}\Delta H = {} & \Delta H \text{ (dilution of SDS micelles and monomers)} \\ & + \Delta H \text{ (demicellization of SDS micelles)} \\ & + \Delta H \text{ (binding of SDS monomers to polymer chains)}\end{aligned} \quad (3)$$

Since the enthalpy changes for the SDS dilution and the demicellization of SDS micelles are small compared to the binding ΔH 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,[36,37] the Gibbs energy for the formation of polymer/SDS aggregates (ΔG_{agg}) can be determined from eq 4

$$\Delta G_{agg} = (1 + K)RT \ln(\text{CAC}) \quad (4)$$

where K is the micellar charge fraction with a value of 0.85 for SDS. All the thermodynamic parameters are summarized in Table 1. Since ΔH_{agg} is positive, the contribution to the Gibbs energy is dictated by the magnitude of $T\Delta S$. Hence, the aggregation process at CAC is an entropic-driven process.

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.[17,18,23,38−40] At C_{SDS} < 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 behavior of SDS micelles. At C_{SDS} > CAC, the ΔH becomes more endothermic, approaching a maxinum 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_{SDS} ~11.16 mM and then merges with the dilution curve of SDS in water at C_2 of 16.26 mM. On the basis of the interpretation of the ITC data for SDS/PEO system,[23,39] the endothermic and exothermic peaks observed for the SDS/25R4 system could be interpreted as follows. At C_{SDS} = 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, followed by binding to PEO segments. The interpretation for the exothermic peak was first proposed by Wang et al.[39] for SDS/EHEC system based on their previous studies on SDS/pentanol-1 system.[41] It was subsequently extended to the PEO/SDS system.[42] The proportion of SDS molecules participating in the polymer/SDS complex increases with each titration, as reflected by the increasing ΔH. A consequence of this is that the electrostatic repulsion between the SDS headgroups 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 a lower ΔH. Further increase in C_{SDS} causes the polymer/SDS complex to reorganize where the 25R4 segments in the hydrophobic core of SDS micelles rehydrate into the water phase due to their amphiphilic property. 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 chains and the polymer chains reside on the outer region of the charged SDS headgroups, 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 increase in the SDS aggregation number. It is reported that the aggregation number of the SDS aggregates is about 30 at CAC and increases to ~60−80 at C_2 for the SDS/PEO system from fluorescence decay measurements.[24,43] At C_2, the aggregation number is slightly smaller than the aggregation number of free SDS micelles in water.[26] 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[26]

$$X_t = X_u + N_f(K_f X_u)^{N_f} + N_b n X_p\left(\frac{(K_b X_u)^{N_b}}{1 + (K_b X_u)^{N_b}}\right) \quad (5)$$

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.[26] Because the thermogram of SDS/25R4 is similar to the thermogram of SDS/PEO system, 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.

From previous discussions on the titration of micellar SDS solution to 25R4, it was observed that SDS concentration affects the binding characteristics. At low C_{SDS}, SDS monomers cooperatively bind to the polymer backbone, producing aggregation complexes containing polymer segments that are solubilized in the hydrophobic core of SDS micelles. At large C_{SDS}, the polymer chains bind to the surface of SDS micelles. 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 2 (filled circles). The ΔH for titrating 25R4 into the SDS solution (filled circles) is much larger than that for 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 on titrating micellar SDS solution into 25R4, thereby confirming that different binding mechanism must be in operation. From Figure 2, ΔH for the 25R4/SDS system is ~78 ± 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 only SDS micelles are present in abundance.

Effect of Surfactant Concentrations. Figure 3 shows the thermograms for titrating 20 to 200 mM SDS solutions into 0.5 wt % 25R4 solution, where the CAC and ΔH_{agg} are independent of C_{SDS}. The computed thermodynamic parameters are summarized in Table 1. The Gibbs 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.

Effect of Polymer Concentrations. Figure 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 %. The surfactant concentrations corresponding to the maximum value of the endothermic peak are also insensitive to the polymer concentration, but the enthalpy changes 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 polymer chains, which is in agreement with previous studies.[15,16,23,26,34]

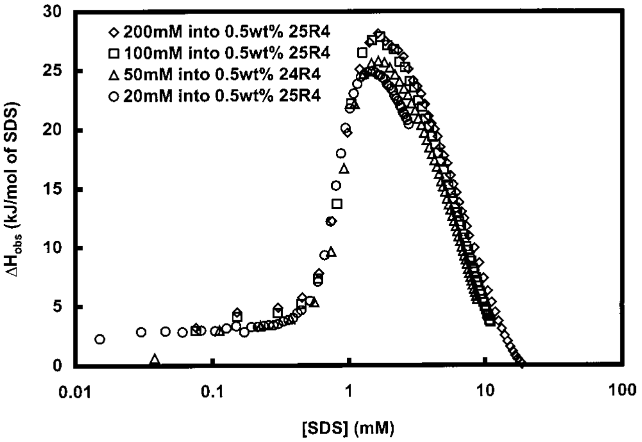

Figure 3. Calorimetric titration curves for titrating different concentrations of SDS into 0.5 wt % 25R4 at 298 K.

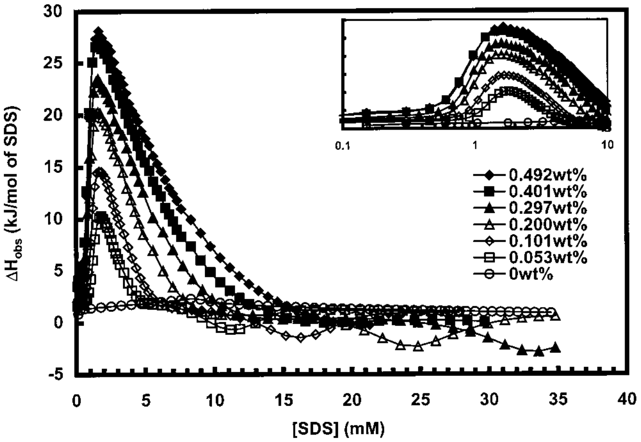

Figure 4. Calorimetric titration curves for titrating 0.2 M SDS into different concentrations of 25R4 at 298 K.

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.[26] The values of C_2 − CAC can be 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 1. By comparing the values of ΔG_{agg}, polymer concentration does not significantly affect the formation of polymer/SDS aggregation complexes at CAC. The contribution from the entropy changes increase with polymer concentrations due to the increase in ΔH.

Figure 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 three times larger than the ΔH_{mic} of SDS (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 solu-

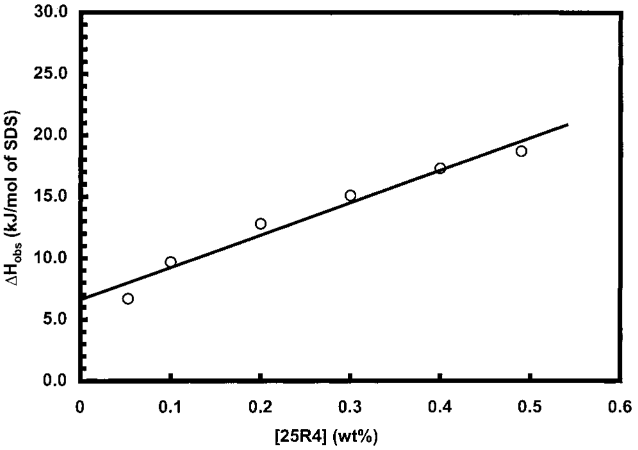

Figure 5. Relationship of ΔH_{agg} and polymer concentrations for a SDS/25R4 system at 298 K.

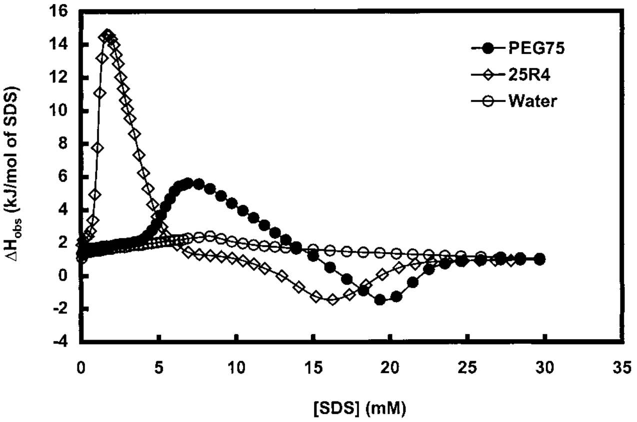

Figure 6. Comparison of the titration curves of 0.2 M SDS into 0.28 mM 25R4 and 0.29 mM PEG75 at 298 K. The open circles represent the dilution curve of 0.2 M SDS in water at 298 K.

tion. With increasing polymer concentration, larger proportions of the 25R4 segments are dehydrated and solubilized in the hydrophobic core of SDS mixed micelles resulting in the corresponding increase in ΔH_{agg}.

Comparison of SDS Titrations into PEP Copolymer and into PEO. To understand the binding behavior between SDS and PEP copolymer, the titration of SDS into PEO at similar molecular weight was compared. Figure 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 masses and molar concentrations, the numbers of polymer chains and the chain lengths are therefore 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. The CAC of SDS/PEP system is much smaller than SDS/PEO system and the endothermic ΔH is more than double that of PEO/SDS system. Because of the fact that PO contains an additional methyl group, it is more hydrophobic than PEO; hence, polymer/SDS aggregation complexes are produced at lower CAC. Thus, 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 use to estimate the amount of SDS bound to the polymer chains. For both PEG75 and 25R4 systems, the molar ratios of (C_2 − CAC)/[polymer] are about 65 and 80, respectively. These numbers indicate that 25R4 can bind more SDS monomers at saturation concentration C_2, but both are smaller than the aggregation number of free SDS micelles in water.

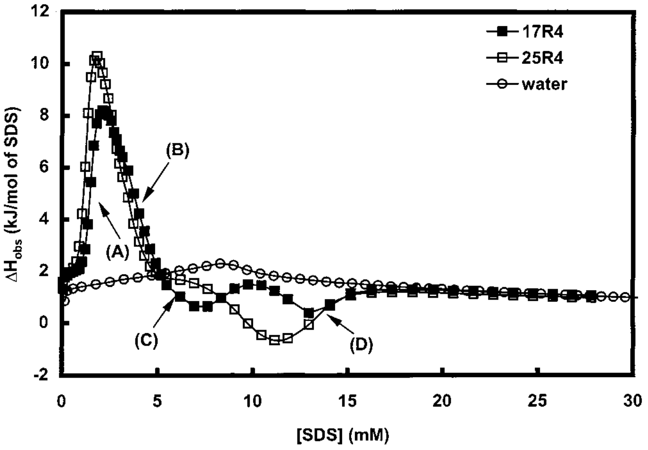

Figure 7. Calorimetric titration curves of 0.2 M SDS into 0.15 mM 25R4 and 17R4 solutions at 298 K. The open circles represent the dilution curve of 0.2 M SDS in water at 298 K.

Effect of Polymer Molecular Weights. For PEO/SDS system, cooperative binding of SDS monomers to PEO will occur when the MW exceeds 900 Da. However, the formation of ion−dipole associated complex (PEO chains wrapping SDS micelles) required a MW greater than 3350 Da.[44] At MW less than 3350 Da, a negligible or very weak exothermic peak is observed in the ITC thermogram. A weak exothermic peak was also observed for PPO/SDS system of MW less than 1000 Da.[42,45] For the PEP polymer with PO and EO segments, the exothermic peak is due to the rehydration of the EO and PO segments into the water phase, and these rehydrated segments could form an ion−dipole association with the hydrophilic headgroups of SDS micelles.

Figure 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 MW of 25R4 is 3600 while that of 17R4 is 2650 Da. 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.[26] 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 weights.

However, both the ΔH_{agg} at CAC and the ΔH of the endothermic peak for 17R4 are smaller compared to 25R4 system. Since both polymers have the same molar concentration, the numbers of polymer chains in the solution are 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 (ΔH_{agg}/MW) are compared, negligible difference is observed. Although the

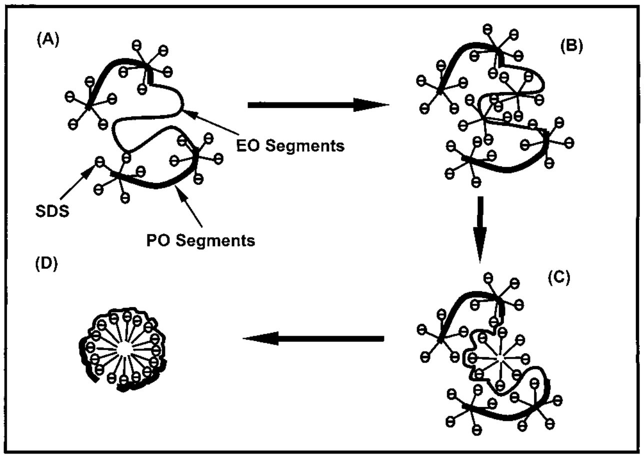

Figure 8. Schematic diagram for the binding process of SDS and PEP copolymers. Regions A−D are marked in Figure 7. A and B represent the polymer-induced micellization process at low SDS concentrations where PPO segments dehydrate from the water phase first followed by PEO segments. C and D indicate the reorganization of SDS/PEP aggregation complex to form ion−dipole association complex, where PEO segments first rehydrate into water phase followed by PPO segments.

contribution to the negative Gibbs 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 enthalpy changes.

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 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 rehydration properties of PPO and PEO segments. It is expected that PEO segments rehydrate 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, rehydration process is dominated by the rehydration of PPO segments. The contribution from the rehydration of PEO is smaller; hence, only a broad exothermic peak dominated by the rehydration of PPO segments is observed. For shorter PPO segments, such as 17R4, both the PEO and PPO segments have equal contribution to the rehydration process, yielding two distinct exothermic peaks. When the length of PO is shorter than EO such as 10R5 (PO/EO = 0.72), the total rehydration process will be dominated by the rehydration process of PEO segments. This is reflected by a distinct exothermic peak caused by the rehydration of PEO segments and a broad shallow second peak attributed to the rehydration of PPO segments as shown in Figure 9.

A schematic description of the binding interactions between SDS and PEP copolymers is shown in Figure 8 (concentration regions A−D are marked in Figure 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). Because of the increase in the aggregation number of SDS, the PEO segments will first rehydrate with the PEO segments binding to the SDS headgroups (region C). In region D, PPO segments rehydrate into the water phase and bind to the SDS headgroups to optimize the aggregation number of SDS micelles.

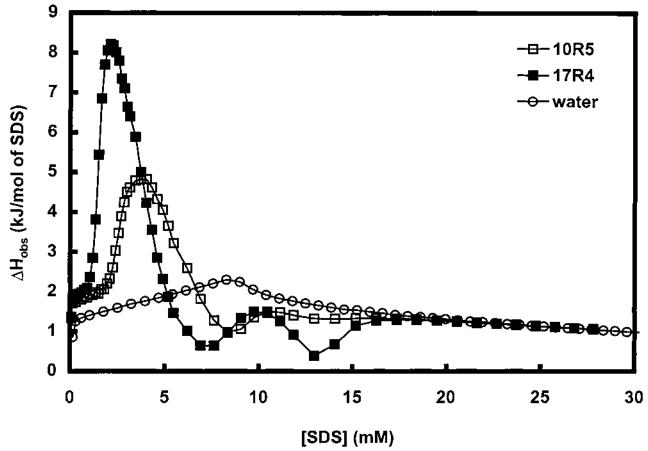

Figure 9. Calorimetric titration curves of 0.2 M SDS into 0.15 mM 10R5 and 17R4 solutions at 298 K. The open circle is the dilution curve of 0.2 M SDS in water at 298 K.

Effect of the Length of PPO. 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 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 EO, but different PO length. It is evident that 10R5 has a higher CAC, but smaller ΔH_{agg}. The Gibbs energy of 17R4 is more negative than 10R5 (see Table 1), which suggests that the interactions between SDS and 17R4 are more favorable than those 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 evident from Figure 9 that the C_2 values of the two polymers are fairly similar. This indicates that C_2 is not sensitive to the polymer composition for PEP copolymers but is only dependent on the 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.

Conclusions

The binding interactions of three Pluronic-R triblock copolymers and SDS were studied by isothermal titration calorimetry. The CAC and C_2 were determined from the titration curves. 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 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 effect. 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 weights, weakly dependent on polymer concentrations, but sensitive to polymer compositions and the hydrophobicity of the polymer. With increasing SDS concentrations, the polymer/SDS aggregation complexes reorganize and the previously dehydrated segments are rehydrated into water phase and then bind to the surface of the SDS micelles through ion−dipole association. 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.

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