

Isothermal Titration Calorimetry Studies of Binding Interactions between Polyethylene Glycol and Ionic Surfactants

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The binding behaviors between poly(ethylene glycol) (PEG) and sodium dodecyl sulfate (SDS) were examined by isothermal titration calorimetry (ITC) technique. The binding interactions between PEG and SDS are dependent on the molecular weights of PEG. At low molecular weight ($MW < 400$ Daltons), SDS does not bind to PEG chains. As PEG molecular weight increases from 900 to 1450 Daltons, an endothermic peak, which is attributed to the formation of SDS/PEG aggregation complex by the polymer-induced surfactant micellization process is observed. SDS micelles of lower aggregation number adsorb on the PEG backbones and the PEG segments are solubilized in the hydrophobic core of SDS micelles. When the molecular weight exceeds 3350 Daltons, an endothermic peak followed by an exothermic peak is observed. The exothermic curve is associated with the re-hydration of PEG segments from the SDS micellar core to form SDS/PEG aggregation complexes through ion–dipole association, where the re-hydrated PEG backbones are bound to the outer surface of the SDS hydrophilic headgroups. The binding behaviors are controlled by the equilibrium between polymer-induced micellization at low SDS concentrations and ion–dipole association at high SDS concentrations. After the polymer saturation concentration, C_2 , free SDS micelles are formed at C_m . Increasing the polymer concentrations causes C_2 and C_m to increase, however, the critical aggregation concentration (CAC) is independent of polymer concentrations. Polymer molecular weights strongly influence C_m and C_2 , but only marginally on the CAC.

Introduction

Mixtures of water-soluble polymer and surfactants have found wide application in many industrial product formulations and have received enormous attention in the past decades.^{1,2} In the polymer/surfactant system, two critical concentrations are used to describe the interactions between the polymer and surfactant molecules.^{1,3–5} The critical aggregation concentration (CAC) or T_1 indicates the onset of the binding. The saturation concentration (C_2) or T_2 implies that the polymer chains are saturated by surfactant molecules, and no additional interactions between surfactants and polymer chains occur. In addition, another critical concentration C_m or T_m , represents the surfactant concentration where free surfactant micelles begin to form. Bloor and coworkers described the determination of these concentrations for polymer/surfactant system using a combination of isothermal titration calorimetric (ITC) and surfactant selective electrode (EMF) techniques.^{6–10} In some cases, C_m is larger than C_2 , which indicates that surfactant molecules will first saturate the polymer. However, for the condition of C_m smaller than C_2 , there is a competition between the formation of free surfactant micelles and the formation of polymer/surfactant aggregation complex at surfactant concentrations between C_m and C_2 . The value of $(C_2 - CAC)$ or $(T_2 - T_1)$ represents the amounts of surfactants bound to the polymer chains.

The system of poly(ethylene glycol) (PEG or PEO) and SDS has been well studied in the past two decades using many different techniques, such as surface tension,¹¹ ITC,^{12,13} neutron scattering,^{14,15} laser light scattering,¹⁶ viscosity,^{17,18} conductiv-

ity,^{17,19} dialysis equilibrium,^{20,21} NMR,^{22–24} and size exclusion chromatography.²⁵ Goddard¹ and Kwak² had written excellent reviews on this topic. When the MW is lower than 1500 Daltons, the interaction is either negligible or nonexistent. However, when the molecular weight exceeds 4000 Daltons, significant interaction between SDS and PEO chains occurs. Beyond this molecular weight, the SDS/PEO interaction becomes independent of molecular weights, but the binding of SDS to PEO is affected by PEO concentrations. 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 concentrations and increase linearly with increasing polymer concentrations. The value of $(C_2 - CAC)$ can be used to determine the amount of SDS bound to polymer chains and this value increases with increasing polymer concentrations. The PEO could either be solubilized in the hydrophobic core of SDS micelles,²³ or absorbed on the surface of SDS micelles to form a necklace-like structure.¹⁵ For PEO/SDS saturation complexes, there are approximately three monomer units of PEO per SDS molecule. SDS micelles absorbed on PEO chains are smaller than free SDS micelles (radius of 2 nm) in water. At CAC, the aggregation number is low and found to be about 1/3 that of the aggregation number of free SDS micelles in aqueous solution.^{16,26,27} The average aggregation number in the SDS/PEO complex increases with SDS concentration and reaches about 60 at saturation, which is slightly smaller than the aggregation number of free SDS micelles in aqueous solutions. The complex increases in size as the SDS concentration increases. The saturated SDS/PEO aggregation complex has the

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TABLE 1: Details of the PEG Used in This Study

| nomenclature | averaged molecular weight | solubility in water @ 20 °C by weight | averaged number of repeat EO units | CAC ^a (mM) | C ₂ ^a (mM) | C _m ^a (mM) |
|--------------|---------------------------|---------------------------------------|------------------------------------|-----------------------|----------------------------------|----------------------------------|
| PEG-8 | 400 | complete | 8.7 | | | |
| PEG-20 | 900 | 86 | 20.0 | 5.9 | 27.0 ^b | 35.0 ^c |
| PEG-32 | 1450 | 72 | 32.5 | 5.3 | 25.0 ^b | 33.0 ^c |
| PEG-75 | 3350 | 67 | 75.7 | 4.6 | 23.5 | 29.9 |
| PEG-100 | 4600 | 65 | 104.1 | 4.4 | 19.8 | 24.6 |
| PEG-150 | 8000 | 63 | 181.4 | 4.2 | 19.1 | 22.5 |

^a PEG concentration is 0.1 wt %. ^b Calculated using $C_2 = C_m - \text{CMC}$, where the CMC is 8 mM for SDS. ^c Obtained from extrapolation of the data in the titration curves.

properties resembling those of polyelectrolytes with similar charge density.

Isothermal titration calorimetry (ITC) is a powerful research tool recently introduced to quantify the binding interactions between polymer and surfactants. Numerous studies can be found in the literature in the past few years.^{2,7–10,12,13,28} From the ITC thermogram, 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 a very developed field and there is significant scope for further research. In this study, the interactions between SDS and PEG of molecular weights ranging from 400 to 8000 Daltons were investigated by ITC. From the ITC thermograms, various binding mechanisms were proposed.

Experimental Section

Materials and Solution Preparation. The poly(ethylene glycol) (PEG) samples (CARBOWAX) were supplied by Dow Chemicals (formerly Union Carbide). The details of the PEG used in this study are listed in Table 1. Sodium dodecyl sulfate (SDS) was purchased from BDH and used as received without further purification. The deionized water was from Alpha-Q Millipore water purification system. A 1 wt % PEG and a 0.2 M SDS aqueous solutions were prepared and used as stock solutions. The samples were diluted from these stock solutions using the filtered (0.22 micron filter) deionized water. All the PEG solutions were stored in the dark, away from light and allowed to equilibrate at room temperature for at least 24 h before measurements were carried out. Before ITC experiments, solutions in both cell and syringe were degassed.

Isothermal Titration Calorimetry. The enthalpy changes of PEG and SDS interactions were measured by a Microcal isothermal titration calorimeter. A detailed description of this power compensated differential instrument could be found in Wiseman et al.²⁹ The microcalorimeter consists of a reference cell and a sample cell of 1.35 mL in volume, with both cells insulated by an adiabatic shield. The titration was carried out by step-by-step injections of concentrated titrant solution from a 250 μ L injection syringe into the sample cell filled with dilute titrate solution. The syringe is tailored-made such that the tip acts as a blade-type stirrer to ensure continuous mixing efficiency at 400 rpm. Using an 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 the ITC experiments, one measures the enthalpy changes associated with processes occurring at a constant temperature. The measurements were performed at a constant temperature of 25.0 ± 0.02 °C where the temperature was controlled using a Poly-Science water bath.

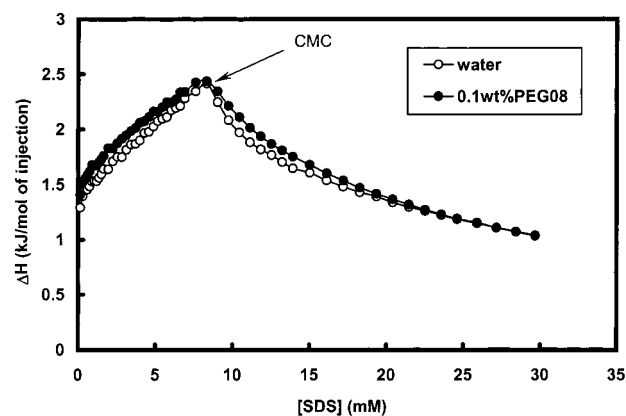


Figure 1. The ITC curves of 0.2 M SDS titrating into water (○) and 0.2 M SDS titrating into 0.1 wt % PEG-8 (●) at 298 K.

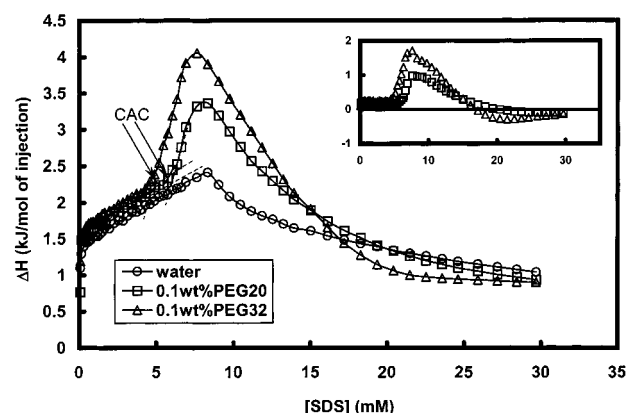


Figure 2. The ITC curve of 0.2 M SDS titrating into 0.1 wt % PEG-20 (□) and 0.1 wt % PEG-32 (△) at 298 K. The open circle is the SDS dilution curve in water. The insert is a plot for the difference curves of titrating 0.2 M SDS into PEGs and water.

Results and Discussion

1. Dilution Properties of SDS and Interactions between SDS and a Low-Molecular-Weight PEG. The dilution behavior of SDS micelles in water can be examined by titrating SDS solution ($c > \text{CMC}$) into deionized water. Figure 1 (open circles) reveals the ITC curve for titrating 0.2 M SDS into water. The transition point of ~ 8.3 mM corresponds to the CMC of SDS, which agrees with previous studies.¹²

The titration curve of 0.2 M SDS into 0.1 wt % PEG-8 (filled circles) is almost identical to that of SDS into water (Figure 1). 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-8 with the molecular weight of 400 Daltons, the hydrophilic nature of the polymer chain dominates and no interaction with SDS is present. Gao et al. also observed similar behavior from their NMR paramagnetic relaxation studies.²³

2. Binding Interactions between SDS and PEGs of Moderate Molecular Weights. Figure 2 shows the ITC curve for titrating 0.2 M SDS into 0.1 wt % PEG-20 (MW = 900 Daltons) solution. A pronounced endothermic peak for the titration of SDS into PEG-20 is observed. The difference between the ITC curves for the SDS/PEG and SDS/water system is attributed to the polymer/surfactant interaction.^{12,30} The insert in Figure 2 reveals the difference thermograms [$\Delta H(\text{SDS/PEG}) - \Delta H(\text{SDS})$] of 0.2 M SDS into 0.1 wt % PEG aqueous solutions and into water. At SDS concentration lower than 5.9 mM, both titration curves are paralleled to each other. The small difference may be due to changes in the solvent quality between

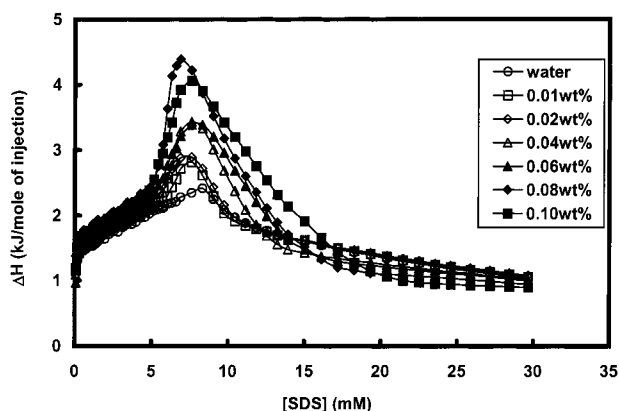


Figure 3. ITC thermograms of 0.2 M SDS titrating into different concentrations of PEG-32 solutions at 298 K. The open circle is the SDS dilution curve in water.

water and 0.1 wt % PEG-20 solution. Beyond 5.9 mM SDS, ΔH increases sharply and reaches a maximum where it decreases and then merges with the SDS dilution curve at SDS concentration greater than 30 mM.

Johnson et al. studied the interactions of SDS and pentanol-1 by isothermal titration calorimetry and they observed an endothermic peak at low SDS concentration.³¹ The peak was attributed to the dehydration of pentanol-1 molecules from water phase into the hydrophobic core of SDS micelles. Since the EO segment contains two methylene groups and an oxygen atom that acts as proton acceptor, PEG possesses amphiphilic properties. Thus, the endothermic peak in the thermogram of SDS/PEG system is due to the dehydration of PEG segments from water phase to the hydrophobic core in SDS mixed micelles.¹² The ΔH for the transfer of one mole of EO groups from water to the dehydrated core is about 7 kJ/mol of EO at 25 °C.³² In the presence of hydrophobic segments such as ether groups in PEG, SDS micelles of lower aggregation number (~ 30) can be induced at the hydrophobic segment of the polymer chain at a 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 observed cooperative binding of SDS with PEG at a molecular weight of about 900 Daltons, which is significantly lower than 4000 reported previously.¹ The onset point for the formation of SDS/PEG mixed micelles or aggregates is defined as the critical aggregation concentration (CAC). At $c > \text{CAC}$, the binding interaction becomes more dominant, causing the aggregation number of SDS to increase. Consequently, the electrostatic repulsion between the anionic headgroups of SDS is enhanced, and this retards the SDS/PEG interaction. At PEG molecular weight of 1450 Daltons (PEG-32), the thermogram exhibits a much larger endothermic peak, while the CAC decreases slightly since the hydrophilicity of the PEG decreases with increasing PEG chain length. A small exothermic peak occurs at higher SDS concentration and the C_m is greater than 30 mM.

Figure 3 shows the dependence of ΔH on polymer concentrations of SDS/PEG-32 system. The endothermic peak increases with increasing polymer concentrations, while the CACs remain constant. The weak exothermic peak becomes more pronounced at higher polymer concentration, while C_m and C_2 shift to higher SDS concentrations.

3. Binding Interactions between SDS and High-Molecular-Weight PEGs. As the molecular weight of PEG increases to

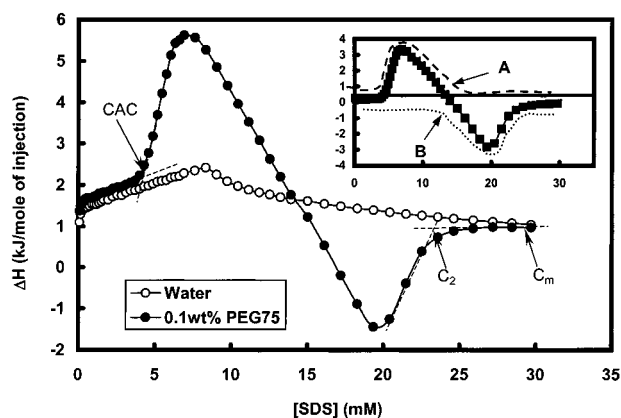


Figure 4. The ITC curve of 0.2 M SDS titrating into 0.1 wt % PEG-75 (●) at 298 K. The open circle is the SDS dilution curve in water. The insert is a plot representing the difference curve of 0.2 M SDS into PEG and water. The dotted lines in the insert figure indicate the two binding processes at different SDS concentrations.

3350 Daltons, the titration curve shows distinct endothermic and exothermic peaks (Figure 4). The insert of Figure 4 reveals the difference curve for titrating 0.2 M SDS into 0.1 wt % PEG-75. For SDS concentration less than 4.6 mM, the deviation between the titration curves is attributed to the changes in the solvent quality. Beyond the CAC of 4.6 mM, the SDS/PEG aggregates begin to form and the CAC is smaller than the values observed for moderate molecular-weight PEGs. The exothermic curve is attributed to the re-hydration of PEG segments from the hydrophobic core of SDS micelles to the water phase and these re-hydrated PEG segments then wrap around the circumference of SDS micelles to form another form of SDS/PEG aggregation complex. The driving force for the re-hydration process of the PEG segments is ion–dipole association between SDS headgroups and EO segments. The stabilization of this SDS/PEG aggregation complex is brought about by two phenomena, i.e.: (1) the electrostatic repulsion between the SDS charge groups is reduced when PEG chains are wrapped around the SDS micelle; and (2) the wrapping of PEG segments around the SDS micelles minimizes the contact between the SDS hydrophobic segments and the water phase. At SDS concentration beyond the minimum of the exothermic curve, the titration curve passes through C_2 , and merges with the SDS dilution curve at C_m . The determinations of CAC, C_2 , and C_m are marked in Figure 4.

The existence of endothermic and exothermic peaks in the ITC curves suggests that the interaction between the 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 micelles to dehydrated PEG segments. The dominant interaction at high SDS concentration is the binding between ionic charged surfaces of SDS micelles and PEG segments driven by PEG/SDS ion–dipole aggregation. In this process, PEG chains re-hydrate from the core of SDS micelles to the water phase (an exothermic process shown by dotted line marked “B”), hence it is the direct opposite to the ΔH for dehydration of PEG from water phase to SDS hydrophobic core groups (an endothermic process shown by dotted line marked “A”).^{12,13,33–35} This binding interaction between SDS and PEG is clearly evident for PEG of high molecular weights, where the energetic is controlled by the equilibrium of the two

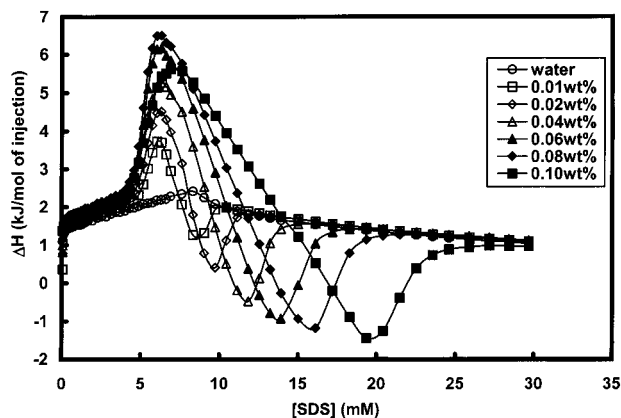


Figure 5. ITC thermograms of 0.2 M SDS titrating into different concentrations of PEG-75 solutions at 298 K. The open circle is the SDS dilution curve in water.

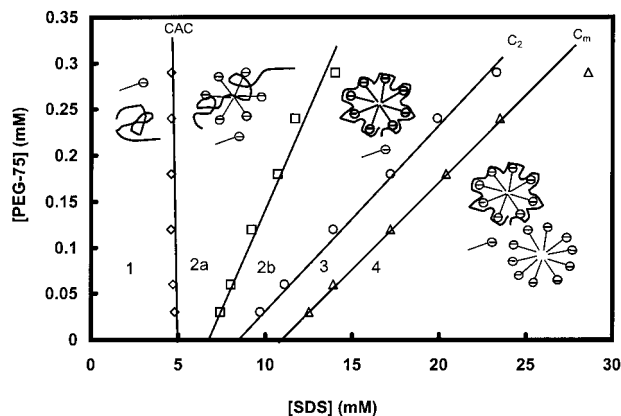


Figure 6. The phase diagram for the SDS/PEG-75 system at 298 K.

processes as shown by the dotted lines in Figure 4. It is evident that the process of the re-hydration of the PEG chains of moderate molecular weights (PEG-20 and PEG-32) is weak because no significant exothermic peak is observed. From the present study, we conclude that the minimum molecular weight for the formation of the re-hydrated PEG aggregation complex is about 3350 Daltons.

The effects of concentrations of PEG-75 polymer were examined and shown in Figure 5. The CAC is independent of polymer concentrations, while C_2 and C_m shift to higher values with increasing polymer concentrations. Since the 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. While C_2 is the saturation concentration for the binding of SDS micelles onto polymer chains, it is proportional to the number of polymer chains present in solution. With increasing polymer concentrations, more surfactants are required to saturate the increasing number of polymer chains.

The phase diagram for the interaction of SDS and PEG-75 is derived from the experiments and summarized in Figure 6. The phase diagram provides a useful tool for describing the dependence of CAC, C_2 , and C_m on polymer concentrations. Included in the figure are the microstructures describing the types of interactions present. No interaction between SDS monomers and polymer chains occurs in region 1. 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

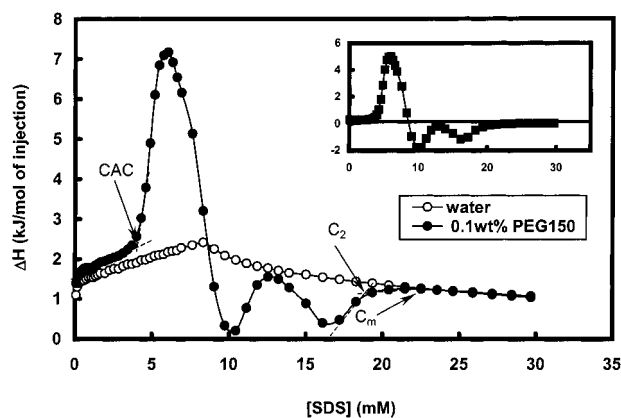


Figure 7. The ITC curve of 0.2 M SDS titrating into 0.1 wt % PEG-150 (●) at 298 K. The open circle is the SDS dilution curve in water. The insert figure is the difference curve of 0.2 M SDS into PEG and water.

micelles. The dividing line for region 2a and 2b (indicated by open square symbols) represents the transition between the dehydration and re-hydration of PEG chains in SDS solutions. With further increase in SDS concentrations, 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 2b and no further interaction between SDS monomers and PEG occurs. In region 4, free SDS micelles exist together with the saturated SDS/PEG aggregation complex.

For PEG-100 with molecular weight of 4600 Daltons, the titration curve exhibits similar trends as PEG-75 with a CAC of 4.4 mM, which is identical to PEG-75. Further increase of the molecular weight to 8000 Daltons (PEG-150) results in a completely different ITC curve (Figure 7), where two exothermic peaks are evident, instead of one broad peak. The CAC is about 4.2 mM, which is fairly close to the literature value of 4.3 mM.¹² C_m and C_2 were determined from the second exothermic peak at high SDS concentrations.

The origin of two exothermic peaks for PEG-150/SDS system is still unclear. Wang and coworkers examined the ITC curve for titrating 10 wt % SDS into 0.1 wt % PEO (MW of 8000 Daltons) and they also observed two exothermic peaks. However, for PEO with MW much greater than 8000 Daltons, the two exothermic peaks disappeared and are replaced by one broad exothermic peak. They attributed this behavior to the phenomenon where only one SDS aggregate per PEG chain was formed.^{12,30} Based on our previous results for low molecular weight PEGs, the behavior of PEG-150/SDS system is unique. We believe the observed trend is probably due to the reorganization of the structure of PEG/SDS complex.

4. Dependence of CAC, C_2 , and C_m on Molecular Weights.

The three critical concentrations are important for interpreting the binding interactions between surfactant and polymer chains in solution. Figure 8 reveals the isothermal titration curves of 0.2 M SDS into 0.1 wt % PEG solutions of different molecular weights. The CAC is not sensitive to the molecular weights of PEG. With increasing molecular weights, CAC decreases slightly and the decrease is more evident for PEG of low molecular weights. The decrease in the CAC is attributed to the decreasing hydrophilicity of PEG chains. However, C_2 and C_m decrease with increasing PEG molecular weights. After normalizing the polymer molecular weight, the values of C_m and C_2 are not similar, which indicates that the number of bound SDS micelles is not proportional to the length of PEG chains,

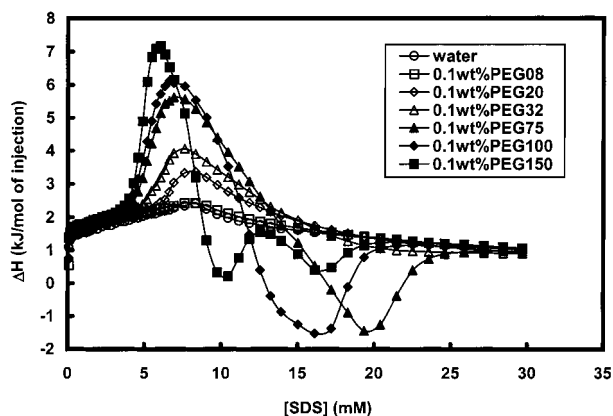


Figure 8. Thermograms for 0.2 M SDS titrating into 0.1 wt % PEG of different molecular weights at 298 K. The open circle is the SDS dilution curve in water.

i.e., the ratio of EO/SDS increase with increasing polymer molecular weights.

Conclusion

For PEG with MW less than 400 Daltons, no interaction is observed. Increasing the molecular weight from 900 to 1450 Daltons, an endothermic peak corresponding to the binding between SDS and PEG through the polymer-induced micellization process is observed. At PEG molecular weight greater than 3350 Daltons, a significant exothermic peak (in addition to the endothermic peak) appears, which is attributed to the re-hydration of PEG segments that bind to the surface of SDS micelles. The binding process is controlled by two different mechanisms, i.e., polymer-induced micellization at low SDS concentration and polymer re-hydration binding at high SDS concentration. For the PEG with the molar mass of 8000 Daltons, two exothermic peaks are observed and this unusual behavior is possibly due to the structural re-organization of the aggregates.

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