Isothermal Titration Calorimetric and Electromotive Force Studies on Binding Interactions of Hydrophobic Ethoxylated Urethane and Sodium Dodecyl Sulfate of Different Molecular Masses

S. Dai,[†,‡] K. C. Tam,*[,†,‡] E. Wyn-Jones,[§] and R. D. Jenkins[||]

Singapore-MIT Alliance and School of Mechanical and Production Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Republic of Singapore, School of Sciences, Chemistry, University of Salford, Salford, M5 4WT, United Kingdom, and The Dow Chemical Company, UCAR Emulsion Systems, 410 Gregson Drive, Cary, North Carolina 27511

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The interactions between hydrophobic ethoxylated urethane (HEUR) and sodium dodecyl sulfate (SDS) were examined by isothermal titration calorimetric (ITC) and surfactant-selective electrode (EMF) techniques. During the isothermal titration of SDS into HEUR aqueous solutions, SDS/HEUR complexes are produced via the polymer-induced micellization process at the critical aggregation concentration (CAC). With increasing SDS concentration, the SDS aggregation number continues to increase, and the SDS/HEUR complexes reorganize to form a necklace-like structure through the ion−dipole association. At the saturation concentration C_2, all of the binding interactions between SDS and HEUR are completed. Because of the increase in the hydrophobicity of polymer chains, the CAC value of SDS/HEUR is lower than that of SDS/PEO. The CAC is independent of HEUR concentrations, but C_2 shifts to higher SDS concentrations when the polymer concentration is increased. The values of CAC and C_2 are not affected by polymer molecular masses (for MM ≥ 17 500 g/mol) and the size of end-capped hydrophobes. The electromotive force measurements revealed the existence of uncooperative binding prior to the cooperative binding at CAC for the $C_{16}H_{33}$ end-capped alkyl hydrophobic chains. Both the CAC and C_2 obtained from ITC and EMF are identical, and the free SDS monomer concentrations during the binding process could be determined from the EMF measurements. During the isothermal titration of HEUR into SDS micellar solutions, SDS/HEUR complexes are formed through ion−dipole association with a necklace-like structure, where the PEO segments along the HEUR chains are bound to the hydrophilic surface of SDS micelles. With increasing HEUR molecular masses, the apparent binding enthalpies increase, but the size of end-capped alkyl hydrophobic chains does not alter the binding characteristics.

Introduction

Hydrophobic ethoxylated urethane (HEUR) is one of the commercially available associative thickeners used for the control of water-borne coating formulations. It contains a long hydrophilic backbone with two hydrophobic segments at both ends. In aqueous media, these telechelic polymers associate through hydrophobic interactions. In dilute solution, different types of aggregates or micelles are formed, depending on the hydrophobicity of the end groups and the length of the hydrophilic spacer chain.[1] For HEUR with a $C_{16}H_{33}$ hydrophobic alkyl chain in dilute aqueous solution, closed association produces rosette-like micelles with both hydrophobic end groups in the same micellar core, where the particle size is independent of polymer concentration. However, for a hydrophobe with an alkyl chain smaller than $C_{12}H_{25}$, open association dominates, where both hydrophobic end groups are located at different hydrophobic cores.[2] In this condition, cluster-like aggregates are produced, and the particle sizes increase with polymer concentrations. At high HEUR concentrations, either micelles or aggregates associate with one another to form a network-like structure, thereby producing interesting rheological behavior.[3,4]

The addition of surfactants to HEUR solutions influences the nature and characteristics of the network structure. Since sodium dodecyl sulfate (SDS) is a common and widely used anionic surfactant, many rheological studies on the SDS/HEUR system have been carried out in past decades.[5−8] It has been reported that the addition of small amounts of SDS increases the viscosity of HEUR solutions but excessive quantities of SDS cause the viscosity to decrease.[5] At low SDS concentrations, hydrophobic tails of SDS molecules replace some of the HEUR end groups in the HEUR micellar core, freeing additional HEUR hydrophobes to produce larger numbers of bridging hydrophobic junctions.[8] At high SDS concentrations, the end groups of HEUR chains are solubilized by the SDS micellar core, which disrupts the network structure, resulting in a rapid reduction in the solution viscosity.[8] In fact, the binding interactions between SDS and HEUR are more complicated than the binding interactions between HEUR and other types of surfactants. In addition to the hydrophobic binding interactions, attractive

* To whom correspondence should be addressed. E-mail: mkctam@ntu.edu.sg. Fax: (65) 6791-1859.
† Singapore-MIT Alliance, Nanyang Technological University.
‡ School of Mechanical and Production Engineering, Nanyang Technological University.
§ University of Salford.
|| The Dow Chemical Company.

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TABLE 1: Characteristics of HEUR Polymers and the Binding Parameters Obtained from Isothermal Titration Calorimetry and Electromotive Force Measurements at 298 K and 1 atm

HEUR name	molecular mass	capped hydrophobes	x	length of PEO	[HEUR] (wt %)	[SDS] (M)	CAC (mM)	C_2 (mM)	C_{DS^-}[a] (mM)	CAC (mM)	C_2 (mM)	ΔG_{ps}[b] (kJ/mol)	n	M^*[c]	EO*[d]	ΔH[e] (kJ/mol)
							EMF Measurement			SDS Titration into HEUR						HEUR Titration into SDS
HEUR−C_{16}18K	17 500	$C_{16}H_{33}$	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	34 200	$C_{16}H_{33}$	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	51 000	$C_{16}H_{33}$	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	67 600	$C_{16}H_{33}$	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	84 300	$C_{16}H_{33}$	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	100 400	$C_{16}H_{33}$	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	50 200	CH_3	6	1080	0.2	0.2	2.5	26	2.6	2.7	29.2	−5.1	10.3	4887	105	4651
	50 200	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	50 700	$C_{12}H_{25}$	6	1080	0.2	0.2	3.1	26	2.7	2.7	28.9	−5.1	10.2	4962	106	4670
	50 700	$C_{12}H_{25}$	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	51 000	$C_{16}H_{33}$	6	1080	0.2	0.2	3.1	26	2.5	2.7	28.9	−5.1	10.4	4924	104	4659
	51 000	$C_{16}H_{33}$	6	1080	0.1	0.2	3.0	17	2.7	2.7	17.9	−5.1	11.9	4276	91	9269

[a] C_{DS^-} is the free monomeric SDS concentration at C_2. [b] $\Delta G_{ps} = (1 + 0.85)RT \ln(\text{CAC/CMC})$. [c] M^* = (molecular mass)/n. [d] EO* = (total EO number)/n. [e] ΔH obtained from the first several injections where enthalpies are independent of HEUR concentrations.

interactions between the charged headgroups of SDS and PEO segments along the HEUR backbone are also present.

Isothermal titration calorimetry (ITC) is a sensitive technique for detecting subtle interactions between polymers and surfactants. From the thermogram of ITC, the critical aggregation concentration (CAC) and the saturation concentration (C_2) can be determined. The former corresponds to the surfactant concentration where a surfactant/polymer complex begins to form cooperatively, and the latter represents the surfactant concentration when the polymer is saturated with surfactant molecules. ITC not only determines these critical concentrations but also provides the thermodynamic parameters during the binding process. Hence, a number of studies on surfactant/polymer systems using the ITC technique have been reported in the last 10 years. Olofsson and co-workers reported on the interactions between SDS and several water-soluble polymers such as poly(ethylene oxide) (PEO),[9,10] poly(propylene oxide) (PPO),[11] poly(2-vinylpyridine) (PVP),[12] and ethyl(hydroxyethyl) cellulose (EHEC).[13] It was found that the CAC was independent of polymer concentration and molecular mass (MM) but depended on the hydrophobicity of the polymer. C_2 increased with polymer concentration but was independent of polymer molecular mass at higher MM values. The electromotive force (EMF) measurement using a surfactant-selective electrode is another versatile research tool for monitoring the polymer/surfactant interactions. In addition to CAC and C_2, the free surfactant monomer concentration during the binding process can be determined. By combining the results determined from ITC and EMF techniques, detailed physical insight can be obtained, which permits us to validate the binding mechanism. Bloor and co-workers conducted numerous studies on the interactions between various types of surfactants and polymers using the isothermal titration calorimetric and surfactant-selective electrode (EMF) techniques.[14−20] They described an analytical method for determining both CAC and C_2 by combining the results from ITC and EMF experiments. In addition, the free surfactant monomer concentration during the binding process could be accurately determined from the EMF data. They also reported that the value of C_2 might be larger than C_m (the critical micellization concentration for the formation of free surfactant micelles in the polymer solution) for some surfactant/polymer systems. Under this condition, competition between the formation of free surfactant micelles and a surfactant/polymer complex occurred at surfactant concentrations ranging from C_m and C_2.

Tam and co-workers used the ITC technique to study the binding interactions between surfactants and different types of water-soluble polymers and associative polymers such as poly(ethylene glycol) (PEG),[21] Pluronic-R copolymers,[22] and HEUR[23,24] as well as hydrophobically modified alkali-soluble emulsions (HASE).[25,26] It was observed that a critical molecular mass of ~900 g/mol was needed for SDS to bind to PEG. When the molecular mass of PEG exceeded 3350 g/mol, a significant exothermic peak began to appear in the ITC thermogram, and the binding process was controlled by the equilibrium between polymer-induced micellization at low SDS concentrations and the ion−dipole association at high SDS concentrations. For PEG with lower molecular masses, both CAC and C_2 decreased with increasing molecular mass. The CAC was weakly dependent on polymer concentration, but C_2 increased with increasing polymer concentration. Hydrophobic modification of the water-soluble polymer chains could lower the CAC. For dilute HEUR solutions with higher concentrations of SDS, SDS/HEUR complexes were produced through the solubilization of several HEUR end groups into a SDS micelle.[24] The microstructure arising from the binding interaction between SDS and HEUR flower micelles was confirmed using a combination of light scattering and calorimetric titration techniques.[24]

As a follow-up to our previous study on the SDS/HEUR system,[24] the effects of molecular mass and the characteristics of the end-capped hydrophobes of HEUR on the SDS/HEUR binding interactions were examined in the present study. On the basis of the EMF data from the SDS-selective electrode and the thermodynamic parameters from ITC, we hope to advance our present understanding on the structural behavior and thermodynamics of interactions between SDS and dilute HEUR polymer in aqueous solutions. In addition, isothermal titrations of SDS into HEUR solutions and HEUR into SDS micellar solutions were compared and discussed.

Experimental Section

Materials and Sample Preparation. The HEUR samples were synthesized by Dow Chemical (formerly Union Carbide), and the details of the synthesis were described by Jenkins.[27] The polymers possess the following chemical structure, and the detailed specifications are described in Table 1:

$$C_nH_{2n+1}-O-(\text{DI-PEO})_x-DI-O-C_nH_{2n+1}$$

where DI is an isophorone di-isocyanate group and PEO is a

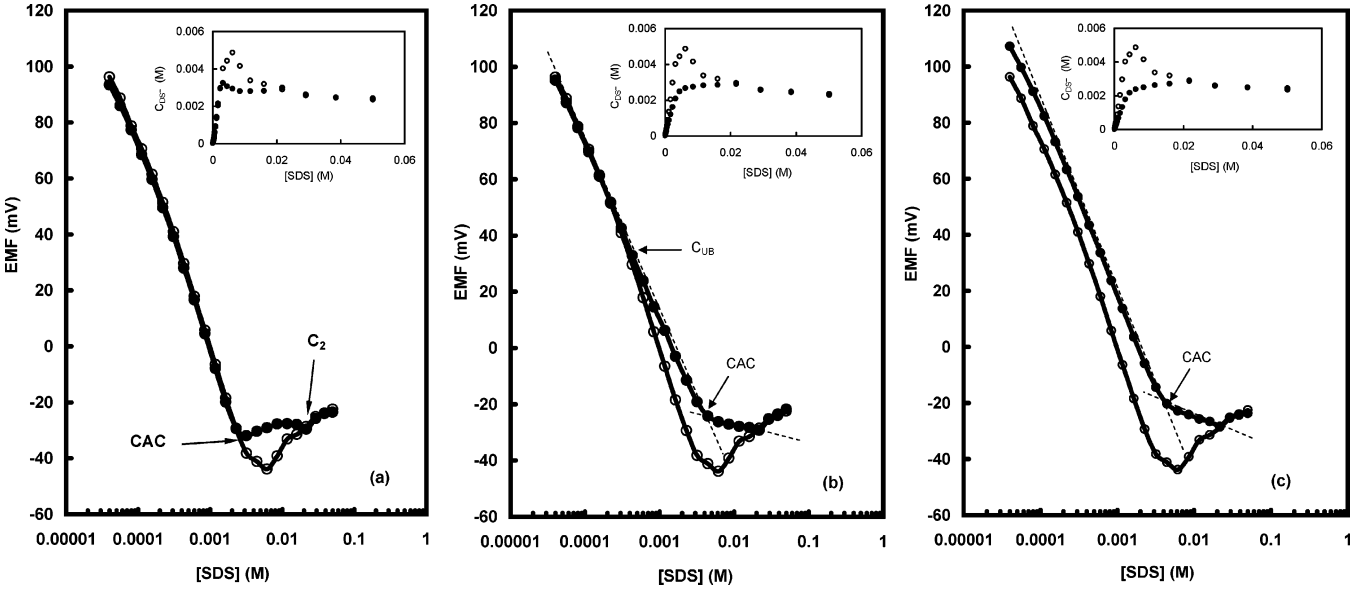

Figure 1. SDS concentration dependence of EMF values on total SDS concentrations at 298 K and 1 atm. Open circles are for SDS in water, and filled circles are for SDS in 0.1 wt % (a) HEUR−$C_1$51K, (b) HEUR−C_{12}51K, and (c) HEUR−C_{16}51K. The insets plot monomeric SDS concentration versus total SDS concentration.

poly(ethylene oxide) segment with a nominal molecular mass of 8200 g/mol. x is the molar number of PEO segments, and C_nH_{2n+1} is the end-capped hydrophobic alkyl group. The molecular mass distribution of M_w/M_n is ∼1.5 to 1.7 as determined from GPC measurements. We designated HEUR−C_nYK for the HEUR polymer with C_nH_{2n+1} alkyl chains with a molecular mass of Y kg/mol. Sodium dodecyl sulfate (SDS) was purchased from BDH and was used as received without further purification. The deionized water was from an Alpha-Q Millipore water purification system. All of the HEUR solutions were stored in the dark, away from light, and were allowed to equilibrate at room temperature for 24 h before the measurements were carried out. Both titrant and titrate solutions in the syringe and the cell were degassed prior to the ITC experiments.

Isothermal Titration Calorimetry. The binding enthalpies of SDS and HEUR were detected using a Microcal isothermal titration calorimeter. A detailed description of this power-compensated differential microcalorimeter can be found in Wiseman et al.[28] The microcalorimeter consists of a reference cell and a sample cell of 1.35-mL volume, with both cells insulated by an adiabatic shield. The titration was carried out by step-by-step injections of concentrated titrant solutions from a 250-μL injection syringe into the sample cell filled with dilute titrate solutions. The syringe is tailor-made such 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 after setting up the number of injections, volume of each injection, and time between each injection. The time interval between each injection was set at 4 min. In the ITC experiments, the enthalpies associated with the interaction processes occurring at constant temperature were recorded. All of the measurements were performed at a constant temperature of 25.0 ± 0.02 °C.

EMF Measurements. A surfactant membrane electrode selective to SDS monomers was kindly supplied by the University of Salford. The electrode was used to monitor the monomeric SDS concentrations during the SDS/HEUR binding process by measuring the EMF values relative to a Metrohm bromide ion reference electrode. The construction of the SDS membrane electrode, solution preparations, and procedures for calculating the monomeric SDS concentration were described previously.[29,30] A constant ionic strength solution of 10^{-4} M NaBr was used as the solvent for all of EMF measurements. An ABU93 tri-burette titrator with modified Aliquot software was used to conduct the titration experiments and to record the EMF values at 25.0 ± 0.1 °C; where the temperature was controlled by a PolyScience water bath.

Results and Discussion

Electromotive Force Measurements. The 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) are shown in Figure 1. Figure 1a compares the dependence of EMF on SDS concentrations in the absence and presence of 0.1 wt % HEUR−$C_1$51K. At SDS concentrations lower than 2.5 mM, the EMF values are identical, and beyond this concentration, they begin to deviate until the concentration of 17.5 mM, where they merge again. The onset of this deviation corresponds to the critical aggregation concentration (CAC) for the cooperative binding between HEUR chains and SDS, and the endpoint is related to the saturation concentration, C_2. Figure 1, parts b and c show the dependence of EMF on SDS concentrations in the presence of 0.1 wt % HEUR−C_{12}51K and HEUR−C_{16}51K in aqueous solutions, respectively. It is evident that the EMF curves of HEUR−C_{12}51K and HEUR−C_{16}51K are different from that of HEUR−$C_1$51K. Besides the CAC for the cooperative binding between SDS and HEUR, uncooperative binding between SDS monomers and the hydrophobic domains of HEUR−C_{12}51K aggregates was detected, where the onset concentration for such binding (C_{UB} as shown in Figure 1b) was observed to be much lower than the CAC and possesses a value of ∼0.4 mM. The C_{UB} for HEUR−C_{16}51K is significantly lower because of the more hydrophobic $C_{16}H_{33}$ 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 co-workers reported the temperature dependence of the binding interactions between SDS and Pluronic copolymer F127 or L64, 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)

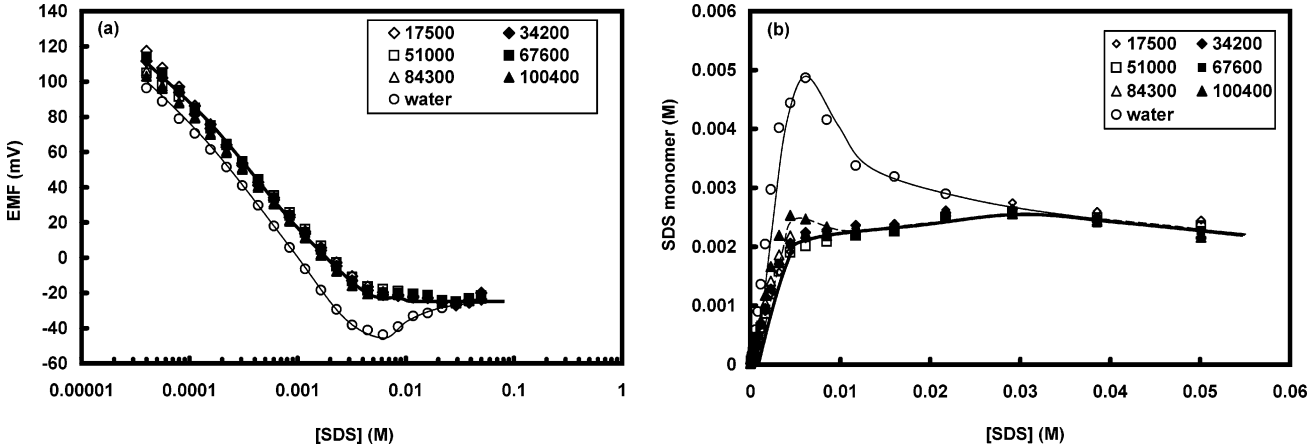

Figure 2. (a) Relationship between EMF values and SDS concentrations for 0.2 wt % HEURs with different molecular masses (end-capped with $C_{16}H_{33}$ alkyl chains) at 298 K and 1 atm. (b) Monomeric SDS concentrations for the binding interaction between SDS and 0.2 wt % HEURs with different molecular masses at 298 K and 1 atm.

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 uncooperative binding occurred at very low concentrations.[15,30] At low temperatures where the PPO segments are not hydrophobic enough, Pluronic micelles are not present 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 first bind uncooperatively to the micelle, giving rise to the divergence in the EMF curves at SDS concentrations lower than the CAC. The onset of uncooperative 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.[31] For HEUR with only methyl group substitution such as HEUR−$C_1$51K, such aggregates are absent, and the solution properties are identical to PEO in water. Hence, the cooperative binding of SDS to HEUR−$C_1$51K chains via the polymer-induced micellization process dominates at the CAC. With increasing length of hydrophobic end-capped segments, the unimeric HEUR chains associate to produce aggregates or micelles in solution. The uncooperative hydrophobic binding between SDS monomers and the hydrophobic core occurs at extremely low SDS concentrations, which gives rise to the trends observed in Figure 1b and c. The uncooperative binding between monomeric SDS and the HEUR micellar core at lower concentrations has been proposed in our earlier publication.[24] The hydrophobicity of HEUR−C_{16}51K is stronger than that of HEUR−C_{12}51K, resulting in the formation of micellar aggregates via the closed-association mechanism. Unimers of HEUR−C_{12}51K associate via the open-association mechanism to form loose micellar clusters with several hydrophobic domains. Because of the fact that the micellar core of HEUR−C_{16}51K is more hydrophobic, the onset of uncooperative hydrophobic binding for the HEUR−C_{16}51K/SDS system is lower and is not detectable over the concentration range investigated. At low SDS concentrations, HEUR micelles or aggregates are stable in solution, and the bound SDS could not disrupt the associated microstructure.[8,24] As SDS concentration reaches the CAC, the cooperative binding between SDS and HEUR chains commences, producing a sharp transition in the EMF curves. EMF measurements of SDS in 0.1 and 0.2 wt % HEUR solutions were conducted, where the CAC is independent of HEUR concentration but C_2 increases with polymer concentration (Table 1).

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

$$E = E_0 - \frac{RT}{nF}\ln\left(\frac{a_{DS^-}}{a_{Br^-}}\right) = E_0 - \frac{RT}{nF}\ln\left(\frac{C_{DS^-}\gamma_{DS^-}}{C_{Br^-}\gamma_{Br^-}}\right) \quad (1)$$

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

$$E = E_0 - \frac{RT}{F}\ln\left(\frac{C_{DS^-}}{C_{Br^-}}\right) = E_0 + \frac{RT}{F}\ln(C_{Br^-}) - \frac{RT}{F}\ln(C_{DS^-}) = E_1 - \frac{RT}{F}\ln(C_{DS^-}) \quad (2)$$

Because the SDS-selective electrode is sensitive only to the SDS monomer in solution, the monomeric surfactant concentration could be determined from eq 2. At low surfactant concentration where all surfactant molecules are in the monomeric form (C < CMC), E_1 and k ($= RT/F$) could be determined by fitting eq 2 to the linear region of the data. Therefore, the monomeric concentration of SDS during the binding or micellization process could be determined from eq 3

$$C_{DS^-} = e\left[\frac{E_1 - E}{k}\right] \quad (3)$$

The insets in Figure 1 show the relationship between the SDS monomer concentration and total SDS concentration in solution. For the SDS micellization process, it is evident that the SDS monomer concentration increases and then decreases after the CMC. However, for the SDS/HEUR binding process, the SDS monomer concentration increases progressively and merges with the equilibrium value for SDS in water beyond C_2.

EMF measurements for SDS and HEUR solutions of different molecular mass were conducted, and the trends are shown in Figure 2a. The SDS monomer concentrations during the binding processes are shown in Figure 2b. It was observed that the polymer molecular masses have negligible effects on the binding isotherms as well as the SDS monomer concentrations, and this

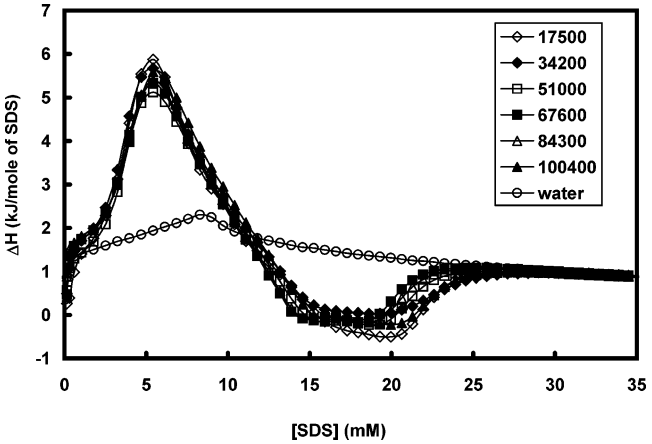

Figure 3. ITC thermograms for titrating 0.2 M SDS into 0.2 wt % HEURs (end-capped with $C_{16}H_{33}$ alkyl chains) with different molecular masses at 298 K at 1 atm. Open circles represent the dilution curve of 0.2 M SDS in water.

will be discussed later. The numerical data from EMF measurements are summarized in Table 1.

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.[24] The titration of micellar SDS into HEUR solutions is discussed here, and the titration of HEUR into SDS micellar solutions will be discussed later. When micellar SDS was titrated into HEUR solutions, SDS micelles first demicellize into SDS monomers, and these SDS monomers bind to HEUR chains in an uncooperative manner at low SDS concentrations. Beyond the critical aggregation concentration (CAC), the SDS/HEUR mixed micellar aggregates appear in solution, where the PEO segments in the HEUR backbones are 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 increases in SDS concentration, the aggregation number of SDS in the mixed micelles is likely to increase, and the SDS/HEUR aggregation complex reorganizes itself. The solubilized PEO segments are removed from the hydrophobic SDS micellar core into the water phase because of 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 coexist 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 3 shows the ITC thermograms for the titration of 0.2 M SDS into 0.2 wt % HEUR (end-capped with $C_{16}H_{33}$) polymer solutions with different molecular masses. The dilution curve of 0.2 M SDS in water is represented by open circles. 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 was evident (after subtracting the dilution enthalpy of SDS in water) at high SDS concentration; these are identical to that observed for the SDS/PEO system. The endothermic and exothermic peaks are 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,[13] where 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 mass, and the C_2 values are also identical when the polymer molecular mass exceeds 17 500 g/mol. The values of CAC and C_2 are summarized in Table 1. It is obvious that both critical values obtained from ITC agree with the data from EMF measurements. However, the heat of uncooperative binding is too small for detection by ITC. In addition, the introduction of polymers into aqueous solution also changes the solvent quality. Hence, ITC is not able to provide additional information on the uncooperative binding process.

The CAC corresponds to the onset of the formation of SDS/HEUR mixed micelles, 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 in the core of SDS mixed micelles dominated by hydrophobic interaction. The Gibbs energies for the surfactant micellization and cooperative binding process can be described by the following equations:[32,33]

$$\Delta G_{mic} = (1 + \beta)RT \ln(\mathrm{CMC}) \quad (4)$$

$$\Delta G_{agg} = (1 + \beta)RT \ln(\mathrm{CAC}) \quad (5)$$

where eqs 4 and 5 are for micellization and cooperative binding processes for ionic surfactants, respectively, where β is the micellar charge fraction with a value of 0.85 for SDS.[34] Both the CMC and CAC are in mole fraction. The Gibbs energy required for driving 1 mol of free SDS micelles into the SDS/HEUR aggregation complex can be calculated from the expression

$$\Delta G_{ps} = \Delta G_{agg} - \Delta G_{mic} = (1 + \beta)RT \ln\left(\frac{\mathrm{CAC}}{\mathrm{CMC}}\right) \quad (6)$$

From the values of ΔG_{ps} shown in Table 1, it is evident that the formation of SDS/HEUR aggregates at the CAC is a thermodynamically favorable process because 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

$$\Delta S_{agg} = \frac{\Delta H_{agg} - \Delta G_{agg}}{T} \quad (7)$$

It is evident that the cooperative aggregation process at the CAC is an entropically 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 mass for MMs of PEO greater than 8000 g/mol.[11,35,36] From Figure 3, the CAC for the SDS/HEUR system is independent of molecular mass for M_n ranging from 17 500 to 100 400 g/mol. This suggests that the polymer−surfactant interaction is dependent only on the local concentration of dehydrated EO

segments and the hydrophobicity of the HEUR chains, but not on the total length of the polymer chains (i.e., the molecular mass). However, the CAC value for the SDS/HEUR system (2.7 mM) is lower than that for the PEO/SDS system (4.2 mM).[11] Because the CAC corresponds to the onset of the cooperative formation of SDS/HEUR mixed micelles through hydrophobic interactions, it is strongly dependent on the hydrophobicity of the solubilized segments. Because of the fact that HEUR chains are more hydrophobic than PEO chains, HEUR polymers have an impact on the binding interactions and CAC values, which is also observed for SDS/(PPO−PEO−PPO) copolymers and the SDS/($C_{12}EO_{200}C_{12}$) system.[10,22]

On the basis of the EMF measurements, the SDS monomer concentration during the binding process could be determined. The value of ($C_2 - C_{DS^-}$) represents the total number of bound SDS molecules on the polymer chains, where C_{DS^-} represents the monomeric SDS concentration at C_2. A smaller value of ($C_2 - C_{DS^-}$) corresponds to a lower binding capacity of the polymer chains. We observed identical C_2 and C_{DS^-} values for SDS and HEURs of different molecular masses as shown in Table 1, 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 C_2 is N_{agg} and the molar concentration of HEUR is C_{HEUR}, then the number of bound SDS micelles per HEUR chain, n, can be approximated by the expression[37]

$$n = \frac{C_2 - C_{DS^-}}{N_{agg} C_{HEUR}} \tag{8}$$

It was reported that the average aggregation number of SDS at saturation concentration C_2 for SDS/PEO system is about 60 ∼ 70.[38,39] Assuming that the aggregation number N_{agg} of each micelle for the SDS/HEUR system is 65, the estimated number of micelles per HEUR chain can be determined using eq 8, where n increases from ∼3 to ∼20 when the MM of the HEUR chain increases from 17 500 to 100 400 g/mol. (See Table 1.) The value of M^* [= (MM)/n] corresponds to the averaged apparent molecular mass of the HEUR segment per SDS micelle in the SDS/HEUR complex. M^* also refers to the equivalent length of the 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 and 5000 g/mol (see Table 1), which is close to the observed value of 3500 to 4000 (minimum MM required for SDS/PEO ion−dipole association) reported previously.[21] We concluded that C_2 is sensitive only to the concentration of these basic binding segments and not to the total HEUR concentration and chain length. At a fixed polymer weight fraction, increasing the polymer molecular mass gives rise to a lower number of HEUR chains. However, the number or the concentration of the basic binding segments and C_2 remain constant.

Figure 4 shows the isothermal titration thermograms for titrating 0.2 M SDS into 0.2 wt % (open symbols) and 0.1 wt % (solid symbols) HEUR of similar molecular masses but different alkyl-modified end-capped hydrophobes. The open circles represent the dilution of 0.2 M SDS in water. It is evident that the titration curves of SDS into HEUR solutions at fixed concentrations do not seem to be influenced by the size of end-capped hydrophobes. The values of CAC and C_2 are listed in Table 1.

As discussed previously, the CAC decreases from 4.2 mM for the SDS/PEO system to 2.7 mM for the SDS/HEUR system, and this is attributed to the more hydrophobic HEUR chains.[24]

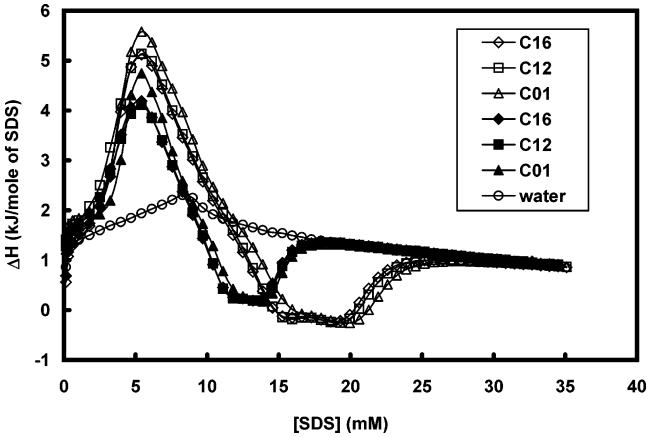

Figure 4. ITC thermograms for titrating 0.2 M SDS into 0.1 wt % (solid symbols) and 0.2 wt % (open symbols) HEUR solutions containing different end-capped hydrophobic groups at 298 K and 1 atm. Open circles represent the dilution curve of 0.2 M SDS in water.

However, the values of CAC for the SDS/HEUR system with different hydrophobic-modified groups are identical, and this means that the length of the hydrophobic end groups (CH_3 to $C_{16}H_{33}$) does not alter the CAC. Because the end groups are significantly hydrophobic, micelles or aggregates are produced in solution, and SDS monomers are bound uncooperatively to the hydrophobic core at low SDS concentrations, as evident from EMF measurements. However, HEUR with CH_3 segments does not aggregate to form micelles, and uncooperative binding is absent. On the basis of these experimental data, it is evident that the end-capped hydrophobes induce only uncooperative 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 composed 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 contributes 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 uncooperatively 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 the SDS/HEUR system is larger than that for the SDS/PEO system because of the smaller CAC, which implies that the binding capability of the SDS/HEUR system is enhanced by the increased hydrophobic characteristics of the whole polymer chains.

From Figure 4, it is also evident that the CAC is independent of HEUR concentration but C_2 increases with increasing HEUR concentration. The concentration dependence of the binding interactions between SDS and HEUR can be described using a phase diagram. Figure 5 shows the phase diagram of the SDS/HEUR−C_{16}51K system as determined from ITC experiments. The uncooperative 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 concentration. Region III, with the onset point determined from the cross point between SDS dilution into HEUR solution,[21] indicates the structural reorganization and formation of the SDS/HEUR complex through the ion−dipole

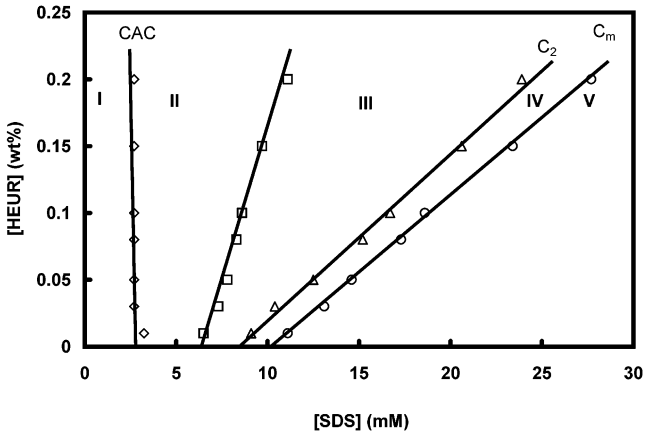

Figure 5. Phase diagram of the SDS/HEUR−C_{16}51K system in water at 298 K. Region I represents uncooperative binding between the SDS monomer and HEUR. Region II represents the SDS/HEUR complex formed by the polymer-induced micellization process, and the delineating line represents the CAC. Region III represents the SDS/HEUR complex formed by ion−dipole association. Region IV represents SDS unimers and the saturated SDS/HEUR complex and the delineating line representing C_2. Region V represents SDS unimers coexisting with the SDS/HEUR saturated complex, and the line indicates C_m.

association process. Region IV represents the saturated necklace-like SDS/HEUR complex coexisting 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 a higher SDS concentration. In region V, the SDS/HEUR aggregation complex coexists with free SDS micelles. The value of ($C_m - C_2$) is smaller than the CMC value of SDS in water (~8.3 mM) because of the presence of polymer chains in solution.

Binding Mechanisms. From the EMF and ITC measurements, the binding mechanisms between SDS and different HEURs can be elucidated and described in Figure 6. HEUR−$C_1$51K 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 that of the SDS/PEO system (Figure 6a). Because the hydrophobicity of linear HEUR chains is greater than that of PEO due to the urethane groups, the onset of cooperative binding (CAC) is lower. At $C \approx$ CAC, polymer-induced SDS mixed micelles are formed first, followed by the formation of SDS/HEUR aggregation complexes through ion−dipole association, where the rehydrated HEUR backbones are bound to the outer surface of the SDS hydrophilic headgroups. For HEUR−C_{12}51K, polymer clusters are produced via the open-association mechanism (Figure 6b). The hydrophobic domains consisting of several $C_{12}H_{25}$ segments induce the uncooperative binding of SDS monomers to these hydrophobic domains at C_{UB}. When the SDS concentration approaches the CAC, cooperative binding between SDS and the HEUR backbones occurs, producing an obvious transition in the EMF curve. For HEUR−C_{16}51K, the $-C_{16}H_{33}$ segments are sufficiently hydrophobic to produce flowerlike micelles in solution. The introduction of minute amounts of SDS monomers produces uncooperative binding of SDS monomers to the hydrophobic core of flower micelles as shown in Figure 6c at $C_{UB} < c <$ CAC. Compared to that in the SDS/HEUR−C_{12}51K system, the onset of uncooperative binding is significantly lower and is not detectable using 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−C_{12}51K and SDS/HEUR−C_{16}51K are similar to that of SDS/HEUR−$C_1$51K.

The binding behaviors between SDS and HEUR can be divided into three concentration regimes, which can be identified using a combination of EMF and ITC techniques. Uncooperative binding may occur at very low SDS concentrations, depending on the character of hydrophobic substitutions. The uncooperative binding process results in a very small enthalpy change, which is not detectable by the sensitive ITC technique, and does not show up on the ITC thermograms. When the SDS concentration reaches the 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 increases in SDS concentration, the aggregation number of SDS in mixed micelles increases, which results in the rehydration of HEUR segments into the water phase. These rehydrated HEUR segments are bound to the surface of SDS micelles through the ion−dipole interaction. Because EMF is sensitive only to the monomeric SDS concentration during the binding process and the monomeric SDS concentrations do not change much during this structural reorganization, such a transition is observable only from ITC thermograms and not from EMF measurements.

Titration of HEUR into Micellar SDS Solutions. 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. In this section, titrations of HEUR into micellar SDS solutions were examined, where the amounts of SDS micelles are in excess and HEUR chains bind only to the surface of SDS micelles via the ion−dipole association to produce the necklace-like SDS/HEUR aggregation complexes.[35,37,40] Figure 7 shows the thermograms of titrating 0.2 wt % HEURs of different molecular masses 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 of these conditions. In addition, the apparent binding enthalpies increase with increasing polymer molecular masses.

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

$$\{(^1/_n)\text{HEUR}\} + \{\text{SDS(micelle)}\} \leftrightarrows \{(^1/_n)\text{HEUR/SDS(micelle)}\} + \Delta H_m$$

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

$$\Delta H_{obs} = \left(\frac{\partial Q}{\partial n_{HEUR}}\right)_{T,P,n_{SDS}} = n\theta\Delta H_m \qquad (9)$$

Because the enthalpy for the binding of one SDS micelle to one basic binding segment, ΔH_m, is a constant, the changes in the apparent enthalpy indicate that the binding capacity ($n\theta$) varies with polymer molecular mass. A linear relationship between the apparent enthalpies and HEUR molecular mass is shown in Figure 8, which indicates the binding enthalpies or the binding capacities ($n\theta$) increase linearly with polymer

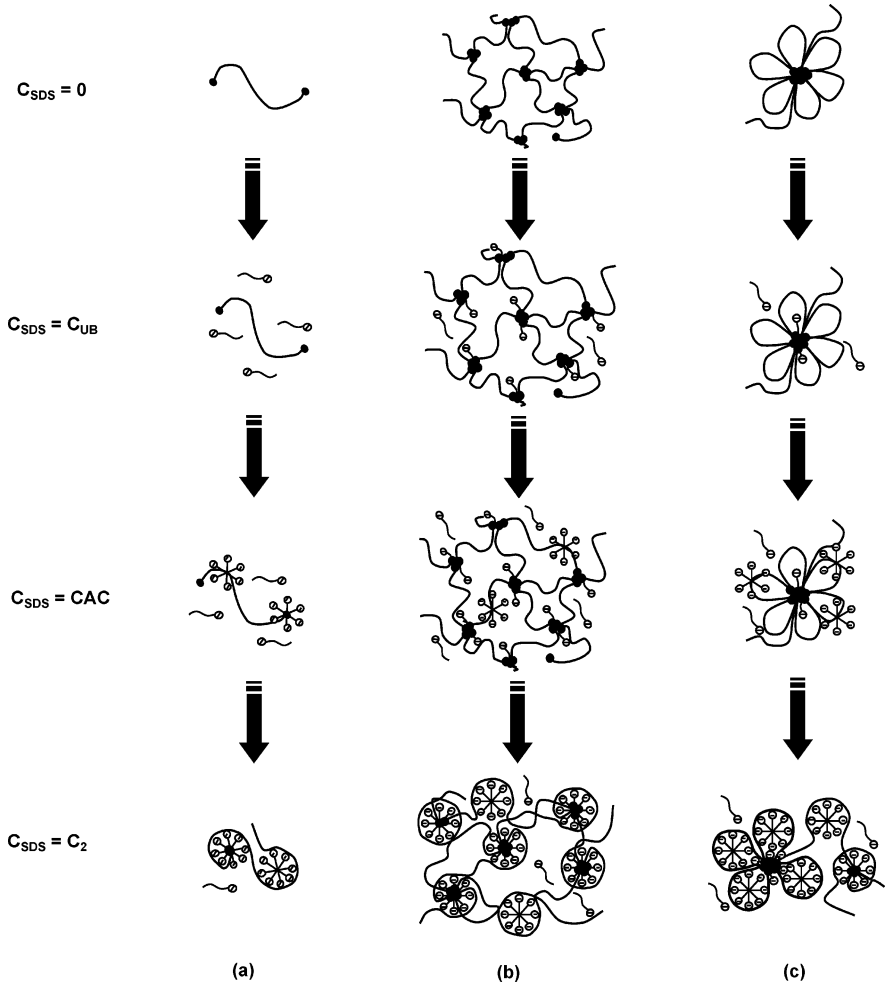

Figure 6. Proposed mechanism for the probable binding interactions between SDS and HEURs with different hydrophobic end-capped groups.

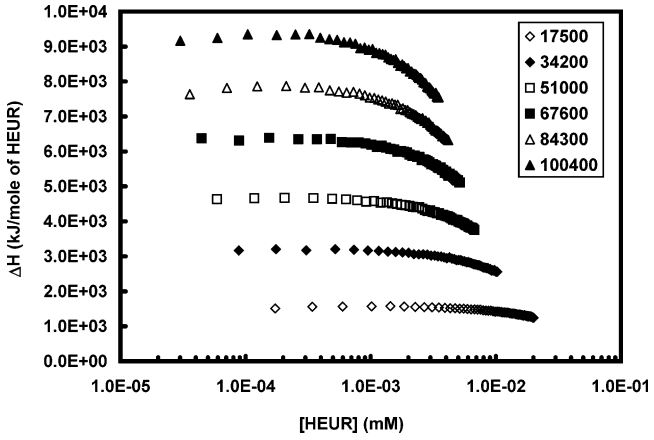

Figure 7. ITC thermograms for titrating 0.2 wt % HEURs with different molecular masses (end-capped with $C_{16}H_{33}$ alkyl chains) into 0.2 M SDS solutions at 298 K and 1 atm.

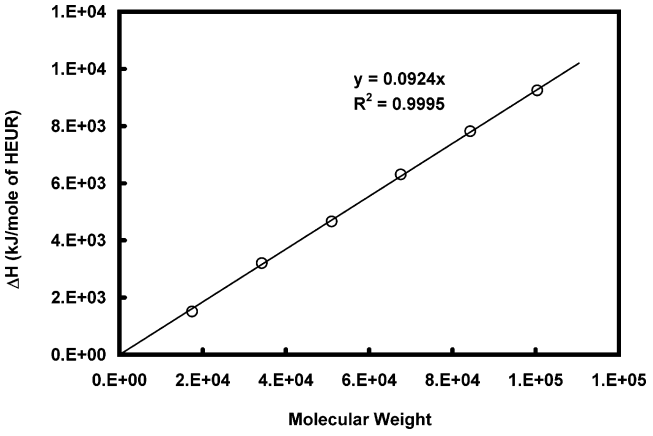

Figure 8. Relationship between the apparent molar binding enthalpies and the molecular masses of HEURs (end-capped with $C_{16}H_{33}$ alkyl chains) for the titration of 0.2 wt % HEURs with different molecular masses into 0.2 M SDS solutions at 298 K and 1 atm.

molecular mass. The number of basic binding segments, *n*, could be determined from the titration of SDS into HEUR solutions as discussed previously. When the number of basic binding segment, *n*, as listed in Table 1 are used, it was found that the values of $\Delta H_{obs}/n$ ($= \theta \Delta H_m$) for 0.2 wt % HEUR are independent of polymer molecular mass, with an averaged value of 450 ± 30 kJ/mol, which indicates that θ does not change with HEUR molecular mass for fixed SDS and HEUR concentrations (wt %) or the main contribution to the increase in the enthalpy with HEUR molecular mass is correlated only to the increasing number of basic binding segments *n*.

It was observed that ΔH_{obs} decreased linearly with HEUR concentrations when titrating different concentrations of HEUR−C_{16}51K into 0.2 M SDS.[24] Because the basic number of binding segments *n* remains constant, the values of $\Delta H_{obs}/n$ are inversely proportional to HEUR concentration, which suggests that the binding fraction θ decreases with increasing titrant polymer concentration. From Figure 7, it is apparent that ΔH_{obs} initially remains constant and begins to decrease when the amount of HEUR in the SDS solution exceeds a critical value. The onset

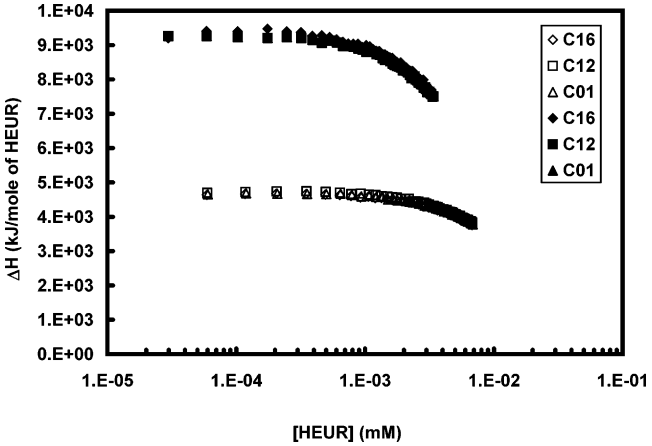

Figure 9. ITC thermograms for titrating 0.1 wt % (solid symbols) and 0.2 wt % (open symbols) HEURs with different hydrophobic end-capped alkyl groups into 0.2 M SDS aqueous solutions at 298 K and 1 atm.

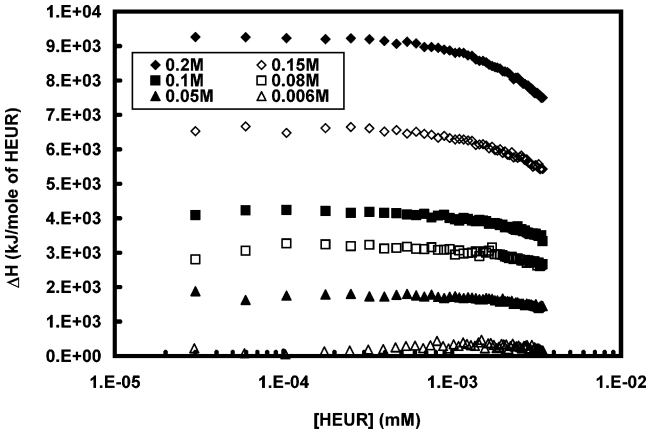

Figure 10. Effects of SDS concentrations on the titration of 0.1 wt % HEUR−$C_1$51K into different concentrations of SDS solutions at 298 K and 1 atm.

of the decrease in ΔH_{obs} is also attributed to the decrease in the binding capacity $n\theta$ or binding fraction θ.

Figure 9 shows the thermograms for titrating 0.1 wt % (open symbols) and 0.2 wt % (solid 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 by the hydrophobic moieties.

To examine the effects of SDS concentrations on the above binding interaction, we titrated a 0.1 wt % HEUR solution into different concentrations of SDS solutions. Figure 10 shows the ITC thermograms for the titration of 0.1 wt % HEUR−$C_1$51K solution into different SDS micellar solutions. The apparent binding enthalpies increase with SDS concentrations. Because of the higher molecular weights of HEUR and the resolution of the microcalorimeter, the dilution heat of HEUR−$C_1$51K and the binding heat between HEUR−$C_1$51K and monomeric SDS are too small to be determined accurately while titrating HEUR into SDS.[24] The relationship between the apparent enthalpy and SDS concentrations is shown in Figure 11. A linear relationship is evident, which is similar to that observed for HEUR−C_{16}-51K and the SDS system.[24] For a fixed concentration of the HEUR polymer chain, n and ΔH_m are constants. Hence, the slope determined from Figure 11 is proportional to the dependence of the binding fraction on SDS concentration, or dθ/d[SDS]. The increase in the apparent binding enthalpies for increasing SDS concentrations is due to the increase in the binding fraction θ. The intercept at the x axis is 11.1 mM, which is larger than the CMC of SDS in aqueous solution. This reinforces the fact that the present binding process occurs only when SDS is in micellar form, resulting in the formation of necklace-like aggregation complexes.

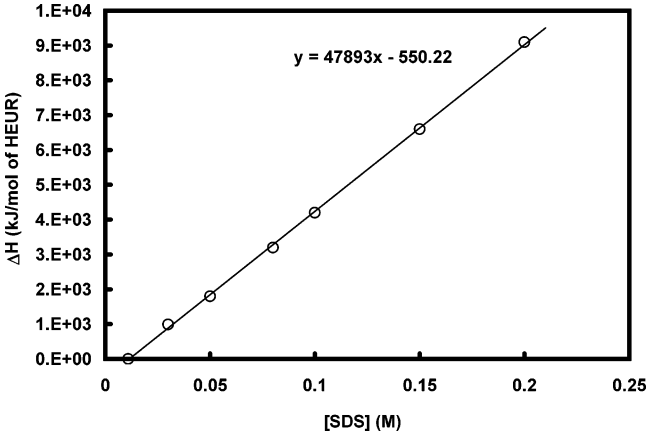

Figure 11. Relationship between the apparent molar binding enthalpies and the SDS concentrations for the titration of 0.1 wt % HEUR−$C_1$51K into SDS at 298 K and 1 atm.

Conclusions

From the EMF measurements, we detected the uncooperative and cooperative bindings between SDS and HEUR at low SDS concentrations. The onset of cooperative binding corresponds to the CAC. Besides the CAC and the saturation concentration C_2, the monomeric SDS concentrations during the binding process were determined from the EMF measurements. However, not only the CAC and C_2 but also the thermodynamic parameters associated with the binding process were determined from ITC. Thermodynamic parameters revealed that cooperative binding between SDS and HEUR at the CAC is an entropy-driven process. Both critical values of CAC and C_2 as determined from EMF and ITC are in agreement. By increasing the end-capped hydrophobic segments, aggregates or micelles are produced in solution, and the monomeric SDS binds uncooperatively to these hydrophobic cores at SDS concentrations lower than the CAC. The presence of hydrophobically modified segments (alkyl chains) and urethane groups along the PEO backbones makes the HEUR more hydrophobic than PEO, which give rise to a lower CAC. The value of C_2 is dependent only on the basic binding segment and not on the total polymer chains. The self-association of HEURs and the uncooperative binding between SDS and HEUR at low SDS concentrations decrease the effects of these end-capped segments on the cooperative binding process. For the titration of HEUR into SDS micellar solutions, HEUR chains are bound to the surface of SDS micelles. The apparent binding enthalpy decreases with decreasing HEUR molecular mass and SDS concentrations as well as increasing HEUR concentrations but is independent of the size of hydrophobes.

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References and Notes

(1) Winnik, M. A.; Yekta, A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 424.
(2) Francois, J.; Maitre, S.; Rawiso. M.; Sarazin, D.; Beinert, G.; Isel, F. *Colloid Surf., A* **1996**, *112*, 251.
(3) Ng, W. K.; Tam, K. C.; Jenkins, R. D. *J. Rheol.* **2000**, *41*, 137.
(4) Tam, K. C.; Jenkins, R. D.; Winnik, M. A.; Bassett, D. R. *Macromolecules* **1998**, *31*, 4149.
(5) Hulden, M. *Colloid Surf., A* **1994**, *82*, 263.
(6) Zhang, K.; Xu, B.; Winnik, M. A.; Macdonald, P. M. *J. Phys. Chem.* **1996**, *100*, 9834.
(7) Binana-Limbele, W.; Clouet, F.; Francois, J. *Colloid Polym. Sci.* **1993**, *271*, 748.
(8) Annable, T.; Buscall, R.; Ettelaie, R.; Shepherd, P.; Whittlestone, D. *Langmuir* **1994**, *10*, 1060.
(9) Olofsson, G.; Wang, G. *Pure Appl. Chem.* **1994**, *66*, 527.
(10) Persson, K.; Wang, G.; Olofsson, G. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3555.
(11) Wang, G.; Olofsson, G. *J. Phys. Chem. B* **1998**, *102*, 9276.
(12) Thuresson, K.; Nystrom, B.; Wang, G.; Lindman, B. *Langmuir* **1995**, *11*, 3730.
(13) Wang, G.; Olofsson, G. *J. Phys. Chem.* **1995**, *99*, 5588.
(14) Li, Y.; Xu, R.; Bloor, D. M.; Holzwarth, J. F.; Wyn−Jones, E. *Langmuir* **2000**, *16*, 10515.
(15) Li, Y.; Xu, R.; Bloor, D. R.; Penfold, J.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **2000**, *16*, 8677.
(16) Ghoreishi, S. M.; Li, Y.; Holzwarth, J. F.; Khoshdel, E.; Warr, J.; Bloor, D. M.; Wyn-Jones, E. *Langmuir* **1999**, *15*, 1938.
(17) Thurn, T.; Couderc, S.; Sidhu, J.; Bloor, D. M.; Penfold, J.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **2002**, *18*, 9267.
(18) Li, Y.; Xu, R.; Couderc, S.; Bloor, D. M.; Wyn−Jones, E.; Holzwarth, J. F. *Langmuir* **2001**, *17*, 183.
(19) Li, Y.; Ghoreishi, S. M.; Warr, J.; Bloor, D. M.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **1999**, *15*, 6326.
(20) Ghoreishi, S. M.; Fox, G. A.; Bloor, D. M.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **1999**, *15*, 5474.
(21) Dai, S.; Tam, K. C. *J. Phys. Chem. B* **2001**, *105*, 10759.
(22) Dai, S.; Tam, K. C.; Li, L. *Macromolecules* **2001**, *34*, 7049.
(23) Dai, S.; Tam, K. C.; Jenkins, R. D. *Macromolecules* **2001**, *34*, 4673.
(24) Dai, S.; Tam, K. C.; Jenkins, R. D. *J. Phys. Chem. B* **2001**, *105*, 10189.
(25) Seng, W. P.; Tam, K. C.; Jenkins, R. D.; Bassett, D. R. *Langmuir* **2000**, *16*, 2151.
(26) Seng, W. P.; Tam, K. C.; Jenkins, R. D.; Bassett, D. R. *Macromolecules* **2000**, *33*, 1727.
(27) Jenkins, R. D. Ph.D. Dissertation, Leigh University, Bethlethem, PA, 1991.
(28) Wiseman, T.; Williston, S.; Brandt, J. F.; Lin, L. N. *Anal. Biochem.* **1989**, *176*, 131.
(29) Wan-Badhi, W. A.; Wan-Yunus, W. M. Z.; Bloor, D. M.; Hall, D. G.; Wyn-Jones, E. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2737.
(30) Xu, R. Ph.D. Dissertation, Salford University, Salford, U.K., 2002.
(31) Wang, C. Ph.D. Dissertation, Nanyang Technological University, Singapore, 2003.
(32) Attwood, D.; Florence, A. T. *Surfactant Systems: Their Chemistry, Pharmacy and Biology*, Chapman and Hall Ltd.: London, 1983.
(33) Lindman, B.; Thalberg, K. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanaban, K. P., Eds.; CRC Press: Boca Raton, FL, 1993; Chapter 5.
(34) Wang, Y.; Han, B.; Yan, H. *Langmuir* **1998**, *14*, 6054.
(35) Goddard, E. D. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanaban, K. P., Eds.; CRC Press: Boca Raton, FL, 1993; Chapter 4.
(36) Gao, Z.; Wasylishen, R. E.; Kwak, J. C. T. *J. Phys. Chem.* **1991**, *95*, 462.
(37) Cabane, B.; Duplessix, R. *J. Phys.* **1982**, *43*, 1529.
(38) Zana, R.; Lianos, P.; Lang, J. *J. Phys. Chem.* **1985**, *89*, 41.
(39) Van Stam, J.; Almgren, M.; Lindblad, C. *Prog. Colloid Polym. Sci.* **1991**, *84*, 13.
(40) Kwak, J. C. T. *Polymer−Surfactant Systems*; Marcel Dekker: New York, 1998.