Calorimetric Studies of Model Hydrophobically Modified Alkali-Soluble Emulsion Polymers with Varying Spacer Chain Length in Ionic Surfactant Solutions

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Received August 17, 1999; Revised Manuscript Received December 16, 1999

ABSTRACT: The binding behavior of SDS onto several model hydrophobically modified alkali-soluble emulsion (HASE) polymers with different spacer chain length was studied using the isothermal titration calorimetric technique. The titration was performed by injecting 0.1 M SDS into 0.1 wt % HASE polymer solution, which yielded a negative enthalpy and a large positive entropy, thus confirming that the interactions between SDS and HASE polymer is entropy-driven. At low degree of ethoxylation (0−5 mol), HASE polymers with short spacer chains form a type I structure consisting of hydrophobic cross-links and hydrophobe−EA junctions. As the length of the spacer chain increases to 10 mol of ethoxylation, the hydrophobes are more accessible to form interchain junctions, yielding a type II cluster. Associative junctions in type II clusters are more accessible to surfactant than those of type I. With increasing spacer chain length, the critical aggregation concentration (cac) and the ΔG of aggregation decrease, while ΔH remains unchanged. A physical model describing the interaction mechanisms between the polymer and surfactant is proposed.

Introduction

In many paint and coating products, the coexistence of both surfactants and polymers is required for colloidal stability and modification of rheological properties. The interactions between polymers and surfactants are complex and at the same time intriguing. The development of commercial microcalorimeters provides an attractive alternative approach to examine these interactions. Besides the extraction of thermodynamic parameters, microcalorimetry allows the characterization of polymer−surfactant systems in terms of critical aggregation concentration (cac) and saturation concentration (C_2).[1] C_2 corresponds to the surfactant concentration at which free micelles start to form when the associative junctions of polymer are fully saturated with bound surfactant. In some cases, a second critical concentration (C_m) is defined to identify the formation of free micelles in the range between cac and C_2. Such a notation was introduced by Bloor and co-workers[2,3] for systems that possess two simultaneous competing surfactant aggregation processes, namely the formation of polymer-bound mixed micelles and free micelles. Most studies emphasized on the interactions of surfactant with unmodified polymers.[2−10] Only a few studies focused on hydrophobically modified polymeric systems.[11−14] Significant endothermic enthalpy and a cac value lower than cmc were detected by Olofsson and co-workers for interactions between ionic surfactants and neutral polymers, both unmodified and hydrophobically modified systems.[7,8,11,12] This was also observed in studies by Wang et al.[14] on the binding of SDS and TTAB with hydrophobically modified and unmodified poly(acrylamide) (HMPAM and PAM). Endothermic heat curves were also reported by Bloor et al. on SDS with poly(propylene oxide) (PPO) and with a copolymer of *N*-(vinylacryloyl)pyrrolidine and 4-vinylpyridine dicyanomethylide (PAPR*).[2,3] Olofsson and Wang[15] published an excellent review on the microcalorimetric studies of polymer−surfactant interactions.

One class of associative polymers that is of interest to us is the hydrophobically modified alkali-soluble emulsion (HASE) polymer. The associative component is comprised of a hydrophobe that is separated from the polymer backbone by a poly(ethylene glycol) spacer chain. In principle, this combination of spacer chain and strong hydrophobe gives the synthetic chemist options for structure modification to control the thickening efficiency, the degree of shear thinning, and the relaxation time of the network. The backbone of the HASE polymer consists of a copolymer of methacrylic acid (MA) and ethyl acrylate (EA) with a small fraction of associative macromonomers (AM) distributed randomly along the backbone (Figure 1). This polymer exists as latexes with a white, milky appearance at low pH. Upon neutralization to pH 9 with a suitable base, the MA groups are ionized and the backbone behaves like an anionic polyelectrolyte. The expanded polymer chains, together with the hydrophobic associations, produce a

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10.1021/ma9913919 CCC: $19.00
Published on Web 02/10/2000

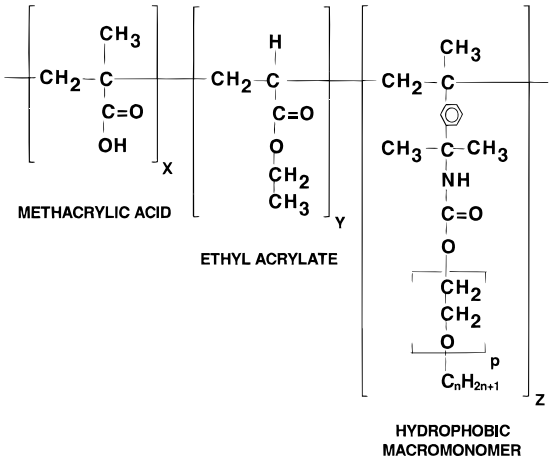

Figure 1. Molecular structure of HASE. R = hydrophobic group; p = number of moles of ethoxylation (spacer length) between polymer backbone and hydrophobic group. x:y:z = 49.05:50.04:0.91.

network structure that significantly increases the viscosity of the solution. The ability of HASE polymers to self-aggregate is analogous to the micellization behavior of free surfactants. We would thus expect a complex structure to evolve from the mixture of these two types of compounds as previously reported for studies using the rheological technique.[16−21] In this paper, we aim to examine the effect of varying the spacer chain length on the interactions between SDS and a series of model HASE polymers. The objective is to obtain a basic understanding of how ionic surfactant binds onto HASE polymer whose hydrophobes are extended away from the backbone using different length of PEO spacer chains.

Experimental Details

Materials. The series of model HASE polymers used in this work were synthesized according to the method described in detail by Jenkins et al.[16] and Tirtaatmadja et al.[22] The chemical structure of HASE is shown schematically in Figure 1. It has an average molecular weight of approximately 200 000−250 000 determined by intrinsic viscosity[23] and static light scattering measurements.[24,25] This copolymer was prepared by conventional semicontinuous emulsion polymerization. The composition of the MAA/EA/AM was kept at 49.05/50.04/0.91 mol %. The structure of the AM comprises of a poly(oxyethylene) chain connected to an alkyl hydrophobic group (R = C_nH_{2n+1}) at one end and a vinyl polymerizable group at the other end. The associative macromonomer was prepared by first ethoxylating a linear alkyl primary alcohol at p moles of ethylene oxide to make a surfactant and subsequently reacting the resulting terminal primary hydroxyl group of the ethoxylate chain portion of the surfactant with an unsaturated isocyanate. This connects the ethoxylated portion of the surfactant to a vinyl polymerizable double bond through a urethane linkage. The polymers are designated as HASE-(EO)p-R, where p is the number of moles of ethoxylation and R is the hydrophobes. Eight model HASE polymers were examined with p equal to 0, 5, 10, 15, 20, 25, 35, and 40 mol of ethoxylation. The hydrophobe R was kept constant at $C_{20}H_{41}$.

The model polymer latex at low pH (ca. 3−4) was dialyzed against distilled−deionized water for about 4 weeks, so as to remove all the impurities and unreacted chemicals. A stock solution of 3 wt % in 0.1 mM KCl was prepared and stored at 4 °C prior to use. From the stock HASE solutions, lower concentration at 0.1 wt % HASE in 0.1 mM KCl was prepared. The alkaline used to neutralize the polymer to the required pH value of approximately 9 is 2-amino-2-methylpropanol-1 (AMP). The anionic surfactant used in this study is sodium dodecyl sulfate (SDS from BDH Laboratory Supplies, 99%, $C_{12}H_{25}OSO_3Na$). They were used as received without further purification. A stock of 0.1 M SDS was prepared in 0.1 mM KCl solutions.

Microcalorimetric Measurements. The experiments were performed using a Microcal isothermal titration calorimeter (Microcal ITC). A detail description of this power compensation, differential instrument can be found in Wiseman et al.[26] The calorimeter 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 SDS solution (in aliquots of 5 μL) from a 250 μL injection syringe into the sample cell filled with 0.1 wt % of the sample HASE 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 interactive software, an injection schedule was automatically carried out after setting up the number of injections, the volume of each injection, and the time between each injection. The measurements of the cmc, cac, enthalpies of micellization, and enthalpies changes associated with polymer−surfactant interactions were performed at a constant temperature (25.0 ± 0.02 °C). The principles and basic thermodynamic conventions of ITC were recently discussed.[27] The thermodynamic data determined from ITC were checked for reproducibility by repeating one of the tests twice. The data are reproducible to within ±5%.

Results and Discussion

Parts a and b of Figure 2 show the thermograms for isothermal titration of 0.1 M micellar SDS into water and 0.1 wt % HASE-(EO)10-C20H41, respectively. These thermograms contain a raw heat signal that is expressed as the electrical power, cell feedback (CFB), required to maintain a constant temperature difference between the sample and reference cells. Each injection of concentrated SDS has a volume of 5 μL when titrated into the sample cell, except the first volume of injection, which is 2 μL. From Figure 2a, the CFB for titration of 0.1 M SDS in the absence of HASE polymer exhibits an increasing endothermic signal until a maximum at the 24th injection, and thereafter, the positive signal decreases. In the presence of HASE-(EO)10-C20H41, the initial portion of the thermogram (see Figure 2b) follows that of Figure 2a. At around the ninth injection, the CFB curve reaches a smaller maximum, which then decreases drastically to reach a minimum near the 24th injection. Beyond this point, the CFB increases slightly.

Integration of the CFB signal with respect to time at the ith injection normalized to the concentration of SDS injected yielded the observed enthalpy change (ΔH_{obs}) between the (i − 1)th and ith injections. Figures 3a and 4a show the differential enthalpic curves for titration of 0.1 M SDS into HASE with varying spacer chain length where the ΔH_{obs} for each injection is plotted against the concentration of SDS. The titration curve of 0.1 M SDS in water is included in both figures. The difference between the titration curve of SDS and the differential enthalpic curves with polymers is ascribed to SDS−HASE interaction. In the premicellar region, the concentration of SDS in the cell at each injection is below the critical micellar concentration (cmc). The added SDS micelles disintegrate into monomers, which generate large endothermic heat, ΔH_{obs}. The curves of HASE polymers follow the demicellization portion of the dilution curve where no polymer−surfactant interaction is observed. These curves then begin to deviate from the titration curve of pure SDS at a critical concentration that corresponds to the onset for binding of SDS onto HASE, which is commonly referred to as the critical aggregation concentration (cac). The ΔH_{obs} becomes less endothermic due to progressive binding of SDS mono-

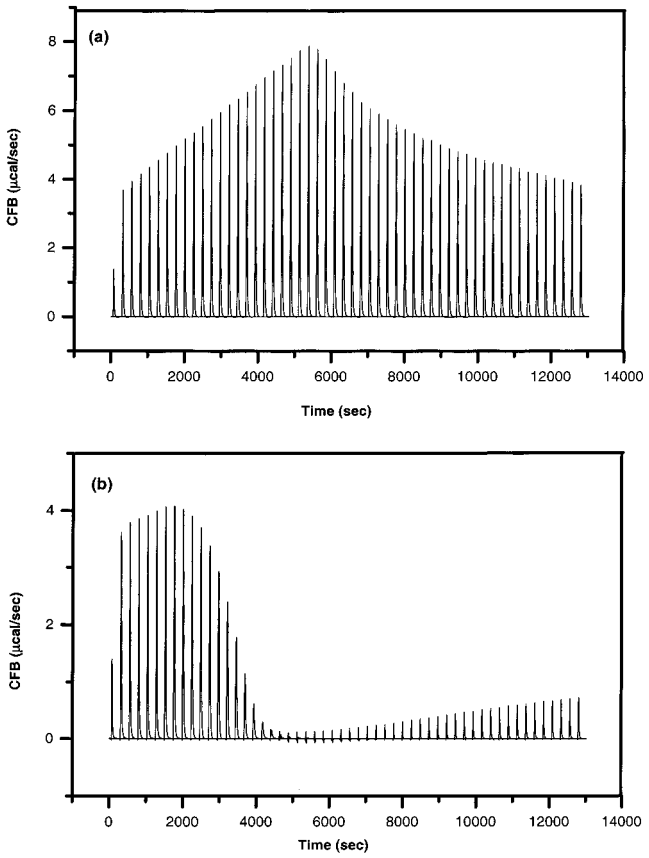

Figure 2. Thermograms showing cell feedback (CFB) versus time for calorimetric titration of 100 mM SDS into (a) water and (b) 0.1 wt % HASE-(EO)10-C20H41 at 25 °C.

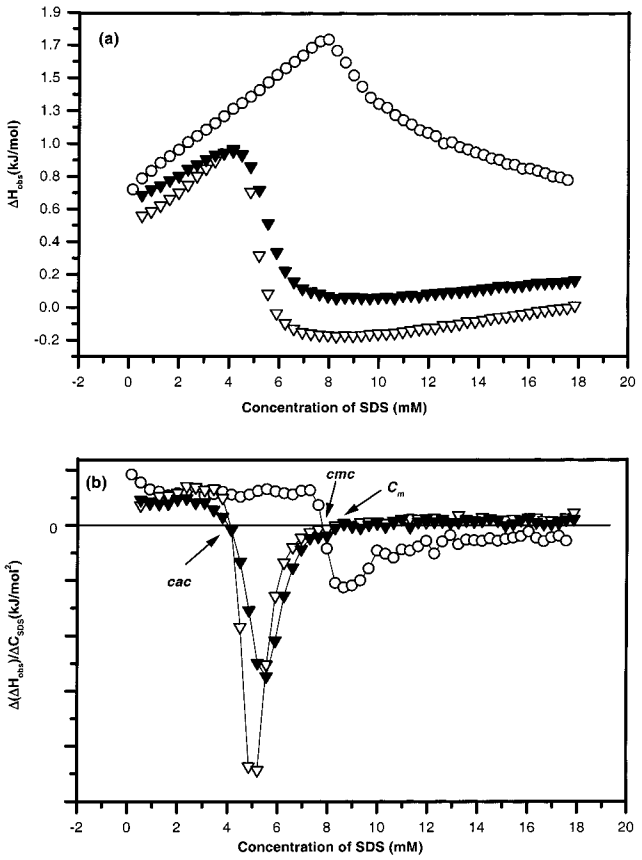

Figure 3. (a) Differential enthalpic curves for titration of 100 mM SDS into water (○) or 0.1 wt % HASE polymers with varying spacer chain length: 0 (▽) and 5 mol (▼) of ethoxylation plotted against concentration of SDS at 25 °C. (b) Difference curves of the differential enthalpic curves in (a) indicating the positions of cmc, cac, and C_m. Type I associative cluster.

mers onto HASE. This reduction in ΔH_{obs} continues until a second critical concentration near the cmc, denoted as C_m. This is the concentration where free micelles start to form between the range of cac and C_2. However, we are unable to identify C_2 since the differential enthalpic curves of HASE do not merge with the dilution curve over the range of concentrations examined.

The critical concentrations, such as cmc, cac, and C_m, described above can be clearly identified from the plots of difference curves of titration of SDS into water and HASE polymers as shown in Figures 3b and 4b. The difference curve contains the incremental enthalpy changes ($\Delta H_{obs}[k] - \Delta H_{obs}[k-1]$) plotted against the change in surfactant concentration (ΔC_{SDS}), where k refers to the kth injection.[8] The cac is defined by Wang and Olofsson[8] as the onset point where the differential enthalpic curve for their polymer deviates from the dilution curve. This is identified as the first peak in the difference curve. In the presence of HASE polymer, the deviation of the curve shifts to a less endothermic enthalpy change and the cac corresponds to the first peak (see Figure 3a). This is identified by the point where the slope of the difference curve is equal to zero. The value of C_m is observed to be independent of the length of the spacer chain. The values of cmc and cac for the titration of SDS into water and HASE polymers are tabulated in Tables 1 and 2.

The shape of the differential enthalpic curves for titration of micellar SDS into HASE-(EO)00-C20H41 and HASE-(EO)05-C20H41 (HASE with no or very short spacer chain) generally follows the same trend as shown in Figure 3a. The position of the endothermic peak remains constant as the degree of ethoxylation increases from 0 to 5 mol. The cac extracted from their difference curves in Figure 3b possesses a constant value of 4.1 mM, which indicates that cac is independent of the spacer chain length at a low degree of ethoxylation. However, as the spacer chain length is increased to ~10 mol, the position of the onset shifts to lower concentration (~3.2 mM) as shown in Figure 4a,b. The depression of cac is mainly due to enhanced hydrophobic interaction between the polymer hydrophobes and the hydrophobic portion of SDS molecules.[14] A further increase in the spacer chain length (from 10 to 40 mol) does not alter the position of the endothermic peak. That is to say, cac is only dependent on the spacer chain length when it varies from 5 to 10 mol. Beyond 10 mol, the value of cac is independent of the degree of ethoxylation (see Figure 4b). This trend is best observed from the plot of cac against degree of ethoxylation as shown in Figure 5. It signifies the existence of two types of associative structure (type I and type II) in the dilute HASE polymer solutions. A spacer chain of 5−10 mol is the

Table 1. Critical Micellar Concentration and Thermodynamic Parameters for Micellization of SDS in Water at 25 °C

surfactant	cmc (mM)	ΔG_{mic} (kJ/mol)	ΔH_{mic} (kJ/mol)	$T\Delta S_{mic}$ (kJ/mol)
SDS	8.2 (6.8)[a]	−22.1 (−23.2)[a]	−1.72 (−2.30)[a]	20.3 (20.3)[a]

[a] Values obtained from ref 14.

Table 2. Critical Aggregation Concentration and Thermodynamic Parameters for Aggregation of SDS in the Presence of 0.1 wt % HASE with Varying Spacer Chain Length at 25 °C

surfactant	polymer	cac (mM)	ΔG_{agg} (kJ/mol)	ΔH_{agg} (kJ/mol)	$T\Delta S_{agg}$ (kJ/mol)	ΔG_{ps} (kJ/mol)
SDS	HASE-(EO)00-C20H41	4.1	−25.2	−1.00	24.2	−3.2
	HASE-(EO)05-C20H41	4.1	−25.2	−1.00	24.2	−3.2
	HASE-(EO)10-C20H41	3.3	−26.3	−0.99	25.3	−4.2
	HASE-(EO)15-C20H41	3.2	−26.4	−0.81	25.6	−4.4
	HASE-(EO)20-C20H41	3.3	−26.1	−0.92	25.2	−4.1
	HASE-(EO)25-C20H41	3.2	−26.4	−0.90	25.5	−4.3
	HASE-(EO)35-C20H41	3.3	−26.3	−0.89	25.4	−4.2
	HASE-(EO)40-C20H41	3.1	−26.5	−0.85	25.6	−4.4

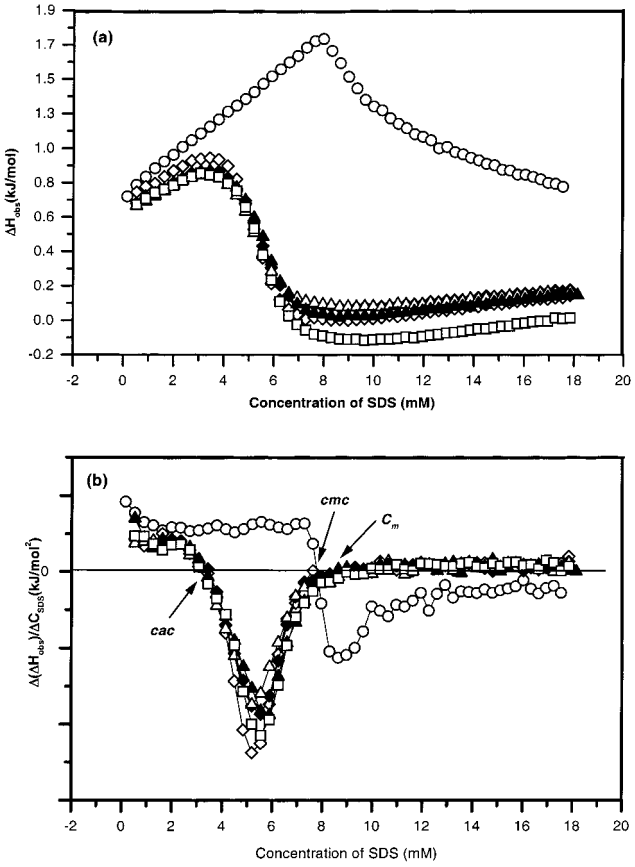

Figure 4. (a) Differential enthalpic curves for titration of 100 mM SDS into water (○) or 0.1 wt % HASE polymers with varying spacer chain length: 10 (◇), 20 (◆), 25 (△), 35 (▲) and 40 mol (□) of ethoxylation plotted against concentration of SDS at 25 °C. (b) Difference curves of the differential enthalpic curves in (a) indicating the positions of cmc, cac, and C_m. Type II associative cluster.

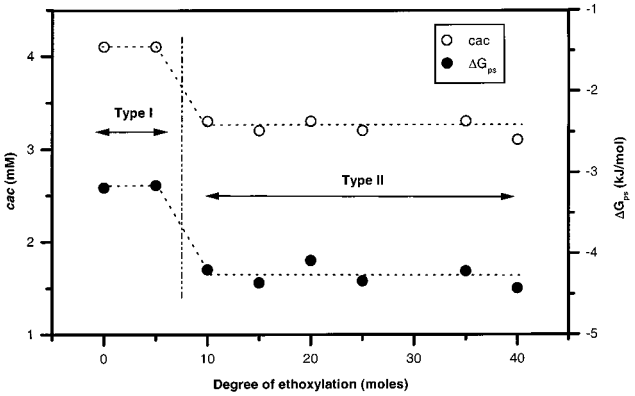

Figure 5. Plot of cac (○) and ΔG_{ps} (●) for titration of SDS into HASE polymers versus moles of ethoxylation. Dotted lines are plotted as guidelines.

critical spacer length for the onset of this transition.

The peak height of the endothermic enthalpic curves is known to be related to the polymer hydrophobicity.[8,14,28] By varying the degree of ethoxylation in the AM, one is able to control the nature of the hydrophobic junctions by changing not only the hydrophobicity but also the accessibility of the hydrophobes in the HASE polymer.[29] From Figures 3a and 4a, the peaks of the endothermic curves remain at around the same value, which means that the enthalpy change of SDS aggregation (ΔH_{agg}) in the presence of HASE polymers is independent of the spacer chain length. The changes in the polymer hydrophobicity resulting from the hydrophilic PEO spacer do not play an important role in altering the value of ΔH_{agg}. Using the thermodynamic equations derived from the charged phase separation and mass-action models,[30,31] the Gibbs free energy change of micellization (ΔG_{mic}) and Gibbs free energy change of aggregation in the presence of polymer (ΔG_{agg}) are determined from the following equations:

$$\Delta G_{mic} = (1 + K)RT \ln[\text{cmc}] \quad (1)$$

$$\Delta G_{agg} = (1 + K)RT \ln[\text{cac}] \quad (2)$$

A factor of $(1 + K)$ is needed to calculate the free energy of ionic SDS, where K is the micellar charge fraction with a value of 0.85.[32] The enthalpy change and free energy change are then used to calculate the entropy change of micellization (ΔS_{mic}) and the entropy change of aggregation in the presence of polymer (ΔS_{agg}). All these parameters are summarized in Tables 1 and 2. The values of enthalpy change obtained calorimetrically are very much smaller than the term $T\Delta S$. The results suggest that both the aggregation processes of SDS in the absence and presence of model HASE polymers are entropy driven. The micellization behavior of surfactant and formation of polymer/surfactant mixed micellar junctions are analogous to each other; therefore, the dominant driving force behind these processes is similarly governed by a positive entropy gain. In the presence of HASE-(EO)00-C20H41 and HASE-(EO)05-C20H41 with 0 and 5 mol of ethoxylation, respectively, ΔS_{agg} of SDS is more positive than ΔS_{mic}, signifying that the entropic contributions to the HASE-SDS interaction tends toward a more disordered environment. With increasing polymer spacer chain length from 5 to 10 mol, this degree of disorderliness increases as indicated by the larger positive entropy. A similar trend is observed for ΔG_{agg}. As the spacer chain length increases from 5 to 10 mol, ΔG_{agg} becomes more negative. This means that the surfactant binding in the presence of HASE with 10 mol of PEO spacer is more favorable than systems with less than 10 mol. A further increase in spacer chain length from 10 to 40 mol shows no change in both ΔG_{agg} and ΔS_{agg}. According to Lindman and Thalberg,[31] the free energy to drive 1 mol of surfactant

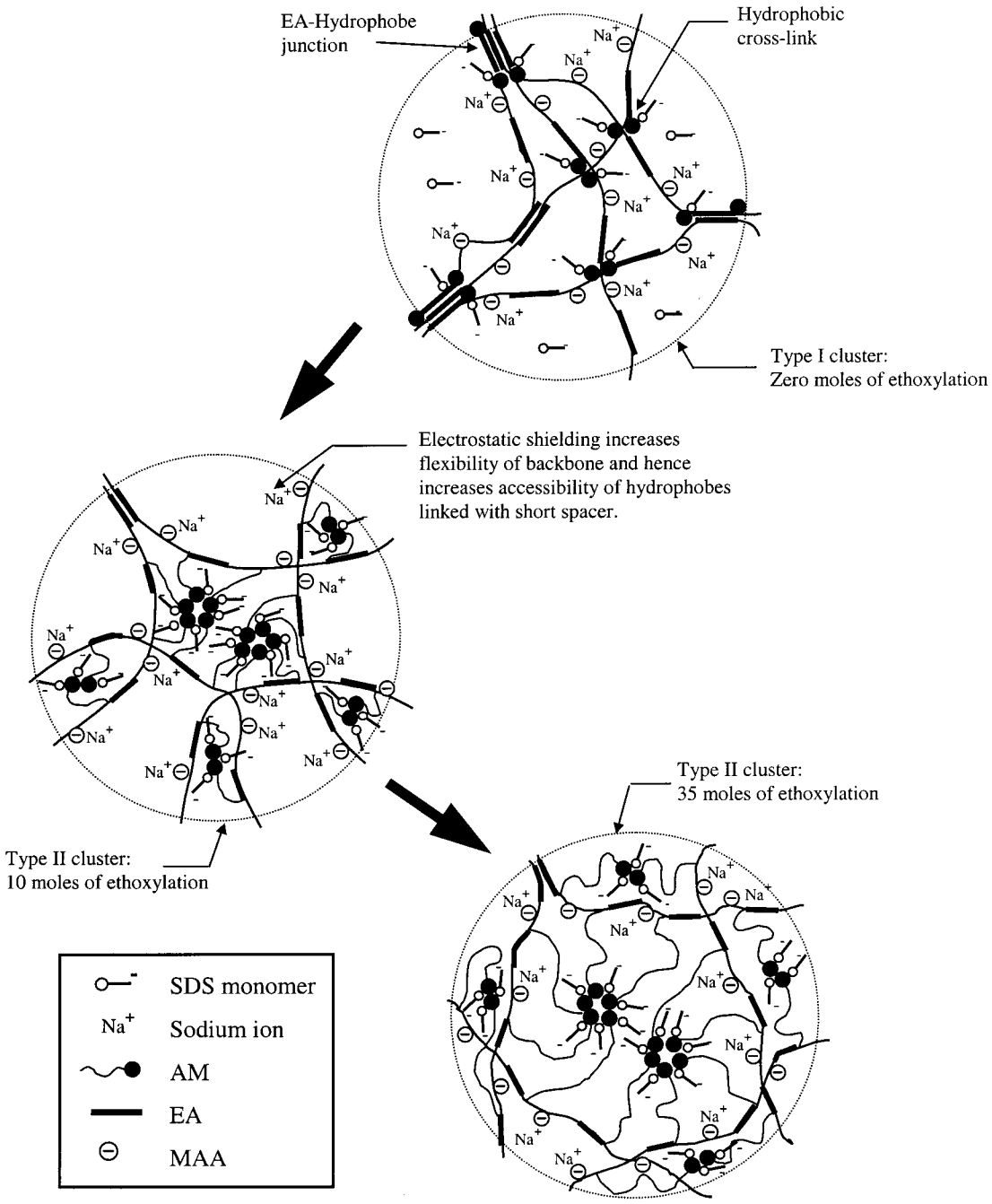

Figure 6. Proposed associating mechanisms between anionic SDS and type I cluster of HASE polymers with 0−5 mol of ethoxylation and type II cluster of HASE polymers with 10−40 mol of ethoxylation.

free micelle into polymer-bound micelle could be derived from the relationship

$$\Delta G_{ps} = \Delta G_{agg} - \Delta G_{mic} \quad (3)$$

This value can be used to define the binding strength of surfactant onto polymer. The result shows that ΔG_{ps} is dependent on the length of the polymer spacer chain around the transition degree of ethoxylation (5−10 mol) (see Figure 5). The more negative ΔG_{ps} at −4.2 kJ/mol for HASE-(EO)10-C20H41 clearly indicates that the interaction between a polymer with type II structure, and SDS is much stronger compared to polymers with type I structure (0 and 5 mol).

There are three important factors to consider when discussing the associative mechanisms for hydrophobic interactions in HASE: first, the hydrophile−lipophile balance (HLB) of the AM; second, the accessibility of spacer chain length; and third, the electrostatic interactions of ionized MAA groups with themselves or with charged surfactants. According to the results determined from laser light scattering studies,[25] HASE polymer in dilute aqueous solution exists as individual clusters, consisting of 5−6 polymer chains. In each cluster, the interchain hydrophobic junctions comprise of hydrophobes linked by spacer chains to the backbones of the polymers. Before the titration with SDS, the HASE polymers are in the form of small individual clusters. The type of cluster depends on the degree of ethoxylation.

Figure 6 shows the proposed microstructures of type I cluster of HASE polymers with 0−5 mol of ethoxylation and type II clusters of HASE polymers with 10−

40 mol of ethoxylation. Because of the constraint of short spacer chain, HASE polymers with low degree of ethoxylation (0−5 mol) are restricted to form hydrophobic cross-link junctions. This kind of junction is extremely close to the polymer backbones, and because of the steric hindrance from the backbones, the number of hydrophobes per junction is constrained by the polymer backbone (see Figure 6). Recent studies conducted at our laboratory on dilute HASE polymer solution using laser light scattering technique showed that the EA segments are blocky and hydrophobic enough to induce hydrophobic association in water.[25] The junctions are in the form of EA block "bundles" as shown in Figure 6. In this case, the hydrophobes linked by short spacer chains are able to associate with these EA "bundles" to form hydrophobe−EA junctions. In the dilute region of HASE polymers with 0−5 mol of ethoxylation, the conformation of the cluster is therefore classified under type I consisting of hydrophobic cross-links between EA blocks and hydrophobe−EA junctions. Upon titration of SDS into type I cluster, the binding of SDS monomers onto the hydrophobic cross-links is hindered by the steric hindrances from the backbone. A similar study on the effect of spacer chain length of HASE using the intrinsic viscosity approach was carried in this laboratory.[33] We observed the existence of hydrophobe−EA junctions, which minimizes the exposure of hydrophobic domain to the aqueous environment as indicated by the low Huggins coefficient. In other words, the driving force for hydrophobic association between the SDS monomers and these junctions is also minimized. Consequently, a larger amount of SDS monomers is required to produce the onset of the aggregation process, and hence the weaker HASE−SDS interaction is observed as indicated by the higher cac and lower negative ΔG_{ps} (see Table 2).

From Table 2, we observe that between 5 and 10 mol of ethoxylation is the critical spacer chain length for an associative cluster to transform from type I to type II cluster. The cac decreases to lower concentration while other thermodynamic parameters such as $-\Delta G_{agg}$, ΔS_{agg}, and $-\Delta G_{ps}$ increase to higher values. At 10 mol of ethoxylation, the accessibility of the hydrophobes is enhanced. This is because the spacer chains are now sufficiently long to allow interchain hydrophobic associations with other polymer chains within the cluster. The formation of the interchain hydrophobic junctions will dominate the formation of hydrophobe−EA junctions since the hydrophobic groups of polymer systems prefer to associate with those species of similar hydrophobicity.[34] In the dilute region of HASE polymers with 10 mol of ethoxylation and above, the conformation of the cluster is classified as type II, which consists of mostly interchain hydrophobic junctions (see Figure 6). The aggregation number of each hydrophobic junction is not at its optimum and hence is not as stable. The reason is that there are 16−18 hydrophobes attached along each polymer backbone. With this limited number of hydrophobes, the stiff backbone restricts the movement of the hydrophobes from forming an optimum micellar cluster in contrast to the mobile free surfactant monomers. The nature of the hydrophobic junction induces the binding of free surfactant monomers to form mixed micellar junctions, which acts to stabilize the junction. The driving force for binding is more significant for the cluster of type II (10−40 mol) conformation compared to the cluster of type I (0−5 mol). This is borne out by the thermodynamic data obtained from isothermal titration calorimetry.

As indicated in Figure 5 and Table 2, the cac and other thermodynamic data are not affected by the length of the spacer chain ranging from 10 to 40 mol. This suggests that the SDS molecules are interacting with hydrophobic junctions with the same morphology, i.e., junctions that contain a similar number of hydrophobes. Besides the accessibility of spacer chain, the cluster conformation is also affected by two other opposing factors. They are the increasing amount of free sodium ion from SDS that shields the charged MAA groups along the backbone and the electrostatic repulsive forces between the SDS charged headgroups in the polymer-bound micelles. If the electrostatic shielding effect can be ignored and the charged backbone is stiff, we should expect that polymers with shorter spacer chain (∼10 mol) will form a cluster that contains more junctions with a smaller number of hydrophobes in each junction. The hydrophobes with longer spacer chain (∼35 mol) will have greater accessibility to extend further and associate with other hydrophobes. The cluster formed will contain fewer junctions, but each junction contains a larger number of hydrophobes. The above hypothesis has been verified using a nonionic surfactant (instead of an ionic one), where the effect of electrostatic shielding was removed. In this work, however, once the repulsive interactions along or between the backbones are substantially removed by electrostatic shielding through the addition of a sufficient amount of sodium free ions from the SDS, the backbones become more flexible. This effect is similar to the addition of salt into a HASE polymer. Guo et al.[23] showed that, with increasing salt concentration ranging from 1 to 10 mM, the stiffness index decreased significantly (persistence chain length decreased from 14.6 to 4.8 nm). The first few injections of SDS yielded a final concentration close to the cac (∼3 mM) and therefore provided sufficient ionic species to cause the stiffness of the backbone to decrease. Within a type II cluster, the backbones that are more flexible will permit the hydrophobes to reorganize and form fewer junctions. However, each junction contains a larger number of hydrophobes (see Figure 6). This type of junction requires approximately the same amount of SDS (∼3 mM) for the initial binding of SDS to occur. The aggregation process exhibits physicochemical properties such as ΔG_{agg}, ΔS_{agg}, and ΔG_{ps} that remain unchanged when the moles of EO varies from 10 to 40 mol as shown in Table 2.

Conclusion

The results show that the binding behaviors of SDS with HASE polymers are dependent on the spacer chain. Polymers with short spacer chain (0−5 mol) are constrained to form a type I associative cluster consisting of hydrophobic cross-links and hydrophobe−EA junctions. As the degree of ethoxylation increases to 10 mol, the polymers are capable of forming a type II cluster consisting of interchain junctions. The junctions in a type II cluster require a lower concentration to initiate surfactant binding and are stronger than in a type I cluster as revealed by the reduction in cac and ΔG_{ps}. A type II cluster also shows higher ΔS_{agg} than type I. However, the thermodynamic parameters are not affected when the spacer chain length of HASE is increased from 10 to 40 mol due to the electrostatic shielding of the polymer backbones.

Acknowledgment. This work was supported by the National Science and Technology Board of Singapore, the Ministry of Education, and the Singapore-Ontario collaborative research program. We acknowledge the useful discussions with W. K. Ng and our collaborative partners involved in this project (i.e., Professors Mitch Winnik and Peter Macdonald from the University of Toronto and Professor Dan Ou-Yang from Lehigh University).

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MA9913919