

Interactions of Cationic Gemini Surfactants with Hydrophobically Modified Poly(acrylamides) Studied by Fluorescence and Microcalorimetry

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Steady-state fluorescence, time-resolved fluorescence quenching, and isothermal titration microcalorimetry have been used to study the interactions of cationic gemini surfactants alkanediyl- α,ω -bis(dodecyldimethylammonium bromide) ($C_{12}C_5C_{12}Br_2$, $S = 3, 6$, and 12) with hydrophobically modified poly(acrylamide) (HMPAM) and unmodified poly(acrylamide) (PAM). Without addition of gemini surfactant, 0.2 wt % HMPAMs except PAM have already self-aggregated into hydrophobic aggregates. Different from single-chain surfactants, $C_{12}C_5C_{12}Br_2$ have stronger interactions with HMPAMs to form surfactant/polymer aggregates, even with PAM. Addition of $C_{12}C_5C_{12}Br_2$ may cause the disruption of HMPAM hydrophobic aggregates and the formation of mixed micelles. It is found that HMPAMs generate lower micropolarity of mixed micelles, larger values of enthalpy of interaction (ΔH_{ps}), and nearly constant values of Gibbs free energy of interaction (ΔG_{ps}). On the other hand, $C_{12}C_5C_{12}Br_2$ with longer spacer brings out slightly lower micropolarity of mixed micelles, owing to the lower electrostatic repulsion between surfactant headgroups. Especially for $C_{12}C_{12}C_{12}Br_2$, the values of ΔH_{ps} are much more endothermic and the values of ΔG_{ps} are much less negative. The weaker interactions of $C_{12}C_{12}C_{12}Br_2$ with HMPAMs arise from the marked reduction of attraction between surfactant headgroups and polymer hydrophilic groups induced by its longer spacer.

Introduction

Increasing attention has been paid to hydrophobically modified (HM) polymers because of their widespread applications and unusual properties.¹ HM polymers consist of a water-soluble backbone on which a small number of hydrophobic groups are chemically attached and the hydrophobic side groups often consist of long alkyl chains. Especially, mixing of surfactant with HM polymer always generates many unique properties involving a more specific interaction pattern than their unmodified relatives. For example, many authors^{2–4} found that the viscosity of an aqueous solution of HM polymers goes through a pronounced maximum as surfactant concentration is increased. Kwak et al.⁵ reported an associative phase separation in a mixture of hydrophobically modified poly(acrylamide) (HMPAM) and sodium dodecyl sulfate (SDS) induced by salt. Meanwhile, Wang et al.⁶ showed that, with the addition of SDS to polymers, the higher hydrophobicity of HM polymers leads to a much more compact packing in the polymer–micelle aggregates. These observations show that the interaction of surfactant with HM polymer is dependent on the hydrophobicity of the polymer as well as the structure of the surfactant.

The aggregation properties of HM polymers with conventional single-chain surfactants have been widely studied with a

variety of methods. However, there have been very few reports on interactions between gemini surfactants and HM polymers. Gemini surfactants comprise two single-chain surfactant moieties joined by a spacer group.^{7–9} This novel class of surfactants has many unique properties that are superior to those of conventional single-chain surfactants, such as remarkably low critical micelle concentration (cmc), much higher surface activity, unusual aggregation morphologies, and better wetting properties. Many works have shown that the spacer of the gemini surfactant plays a major role in the aggregation properties of these surfactants, attributing to the conformational change of the surfactant molecules and to the change of the spacer location in the micelles.¹⁰ To our knowledge, only two previous studies were reported on the interactions between gemini surfactants and HM polymers. Bai et al.¹¹ found that the interactions between polymers are much stronger for gemini surfactants in comparison with single-chain surfactants. Moreover, gemini surfactants with different spacer length have a similar magnitude of interaction with HMPAM, while the gemini surfactant with a shorter spacer has a stronger interaction with hydrophobically modified poly(acrylamide-*co*-acrylic acid) (HMPAM-AA) compared with the gemini surfactant with a longer spacer. In addition, Zana et al.¹² showed that the interaction of gemini surfactants with hydrophobically modified hydroxypropylguar (HMHPG) depends strongly on the ranges of surfactant concentration, which depend slightly on the spacer length. These studies have to some extent clarified the association behavior of gemini surfactants with HM polymers. However, to gain deeper insights into the role of the

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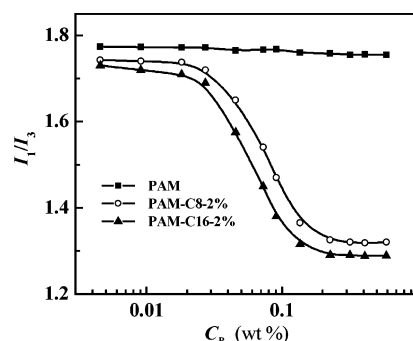
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In the present work, we focus on the effect of the spacer length of gemini surfactant on the interactions of cationic gemini surfactants with hydrophobically modified poly(acrylamide) (HMPAM) using steady-state fluorescence, time-resolved fluorescence quenching, and isothermal titration microcalorimetry. The cationic gemini surfactants alkanediyl- α,ω -bis(dodecyltrimethylammonium bromide) have the structure $[\text{C}_{12}\text{H}_{25}(\text{CH}_3)_2\text{N}(\text{CH}_2)_S\text{N}(\text{CH}_3)_2\text{C}_{12}\text{H}_{25}]\text{Br}_2$, $\text{C}_{12}\text{C}_5\text{C}_{12}\text{Br}_2$, where $S = 3, 6$, and 12 , indicating the number of carbons in the spacer. Two HMPAMs examined in this work carry different alkyl chains, octyl and hexadecyl chains, respectively. For comparison, parallel measurements have also been made on the interactions between gemini surfactants and unmodified poly(acrylamide) (PAM).

Materials. Gemini surfactants $C_{12}C_5C_{12}Br_2$ ($S = 3, 6,$ and 12) were synthesized and purified according to the method of Menger and Littau.⁹ Polyacrylamide (PAM) was purchased from ACROS. The hydrophobically modified polyacrylamides (HMPAMs) were prepared by *N*-alkylation of PAM in dimethyl sulfoxide (DMSO).^{13–14} A typical procedure for preparing PAM-C8-2% was as follows: First 2.0 g of PAM and 200 mL of anhydrous DMSO were introduced into a 1 L three-necked round flask. When the dissolution of PAM in DMSO was completed after 24 h of constant stirring at 80 °C under nitrogen atmosphere, the solution was cooled to room temperature. Then 10 mL of DMSO solution containing potassium *tert*-butoxide (0.17 g) was added into the flask. Afterward octyl bromide (0.12 g) dissolved in 10 mL of DMSO was also added. The alkylation reaction proceeded at 65 °C with agitation for 24 h. The final reaction mixture was dialyzed and then freeze-dried to give a white powder. The structures of the polymers are shown in Figure 1. The average molecular weight determined by viscometry was approximately 200 000 for these three polymers. The fluorescence probe pyrene (Aldrich) and a quencher of the fluorescence probe benzophenone (Fluka) were recrystallized from ethanol. Triply distilled water was used throughout this work.

Time-Resolved Fluorescence Quenching. This method was used to determine the micelle aggregation number of surfactant or polymer alkyl chain, using a Horiba NAES-1100 single photon counting spectrophotometer. For each sample, the decay of the fluorescence probe was recorded separately in the absence



of quencher and in the presence of quencher at 298.15 ± 0.05 K. The long-time slopes of the decay curves in the presence of quencher are always identical with those without quencher within experimental error. This behavior indicates that the probe and quencher are immobile on the fluorescence time scale. In this case, the quenched decays were fitted to the following equation¹⁷⁻²⁰

$$I(t) = I(0) \exp\{-A_2 t - A_3[1 - \exp(-A_4 t)]\} \quad (1)$$

$$N_s = A_3(C_s - \text{cac})/[\text{quencher}] \quad (2)$$
$$N_H = A_3[H]/[\text{quencher}] \quad (3)$$

Isothermal Titration Microcalorimetry. The calorimeter used in this work was a TAM 2777-201 microcalorimeter with a 1 mL stainless steel sample cell. The cell was initially loaded with 0.6 mL of water or 0.2 wt % polymer solution. The concentrated gemini surfactant solutions of 10 mM were injected into the stirred sample cell in small aliquots of 2–5 μL , using a 500- μL Hamilton syringe controlled by a Thermometric 612 Lund pump. The observed enthalpy (ΔH_{obs}) was obtained by integration over the peak in the plot of thermal power against time. During the whole titration process of gemini surfactants into 0.2 wt % polymer solutions, the polymer concentration was kept constant by including polymer of the same concentration in the added surfactant solution.²³ All the measurements were conducted at 298.15 ± 0.01 K.

Self-Aggregation of HMPAMs and PAM in the Absence of Surfactant. Figure 2 shows the variations of the pyrene polarity ratio I_1/I_3 for HMPAMs and PAM in the absence of surfactant from steady-state fluorescence measurement. The I_1/I_3 curve for PAM is found to exhibit a distinct difference from those for the two HMPAMs. Through the investigated polymer concentration (C_p), I_1/I_3 for PAM remains nearly constant and a high value, which is practically equivalent to that measured

in pure water. However, for the two HMPAMs, as C_P increases, a marked decrease of I_1/I_3 is observed and the I_1/I_3 values of the almost-horizontal part of the curves at high C_P are close to those of nonionic surfactant micelles.¹⁵ These sigmoidal I_1/I_3 curves for HMPAMs reveal the formation of aggregates by the alkyl chains in HMPAM solutions. When the HMPAM molecules are dissolved in aqueous solution, the polymer alkyl chains tend to associate with each other forming micelle-like hydrophobic aggregates to minimize their exposure to water. Like cmc for surfactant systems, a critical polymer concentration (C_P') can be designated, which corresponds to the polymer concentration at which HMPAM alkyl chains start to associate into hydrophobic aggregates. Here, the values of C_P' for PAM-C8-2% and PAM-C16-2%, determined from the intercept between the linear extrapolations of the rapidly varying portion of the curve and of the almost-horizontal portion at high C_P ,²⁴ are 0.15 and 0.12 wt %, respectively. The I_1/I_3 curves for the two HMPAMs show only a slight difference in C_P' values and I_1/I_3 values at high C_P . However, the small difference between these two I_1/I_3 curves is still larger than the experimental error. Comparing with PAM-C8-2%, a slightly lower value of C_P' together with a slightly lower value of I_1/I_3 at high C_P suggest that PAM-C16-2% has a somewhat greater tendency to form a little more hydrophobic aggregates. Nevertheless, hydrophobic aggregates cannot be generated in the PAM solution.

Interactions of Gemini Surfactants with HMPAMs and PAM. On the basis of the above studies on the polymer solutions, we know that HMPAMs can generate hydrophobic aggregates above C_P' , whereas PAM does not have this behavior. During the following studies on the interactions of gemini surfactants $C_{12}C_5C_{12}Br_2$ with HMPAMs and PAM, C_P is fixed at 0.2 wt % above C_P' of HMPAMs. The aim of these studies is to disclose the impact of the structure of gemini surfactants on their interactions with the hydrophobic aggregates of HMPAMs.

Steady-state fluorescence measurement is first used to study the variations of I_1/I_3 for the three gemini surfactants $C_{12}C_5C_{12}Br_2$ with polymers. Figure 3 shows the dependence of the I_1/I_3 values for the mixtures of gemini surfactants with polymers on the surfactant concentration (C_s), together with the curves of the corresponding surfactants with water for comparison.

The I_1/I_3 plots for pure gemini surfactants have an usual sigmoidal shape, with a sharp decrease of I_1/I_3 at C_s slightly below cmc and with a stabilization at high C_s , which indicates the formation of micelles. The cmc can be taken as the concentration corresponding to the intercept between the linear extrapolations of the rapidly varying portion of the curve and of the almost-horizontal portion at high C_s ,^{25–26} as shown in the inset of Figure 3a. The obtained cmc values of $C_{12}C_3C_{12}Br_2$, $C_{12}C_6C_{12}Br_2$, and $C_{12}C_{12}C_{12}Br_2$ are listed in Table 1, in good agreement with the literature values.²⁷

When gemini surfactants $C_{12}C_5C_{12}Br_2$ are added into 0.2 wt % unmodified PAM, the values of I_1/I_3 decrease markedly toward a plateau region, then increase gradually and finally converge with the curves of pure gemini surfactants. The above changes of I_1/I_3 reflect the formation of surfactant/polymer aggregates, similar to the observation in SDS and poly(*N*-vinylpyrrolidone) systems.²⁸ The end of the first transition is designated as critical aggregation concentration (cac), while the end of the second transition is taken as the saturation concentration (C_2), as shown in the inset of Figure 3a. Beyond cac , gemini surfactant molecules may start to form micelle-like aggregates on PAM chains, indicated by lower I_1/I_3 values in the plateau region. Usually, these surfactant/polymer aggregates can be

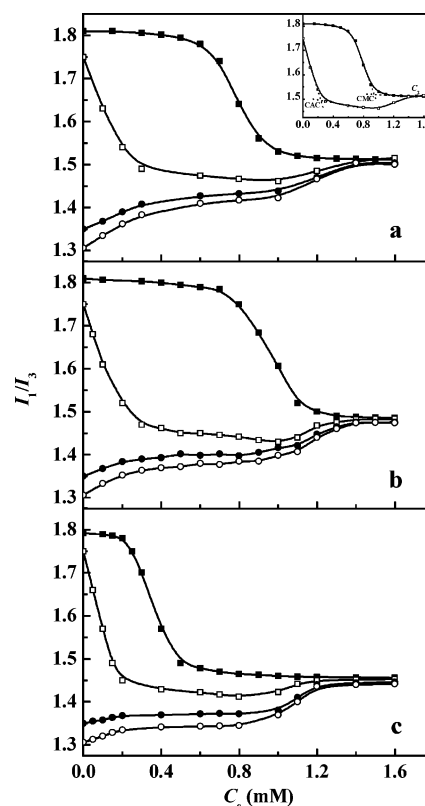


Figure 3. Variations of I_1/I_3 for (a) $C_{12}C_3C_{12}Br_2$, (b) $C_{12}C_6C_{12}Br_2$, and (c) $C_{12}C_{12}C_{12}Br_2$ with 0.2 wt % polymers and with water: (■) H_2O ; (□) PAM; (●) PAM-C8-2%; (○) PAM-C16-2%.

TABLE 1: Critical Micelle Concentrations and Thermodynamic Parameters for the Gemini Surfactants $C_{12}C_5C_{12}Br_2$

surfactants	cmc ^a (mM)	cmc ^b (mM)	ΔH_{mic} (kJ/mol)	a	ΔG_{mic} (kJ/mol)	$T\Delta S_{mic}$ (kJ/mol)
$C_{12}C_3C_{12}Br_2$	0.96	0.85	-10.2	0.16	-44.1	33.9
$C_{12}C_6C_{12}Br_2$	1.09	0.89	-4.8	0.20	-42.5	37.7
$C_{12}C_{12}C_{12}Br_2$	0.46	0.29	-14.6	0.31	-45.7	31.1

^a By steady-state fluorescence. ^b By microcalorimetry.

described as a series of micelles whose surfaces are covered by polymer segments and connected by polymer strands.²⁹ After C_2 , PAM chains are saturated by bound gemini surfactant micelles and free micelles start to appear in the system, leading the I_1/I_3 curves to coincide with those of pure gemini surfactants. Generally, single-chain surfactants do not significantly interact with PAM.⁵ The present fluorescence result may give an indication that the interactions of polymer with gemini surfactants are much stronger than those with single-chain surfactants.

In the presence of HMPAMs, the I_1/I_3 curves show noticeable differences from the systems of gemini surfactants with PAM. Without addition of gemini surfactants, the I_1/I_3 values for HMPAMs are much lower than those of PAM. With increasing C_s , the values of I_1/I_3 increase gradually and then remain nearly constant. Here, cac is taken as the concentration at the intercept between the linear extrapolations of the gradually increasing portion of the curve and of the almost-horizontal portion. Further addition of gemini surfactant makes I_1/I_3 values increase gradually again. The end of the second transition is designated as C_2 . Beyond C_2 , the I_1/I_3 curves for HMPAMs eventually join pure gemini surfactants and join the systems of gemini surfactants with PAM. Such changes of I_1/I_3 curves suggest a specific mechanism of interaction of gemini surfactants with HMPAMs. Because hydrophobic aggregates already exist in 0.2 wt %

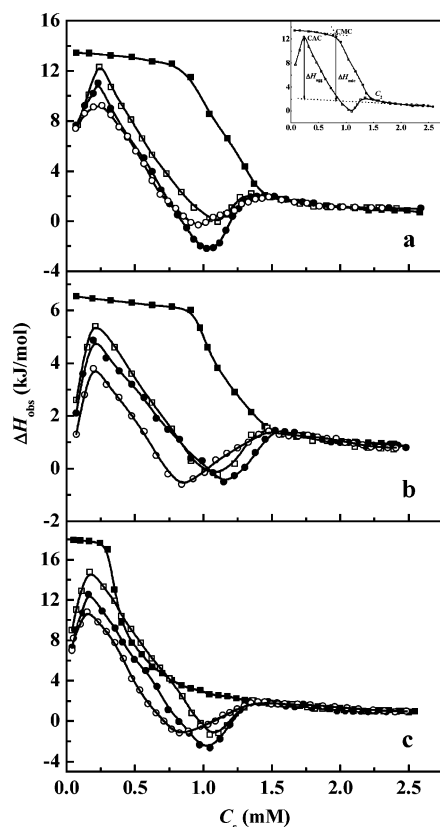


Figure 4. Calorimetric titration curves for (a) $C_{12}C_5C_{12}Br_2$, (b) $C_{12}C_6C_{12}Br_2$, and (c) $C_{12}C_{12}C_{12}Br_2$ with 0.2 wt % polymers and with water: (■) H_2O ; (□) PAM; (●) PAM-C8-2%; (○) PAM-C16-2%.

HMPAM solution, the I_1/I_3 values for pure HMPAMs are much lower than those of PAM. Below cac , the increase of I_1/I_3 with addition of gemini surfactant may arise from the progressive incorporation of ionic gemini surfactant monomers into HMPAM hydrophobic aggregates. After cac , more gemini surfactant molecules may aggregate on HMPAM chains to form mixed micelles, involving alkyl chains of HMPAM. This leads I_1/I_3 curves to obtain a plateau region. Probably because of the smaller difference in micropolarity of mixed micelles and HMPAM hydrophobic aggregates, the first transition for HMPAM is not as clear as that for PAM. In the second transition, the gradual increase of I_1/I_3 possibly stems from the progressively increasing content of gemini surfactants in mixed micelles, which tends to lead the mixed micelles more like the micelles of gemini surfactants. After C_2 , mixed micelles could saturate HMPAM chains and more added surfactant molecules start to form free micelles. Then, the I_1/I_3 values are close to those of pure gemini surfactants.

The interactions between $C_{12}C_5C_{12}Br_2$ and HMPAMs have also been investigated by isothermal titration microcalorimetry. The calorimetric titration curves of the observed enthalpy (ΔH_{obs}) of $C_{12}C_5C_{12}Br_2$ solution diluted into polymer solutions with the final surfactant concentration C_s are shown in Figure 4. In contrast, the corresponding dilution enthalpy curves of $C_{12}C_5C_{12}Br_2$ into water are also included in this figure.

All the pure gemini surfactant titration curves have a sigmoidal shape with an abrupt decrease at a threshold concentration corresponding to the micelle formation, allowing identification of cmc by an extrapolation of the initial portion of the curve and of the rapidly decreasing portion of the curve.^{30,31} Meanwhile, the enthalpy of micellization (ΔH_{mic}) can be determined from the difference at the cmc between ΔH_{obs}

of the two linear segments of the plots,³² as shown in the inset of Figure 4a.

The calorimetric titration curves for gemini surfactants into polymer solutions exhibit a pronounced endothermic peak followed by a shallow exothermic one. Then all the curves join together and join the dilution curves of surfactants. The difference in titration curves in the presence of polymer from those without polymer can be attributed to the interactions between surfactants and polymers. At the beginning of the titration, the added micelles break up into monomers, and the monomers are further diluted and then bind onto PAM chains or insert into hydrophobic aggregates of HMPAMs through hydrophobic interaction. This endothermic binding results in an increase of ΔH_{obs} in the initial part of titration curves. Until the maximum point of the endothermic peak, corresponding to cac , the micelle-like aggregates may start to form on PAM chains or the mixed micelles of surfactant molecules with polymer alkyl chains may start to form on HMPAM backbones. This exothermic process makes ΔH_{obs} decrease sharply to a minimum. The values of ΔH_{obs} then increase gradually, because of the electrostatic repulsion among more and more bound micelles and the resulting stretch of polymer chains. After C_2 , estimated from the point of convergence of the curves of surfactants into polymers with those into water, the polymer chains are fully saturated and free micelles start to appear. Further addition of surfactant will only lead to dilution of the micellar solution. From the calorimetric curves, the enthalpy of aggregation (ΔH_{agg}) is determined by a similar procedure as for ΔH_{mic} , shown in the inset of Figure 4a. The values of cac and C_2 determined by microcalorimetry are listed in Table 2 and are consistent with the results from fluorescence measurements.

On the basis of cmc and cac from microcalorimetry, Gibbs free energy of micellization ΔG_{mic} without polymer and Gibbs free energy of aggregation ΔG_{agg} with polymer can be calculated with the following equations³³

$$\Delta G_{mic} = RT(3 - 2\alpha) \ln(CMC) - RT \ln 2 \quad (4)$$

$$\Delta G_{agg} = RT(3 - 2\alpha') \ln(CAC) - RT \ln 2 \quad (5)$$

where CMC and CAC are expressed in molarity of alkyl chain, twice as much as cmc or cac expressed in molarity of gemini surfactant. The α and α' are the ionization degrees of micelles and surfactant/polymer aggregates, respectively. Here, the values of α are taken from ref 34. However, the values of α' cannot be directly obtained by experiment measurements for such complicated aggregates. Supposing that the surfactant aggregates bond on nonionic polymer chains might be similar to those of normal micelles, it is thus assumed that $\alpha = \alpha'$.^{11,35,36} The entropy changes ΔS_{mic} and ΔS_{agg} then can be derived from ΔH_{mic} and ΔG_{mic} or ΔH_{agg} and ΔG_{agg} . Moreover, the aggregation of surfactant with polymer can be thought of as including the surfactant micellization and the binding of micelle to polymer. Therefore, the thermodynamic parameters ΔX_{ps} for the interaction of surfactant with polymer can be obtained from the difference of $\Delta X_{agg} - \Delta X_{mic}$. All the thermodynamic parameters for the interactions of $C_{12}C_5C_{12}Br_2$ with polymers are also presented in Table 2.

The combination of the steady-state fluorescence and microcalorimetry results can reflect more insight into the interaction of $C_{12}C_5C_{12}Br_2$ with HMPAMs. It is worthy to note that the I_1/I_3 values above C_2 are higher than those of mixed micelles between cac and C_2 , which are again higher than those of HMPAMs without surfactants. This suggests that the micro-

TABLE 2: Critical Aggregation Concentrations, Saturation Concentrations, and Thermodynamic Parameters for the Gemini Surfactants $C_{12}C_5C_{12}Br_2$ with Polymers

surfactants	polymers	cac ^a (mM)	cac ^b (mM)	C_2^a (mM)	C_2^b (mM)	ΔH_{agg} (kJ/mol)	ΔG_{agg} (kJ/mol)	$T\Delta S_{agg}$ (kJ/mol)	ΔH_{ps} (kJ/mol)	ΔG_{ps} (kJ/mol)	$T\Delta S_{ps}$ (kJ/mol)
$C_{12}C_3C_{12}Br_2$	PAM	0.24	0.24	1.40	1.46	-9.1	-52.5	43.4	1.1	-8.4	9.5
	PAM-C8-2%	0.25	0.22	1.41	1.51	-8.2	-53.1	44.9	2.0	-9.0	11.0
	PAM-C16-2%	0.25	0.23	1.41	1.48	-7.7	-52.8	45.1	2.5	-8.7	11.2
$C_{12}C_6C_{12}Br_2$	PAM	0.22	0.21	1.32	1.46	-3.0	-51.8	48.8	1.8	-9.3	11.1
	PAM-C8-2%	0.20	0.20	1.35	1.52	-2.4	-52.1	49.7	2.4	-9.6	12.0
	PAM-C16-2%	0.21	0.20	1.36	1.50	-1.9	-52.1	50.2	2.9	-9.6	12.5
$C_{12}C_{12}C_{12}Br_2$	PAM	0.17	0.17	1.19	1.36	-10.8	-48.8	38.0	3.8	-3.1	6.9
	PAM-C8-2%	0.16	0.16	1.23	1.39	-9.7	-49.2	39.5	4.9	-3.5	8.4
	PAM-C16-2%	0.17	0.16	1.23	1.40	-8.5	-49.2	40.7	6.1	-3.5	9.6

^a By steady-state fluorescence. ^b By microcalorimetry.

polarity of these three kinds of aggregates follows the order of gemini surfactant micelles > mixed micelles > polymer hydrophobic aggregates. Moreover, the value of ΔG_{ps} is found to be negative, which means that the formation of mixed micelles and the disruption of HMPAM aggregates are spontaneous in nature. However, probably because the disruption of polymer aggregates may bring about a larger endothermic effect, ΔH_{ps} exhibits a positive value, which suggests that the interaction is mainly entropy-driven.

On the basis of the above results, we could further understand the effect of the polymer hydrophobicity on the interaction. As shown in Figure 3, the I_1/I_3 values between cac and C_2 for $C_{12}C_5C_{12}Br_2$ /PAM-C16-2% systems are only a little lower than those for $C_{12}C_5C_{12}Br_2$ /PAM-C8-2% systems. But both of them are obviously lower than those of $C_{12}C_5C_{12}Br_2$ /PAM systems. This suggests that the enhancement of polymer hydrophobicity results in the lower micropolarity of the surfactant/polymer aggregates. From the thermodynamic results for the same gemini surfactant, an increase in the polymer hydrophobicity leads to more endothermic ΔH_{ps} , whereas all ΔG_{ps} values for different polymers are nearly the same. As expected, more energy might be required to disrupt the more hydrophobic aggregates, accompanied by an increase in ΔH_{ps} with the increasing hydrophobicity of polymer. However, an increase of $T\Delta S_{ps}$ will compensate the increase of ΔH_{ps} . This finally results in a constant ΔG_{ps} , i.e., the hydrophobicity of polymer does not markedly influence the tendency of interaction.

The effect of the spacer length on the interaction also can be seen from the experimental results. For the same polymer, the gemini surfactant with a longer spacer brings on a little lower I_1/I_3 value of mixed micelles. Note that the values of α^{34} are 0.16, 0.20, and 0.31 for $C_{12}C_3C_{12}Br_2$, $C_{12}C_6C_{12}Br_2$, and $C_{12}C_{12}C_{12}Br_2$, respectively. The larger value of α means that the longer spacer may reduce the charge density of gemini surfactant headgroups to a greater extent.³⁷ For the mixed micelle including the gemini surfactant with a longer spacer, its slightly more hydrophobic structure could be ascribed to the smaller magnitude of repulsion among surfactant headgroups. Meanwhile, the reduction of the charge density of surfactant headgroups induced by the longer spacer could be expected to decrease attraction between surfactant headgroups and polymer hydrophilic groups much more significantly. This spacer effect would lead to more endothermic ΔH_{ps} and less negative ΔG_{ps} for $C_{12}C_5C_{12}Br_2$ with a longer spacer. As seen, much weaker interaction exists between $C_{12}C_{12}C_{12}Br_2$ and HMPAMs. However, this spacer effect is much less obvious for $C_{12}C_3C_{12}Br_2$ and $C_{12}C_6C_{12}Br_2$, owing to their short and close spacers.

To further understand the structure of $C_{12}C_5C_{12}Br_2$ /HMPAM mixed micelles, time-resolved fluorescence quenching has also been used to determine the aggregation number of the surfactants (N_s) and the aggregation number of polymer alkyl chains (N_H)

TABLE 3: The Micelle Aggregation Number of Surfactant or Polymer Alkyl Chains for the Gemini Surfactants $C_{12}C_5C_{12}Br_2$ Mixed with Polymers

surfactants	polymers	C_s (mM)	N_H	N_s
$C_{12}C_3C_{12}Br_2$	PAM-C8-2%	0	15.8	0
		0.4	10.1	7.1
		0.6	6.8	10.0
		0.8	4.8	14.1
		1.5	1.1	17.9
	PAM-C16-2%	0	29.9	0
		0.4	17.5	8.5
		0.6	12.0	11.2
		0.8	7.4	15.4
		1.5	1.2	18.5
	$C_{12}C_6C_{12}Br_2$	0	15.8	0
		0.4	10.2	6.8
		0.6	6.8	9.8
		0.8	4.7	14.0
		1.5	1.0	17.6
	PAM-C16-2%	0	29.9	0
		0.4	17.6	8.1
		0.6	11.8	11.0
		0.8	7.2	15.2
		1.5	0.9	18.3
$C_{12}C_{12}C_{12}Br_2$	PAM-C8-2%	0	15.8	0
		0.4	10.0	6.5
		0.6	6.6	9.6
		0.8	4.6	13.7
		1.5	0.8	17.4
	PAM-C16-2%	0	29.9	0
		0.4	17.4	7.5
		0.6	11.6	10.8
		0.8	7.3	15.0
		1.5	1.0	18.4

in mixed micelles, as summarized in Table 3. It is noted that the aggregates of PAM-C16-2% have a larger size than those of PAM-C8-2%. Moreover, N_H decreases continuously with increasing C_s , whereas N_s increases gradually. Because of the electrostatic repulsion among the headgroups of gemini surfactants, the increase of N_s and the decrease of N_H together contribute to the higher micropolarity of mixed micelles than those of the aggregates of HMPAMs themselves. Beyond C_2 , the N_H values for different surfactant/polymer systems are all close to 1. That is to say, the mixed micelles in this case only solubilize about one polymer hydrophobic chain. These observations are consistent with the reported variation of the viscosity of HM polymers on the surfactant concentration C_s .²⁻⁴ With addition of surfactant, the viscosity of HM polymers passes a maximum at intermediate C_s but then decreases again at higher C_s .

Conclusions

Hydrophobically modified polymers HMPAMs can form hydrophobic aggregates in the solution whereas unmodified

PAM does not have this behavior. Cationic gemini surfactants $C_{12}C_5C_{12}Br_2$ have strong interaction with HMPAMs, even with unmodified PAM. Addition of $C_{12}C_5C_{12}Br_2$ into HMPAMs will gradually disrupt polymer hydrophobic aggregates and result in the formation of mixed micelles. The hydrophobically modified polymers tend to form more hydrophobic mixed micelles with gemini surfactants and the polymer hydrophobic aggregates will be disrupted to a greater extent. The longer spacer of the gemini surfactant could reduce the electrostatic repulsion among surfactant headgroups, resulting in slightly lower micropolarity in the mixed micelles. Especially for $C_{12}C_{12}C_{12}Br_2$ with a long spacer, the attraction between surfactant headgroups and polymer hydrophilic moieties could be depressed markedly, which weakens the final interaction between $C_{12}C_{12}C_{12}Br_2$ and HMPAMs.

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