# Hydrophobically Modified Acrylamide-Based Polybetaines. II. Interaction with Surfactants in Aqueous Solution[†]

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**ABSTRACT:** The interaction of hydrophobically modified (HM) polybetaines with selected small molecule surfactants in aqueous solution was investigated using rheological and surface tension analyses. The polymers included acrylamide-based, HM polybetaines containing *N*-butylphenylacrylamide (BPAM) and specified amounts of sulfobetaine, 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulfonate (AMPDAPS), or carboxybetaine, 4-(2-acrylamido-2-methylpropyldimethylammonio)butanoate (AMPDAB); corresponding control (co)polymers lacking BPAM and/or betaine comonomer(s) were also examined for comparative purposes. Low charge density terpolymers exhibited greater viscosity enhancement with the addition of surfactant compared to the high charge density terpolymers. The addition of sodium dodecyl sulfate (SDS) produced the largest increase in solution viscosity, while *N*-dodecyl-*N,N,N*-trimethylammonium bromide (DTAB), *N*-dodecyl-*N,N*-dimethylammonio-1-propanesulfonate (SB3–12), and Triton X-100 enhanced polymer solution viscosity to a lesser degree. In most cases, the high charge density carboxybetaine terpolymer exhibited diminished solution viscosity upon surfactant addition. The polymers lacking hydrophobic modification showed no detectable viscosity enhancement in the presence of surfactants. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 658—671, 2004

**Key words:** amphiphilic polymers; polyzwitterions; surfactants; surface tension; viscosity; water-soluble polymers

## INTRODUCTION

The synergistic interaction of water-soluble polymers with surfactants is critical to the success of many applications, including petroleum production, (bio)-chemical separations, and the formulation of coatings, detergents, cosmetics, and personal care products.[1] In enhanced oil recovery (EOR) processes, surfactants and water-soluble polymers are used together to mobilize crude oil trapped in underground reservoir formations.[2–4] The surfactants are necessary for reducing interfacial tension and solubilizing trapped oil, while the water-soluble polymers are required to viscosify the waterflood that drives the solubilized oil from the porous rock media. Ideally, water-soluble polymers employed as viscosifiers in EOR processes should exhibit increased thickening efficiency in the presence of surfactants and also act cooperatively with surfactants to reduce interfacial tension and to solubilize oil.

The rheological properties of water-soluble polymers can be readily altered by the addition of surfactants, as indicated in numerous studies.[5–10] Much of the research in this area has focused on the interaction of nonionic polymers with charged surfactants[11–19] and the interaction of polyelectrolytes with surfactants of opposite charge.[20–25] Polyelectrolyte interaction with surfactant systems having the same charge have also been investigated.[5,6,9,10,26] In these studies, the polymers were often hydrophobically modified (HM) to induce interaction between the polymer and the surfactant.

Relatively few studies of the interaction of surfactants with HM polyzwitterions have been conducted. Bekturov and coworkers[27] studied the effect of adding sodium dodecyl sulfate (SDS) and cetyltrimethylammonium chloride (CTAC) to polyampholytes composed of acrylic acid and 1,2,5-trimethyl-4-vinylethynyl-4-piperidinol. The addition of either surfactant to the polyampholyte solution produced a decrease in viscosity, although the effect of SDS was more pronounced than that of CTAC. Unlike polyelectrolyte–surfactant complexes, which tend to precipitate at certain ratios of polyelectrolyte to surfactant, the polyampholyte–surfactant complexes remained soluble over the entire composition range. It was postulated that the hydrophilic components of the polyampholyte chain prevented precipitation of the polymer–surfactant complexes. More recently, Harrison and coworkers[28] have examined the interactions of polyampholyte terpolymers based on acrylamide (AM), sodium 2-acrylamido-2-methylpropanesulfonate, and (2-methacroyloxyethyl)trimethylammonium chloride
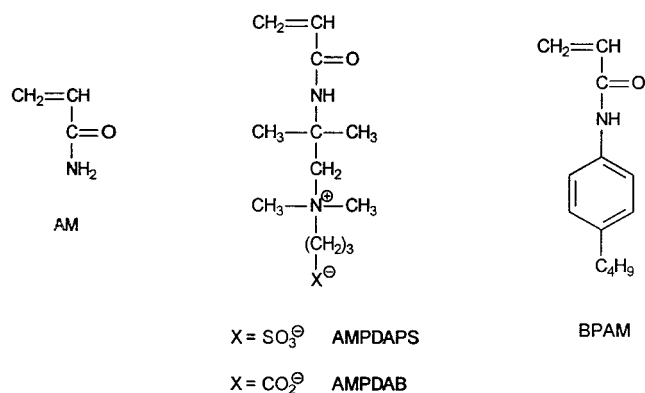
**Figure 1** Monomers employed in synthesis of HM polybetaines via micellar copolymerization.

with either SDS or tetradecyltrimethylammonium bromide. Polyampholyte–surfactant interactions were found to be highly dependent on the charge balance of the polyampholytes and the type of surfactant employed.

In Part I of this study, we described the synthesis, characterization, and stimuli-responsive solution behavior of terpolymers composed of AM, either 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulfonate, (AMPDAPS) or (4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate (AMPDAB), and N-butylphenylacrylamide (BPAM).[29] The terpolymers were prepared from the monomers shown in Figure 1 using micellar copolymerization techniques to yield HM polybetaines. These systems were shown to combine the unique attributes of polyzwitterions (i.e., salt-tolerance, antipolyelectrolyte effect) and associative thickeners (i.e., enhanced viscosification via intermolecular hydrophobic association). Additionally, the amphoteric character of the HM polycarboxybetaines allowed changes from polyzwitterion to polyelectrolyte behavior in response to changes in solution pH.

In Part II of this study, we assess the solution behavior of HM AM-based polybetaines containing either sulfobetaine or carboxybetaine comonomers with the addition of nonionic, zwitterionic, anionic, and cationic surfactants. The properties of the resulting terpolymer solutions were followed by rotational viscometry and surface tensiometry, and models consistent with others in the literature have been proposed to explain solution behavior as functions of surfactant type (i.e., type of head/tail group) and surfactant concentration.

## EXPERIMENTAL

### Materials

Triton X-100 was purchased from Bio-Rad Laboratories. All other chemicals were purchased from Aldrich and used as received except where indicated. Deionized (DI) water was obtained from a Barnstead NANOPure reverse osmosis/filtration unit (resistivity = 18.0 MΩ).

Table I lists the polymers examined in this work and their properties.[29,30] The HM polybetaine terpolymers are designated as either HSB# (sulfobetaine series) or HCB# (carboxybetaine series), where # indicates the mol % of betaine comonomer present in the feed. Copolymers lacking either BPAM (the hydrophobic comonomer) or betaine comonomer were prepared for the purpose of performing comparative studies; these copolymers are designated SB#, CB#, and HAM, respectively. A polyacrylamide homopolymer was also synthesized under the micellar conditions and is designated PAM.

### Instrumentation and analysis

#### Solution rheology

Polymer stock solutions were prepared by dissolving lyophilized polymers in DI water and allowing them

**TABLE I**
**Properties of the HM Polybetaine Terpolymers and the Control (Co)polymers**

| Sample ID | AM (mol %) | Betaine comonomer[a] (mol %) | BPAM[d] (mol %) | $M_w^e$ ($10^6$ g/mol) | $A_2^e$ ($cm^3$ mol/$g^2$) | $pK_a^f$ |
|---|---|---|---|---|---|---|
| HSB5 | 95 | 4.1[b] | 0.88 | 0.827 | $1.3 \times 10^{-3}$ | — |
| HSB25 | 76 | 23[b] | 1.0 | 1.13 | $-4.82 \times 10^{-5}$ | — |
| SB5 | 95 | 5.0[b] | — | 0.819 | $4.08 \times 10^{-4}$ | — |
| HCB5 | 96 | 3.6[c] | 0.64 | 1.29 | $-9.18 \times 10^{-5}$ | 6.2 |
| HCB25 | 82 | 17[c] | 1.0 | 0.419 | $-5.77 \times 10^{-5}$ | 7.2 |
| CB5 | 91 | 8.9[c] | — | 1.16 | $1.36 \times 10^{-4}$ | 4.1 |
| HAM | 99.5 | — | 0.55 | 0.806 | $-2.52 \times 10^{-3}$ | — |
| PAM | 100 | — | — | 0.850 | $4.2 \times 10^{-3}$ | — |

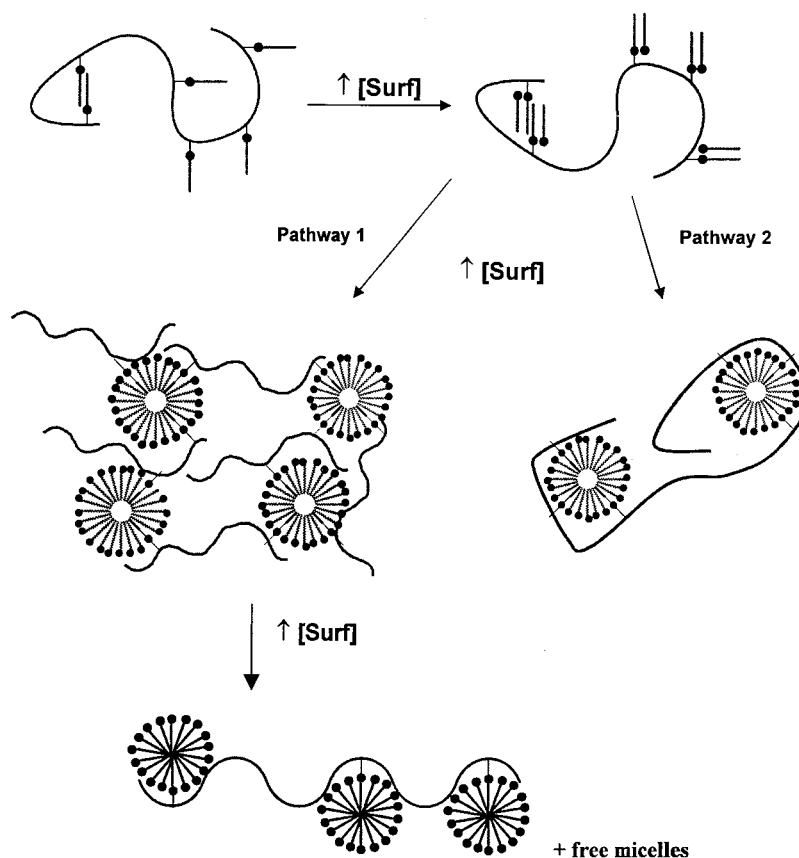[a] Determined via inverse gated decoupled $^{13}$C NMR spectroscopy.
[b] AMPDAPS.
[c] AMPDAB.
[d] Determined via UV-Vis spectroscopy.
[e] Determined via classical light scattering in 0.5 M NaCl.
[f] Determined via potentiometric titration.

**Figure 2** Proposed mechanisms of surfactant-induced viscosity modification in HM polymer solutions.

to age 7 to 10 days while agitating gently on an orbital shaker. Following dilution of the stock solutions with DI water, surfactants were added to the solutions to achieve the desired concentration. The polymer–surfactant solutions were allowed to age for several weeks on an orbital shaker prior to analysis. All polymer–surfactant solutions were analyzed at ambient pH (pH 7.5 ± 0.5). Solution viscosity measurements were performed using a Contraves LS-30 low shear rheometer. The measurements were conducted at 25°C and at a shear rate of 5.96 s$^{-1}$. Reported viscosities are the average of five measurements. The upper viscosity limit of the rheometer was taken as 125 cP.

Surface tensiometry

A Kruss K12 Processor Tensiometer was utilized to conduct Wilhemy plate surface tension measurements. All solutions were prepared using doubly distilled water (surface-quality water). A minimum surface tension reading of 72 mN/m confirmed the required purity. Surfactants were purified as follows: SDS was recrystallized three times from absolute ethanol, N-dodecyl-N,N,N-trimethylammonium bromide (DTAB) was recrystallized three times from a mixture of ethyl acetate and ethanol (10/1 v/v), and N-dode-

cyl-N,N-dimethylammonio-1-propanesulfonate (SB3–12) was recrystallized twice from 2-propanol. Polymer solutions were prepared at a concentration of 0.2 g/dL. The necessary amount of surfactant was added to the polymer solutions to bring the surfactant concentration to the desired value, and the solutions were allowed to age 7 to 10 days while agitating gently on an orbital shaker prior to analysis. All polymer–surfactant solutions were analyzed at ambient pH (pH 7.5 ± 0.5). Experimental error in reported surface tension values is ≤ ±1.5%.

**RESULTS AND DISCUSSION**

Addition of surfactants to HM polymer solutions can increase the viscosity of polymer solutions, provided comicellization between the polymer and surfactant provides bridging between polymer chains.[5,7,9,31–34] In this respect, an accepted model for associative complexes of HM polymers and surfactants involves formation of mixed micelles, or hemimicelles, composed of polymer-bound hydrophobes comicellized with surfactant molecules (Fig. 2, Pathway 1). If multiple polymer-bound hydrophobes from different polymer chains participate in the same mixed micelle, a physical crosslink is formed between the polymer

chains.[5,34] A dramatic increase in solution viscosity is often observed upon formation of these intermolecular physical crosslinks. As the concentration of surfactant in the polymer solution is increased, the stoichiometry of the system will eventually disfavor comicellar bridging and the viscosity will decrease to levels close to or even lower than that of the original polymer solution.[35]

The electrostatic repulsions of ionically charged hemimicelles adsorbed along the polymer may cause chain expansion, leading to an increase in viscosity below the critical overlap concentration, $c^*$.[36,37] In some cases, the addition of surfactant to HM polymer solutions below $c^*$ has been reported to cause viscosity reduction.[32,33,38,39] In these cases, contraction of the hydrodynamic dimensions of the polymer chain results from intramolecular associations induced by comicellization (Fig. 2, Pathway 2).

Our goal in this research was to induce intermolecular associations (and thus enhanced viscosity) via the addition of surfactants to polymer solutions. Therefore, we selected polymer concentrations slightly lower than $c^*$ to facilitate observation of any viscosity enhancement caused by comicellar bridging. Thus, based on the findings from viscosity versus polymer concentration experiments reported in Part I,[29] we elected to conduct polymer–surfactant solution rheological studies at polymer concentrations of 0.4 g/dL. (Note: To prevent exceeding the upper viscosity limit of the Contraves LS-30 rheometer, it was necessary to examine HCB25 at a concentration of 0.1 g/dL due to the exceptionally high viscosity of this sample in DI water.)

While the effects of surfactant addition on solution viscosity are readily probed on the macroscopic level via rheological analysis, surface tension experiments were also conducted to further elucidate the effects of surfactant addition to polymer solutions. Figure 3 depicts an idealized surface tension profile for a small molecule surfactant in aqueous solution.[36,37,40] A plateau region is observed at very low surfactant concentrations. In the usual experimental concentration ranges, this region is so small that it is undetectable. Adsorption of amphiphilic molecules at the air–water interface causes the surface tension to be lowered as the surface excess concentration of surfactant at the interface increases. At the *cmc*, the chemical potential of surfactant adsorbed at the air–water interface becomes equal to the chemical potential for micelle formation. Thus, surfactant added in excess of the *cmc* is preferentially solubilized in micelles, and the surface tension reaches a plateau value.

The addition of a polymer capable of associating with surfactants (e.g., a HM polymer or oppositely charged polyelectrolyte) to a surfactant solution modifies the surface tension profile.[36,37,40] Figure 4 shows an idealized plot of surface tension against surfactant
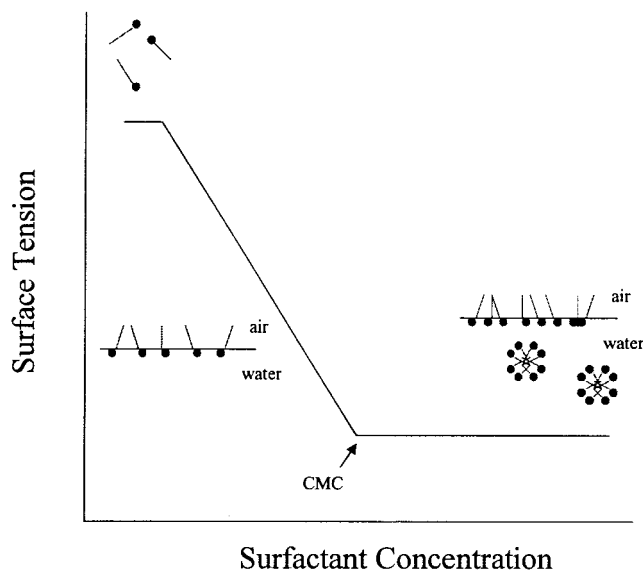


**Figure 3** Idealized surface tension curve for small molecule surfactants.

concentration for such a system. Initially, surfactant adsorption at the air–water interface results in a decrease in surface tension. At the crossover concentration ($C_1$), the chemical potential becomes favorable for polymer–surfactant interaction; the surface excess concentration of the surfactant remains unchanged at $C_1$, as surfactant interacts preferentially with polymer in the bulk solution to form complexes. Upon reaching a saturation point ($C_2$), the chemical potential of surfactant migration to the air–water interface again becomes favored, and the surface tension is lowered until the chemical potential of the surface becomes equal to that in a regular surfactant micelle. At $C_2$, any excess surfactant added to the polymer–surfactant solution will form micelles in solution. The point $C_2$ is detected as a plateau in the surface tension profile that has the same magnitude of the surface tension at the *cmc* in the absence of polymer. In experimentally observed systems, polymer–surfactant solution surface tension profiles deviate from the depicted ideality due to the changes in polymer conformation and resulting changes in detailed polymer–surfactant interactions. Values of $C_1$ and $C_2$ are usually still detectable, but the graphical surface tension plot between these points is typically curved.

### Effect of nonionic surfactant

The effect of nonionic surfactants on the solution rheology of the HM polybetaine terpolymers and control (co)polymers was examined using Triton X-100, an ethoxylated nonylphenol surfactant. Figure 5 shows the effects of Triton X-100 addition to solutions of the HM polysulfobetaine terpolymers and the corresponding control (co)polymers. Using the PAM con-
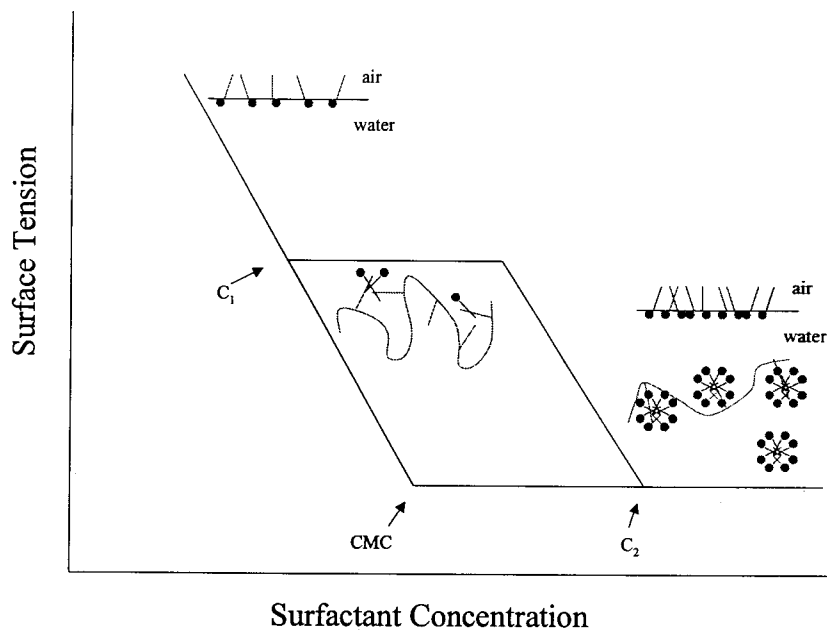
**Figure 4** Idealized surface tension profile of a small molecule surfactant in the presence of polymer.[36]

trol polymer as a basis for comparison, the effects of sulfobetaine comonomer incorporation and hydrophobic modification are readily observed. HSB25, which contains 23 mol % AMPDAPS, exhibits a solution viscosity lower than that of PAM (despite being of higher MW), indicating that the high level of sulfobetaine comonomer incorporation significantly reduces the hydrodynamic volume of the HSB25 terpolymer. However, the polymers containing lowering sulfobetaine comonomer contents (SB5 and HSB5) display greater apparent viscosities and thus greater hydrodynamic volumes relative to PAM. Therefore, it appears that there is an optimum level of sulfobetaine comono-

mer incorporation (irrespective of hydrophobic modification), below which the polymer chain expands and above which the polymer chain is constrained.

Interestingly, the HAM copolymer containing 0.55 mol % BPAM exhibits a higher solution viscosity than the PAM homopolymer. *A priori*, hydrophobic modification of the hydrophilic PAM chain (to yield the HAM copolymer) would be expected to cause intramolecular hydrophobic association and to reduce the hydrodynamic volume of the isolated HAM chain in solution, leading to a lower solution viscosity. It is reasonable, therefore, to conclude that the observed viscosity increase is due to aggregation of HAM poly-
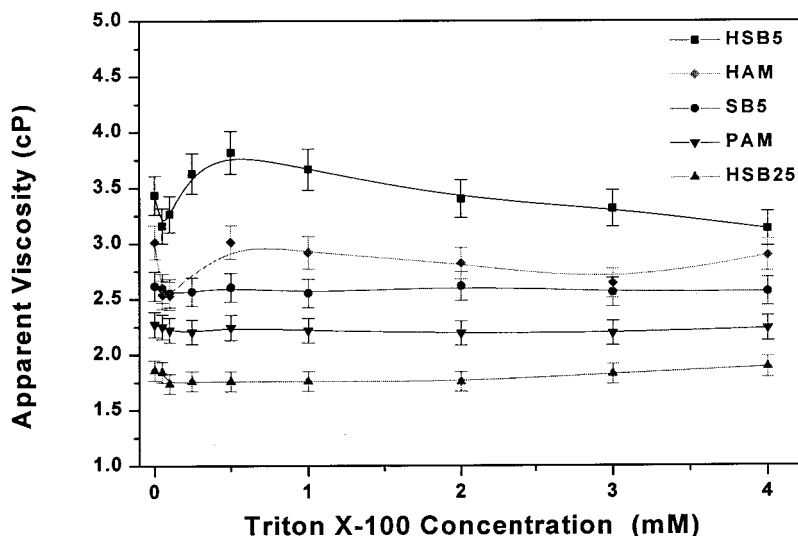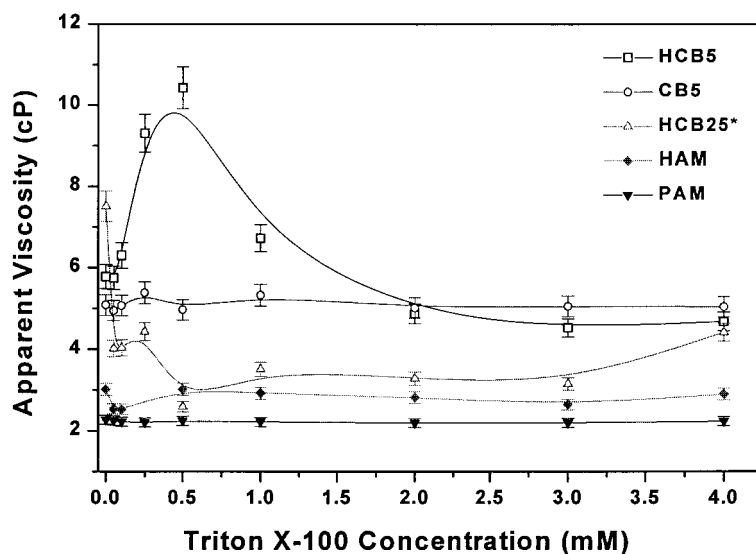


**Figure 5** Apparent viscosity of the HM sulfobetaine terpolymers and the control polymers as a function of Triton X-100 concentration. Polymer concentration = 0.4 g/dL.

**Figure 6** Apparent viscosity of the HM carboxybetaine terpolymers and the control polymers as a function of Triton X-100 concentration. Polymer concentration = 0.4 g/dL, except HCB25, polymer concentration = 0.1 g/dL.

mer chains in solution to form multimeric species. Addition of Triton X-100 causes an initial reduction in the apparent viscosity of the HAM copolymer. This could be attributed to disaggregation of the HAM copolymer due to competitive hydrophobic interaction with the surfactant. It is notable that the viscosity goes through a sharp minimum in the region of the surfactant *cmc* (~0.1 mM) and increases sharply to a plateau at ~0.5 mM Triton X-100. Similar behavior is observed for the HSB5 polymer that contains 4.1 mol % sulfobetaine and 0.88% BPAM; indeed, HSB5 exhibits the highest solution viscosities and the most profound viscosity enhancement upon addition of Triton X-100. The viscosity enhancement of HAM and HSB5 is attributed to comicellar network formation of the polymer and surfactant micelles (Fig. 2, Pathway 1). Unlike the other HM polymers in the series, HSB25 did not exhibit surfactant-induced viscosity enhancement. This maybe be attributed to the high degree of intramolecular electrostatic association between sulfobetaine repeat units, which causes collapse of the HSB25 chain, making the pendant BPAM moieties unavailable for intermolecular association and comicellization.

Similar trends were observed with the carboxybetaine terpolymers, although it is notable in this case that all of the terpolymers displayed significantly higher apparent viscosities than the nonionic control polymers PAM and HAM (Fig. 6). As in the sulfobetaine series, the low charge density terpolymer (HCB5) displayed a dramatic increase in viscosity upon addition of Triton X-100, and a maximum viscosity was reached at surfactant concentrations that were moderately higher than the *cmc*. However, in this series, the high charge density carboxybetaine terpolymer (HCB25) actually exhibited a dramatic decrease in viscosity upon addition of Triton X-100, possibly due

to the intramolecular comicellization mechanism shown in Figure 2, Pathway 2. This is a further indication that the type (e.g., sulfobetaine versus carboxybetaine) and content of zwitterionic monomer employed in the HM polybetaines plays an important role in determining the solution behavior of such polymers in the presence of surfactants.

Surface tension measurements shed light on the mechanisms that underpin these polymer–surfactant interactions. Figure 7 demonstrates that there is little or no difference in the surface tension with respect to Triton X-100 concentration in the presence and absence of PAM. Based on the surface tension and rheological data, it can be concluded that the PAM control polymer does not interact with Triton X-100. Similar surface tension profiles provided evidence that SB5 and CB5 do not interact with Triton X-100 (data not shown).[30] However, as shown in Figure 8, there is clear evidence indicating that the HM polymers interact with Triton X-100 to form mixed micelles. The surface tension values for Triton X-100 in the presence of HSB5 and HCB5 tend to be higher than those of HAM as a function of increasing Triton X-100 concentration. The surface tension values below $C_1$ for the HAM system show that the polymer–surfactant system is more surface active than the surfactant alone, whereas the HCB5 and HSB5 systems display higher surface tensions at concentrations below the surfactant *cmc*. This is consistent with the viscosity results (Figs. 5 and 6) that indicate the betaine-containing hydrophobic terpolymers, HCB5 and HSB5, are more expanded in solution than the HM polyacrylamide copolymer, HAM. It is notable that the maxima in the viscosity curves for the HM polymers HAM, HSB5, and HCB5 occur at the surfactant concentration corresponding to $C_2$. This is consistent with comicellar
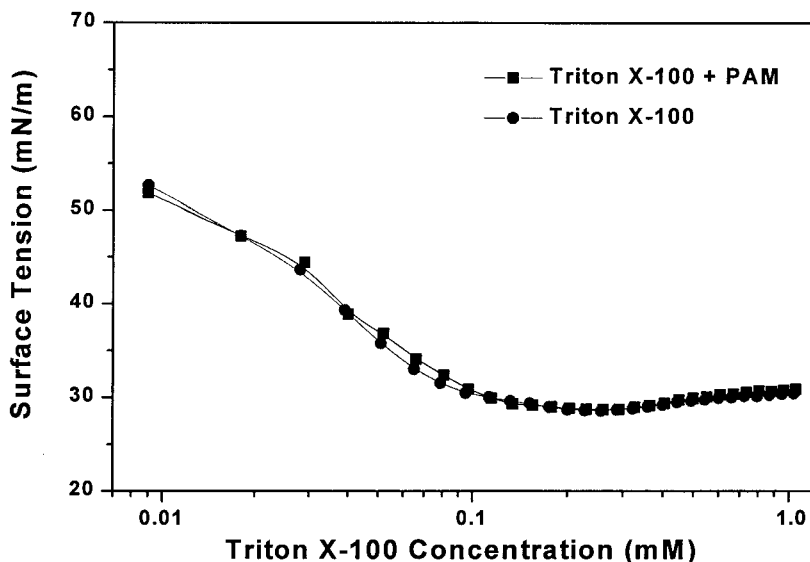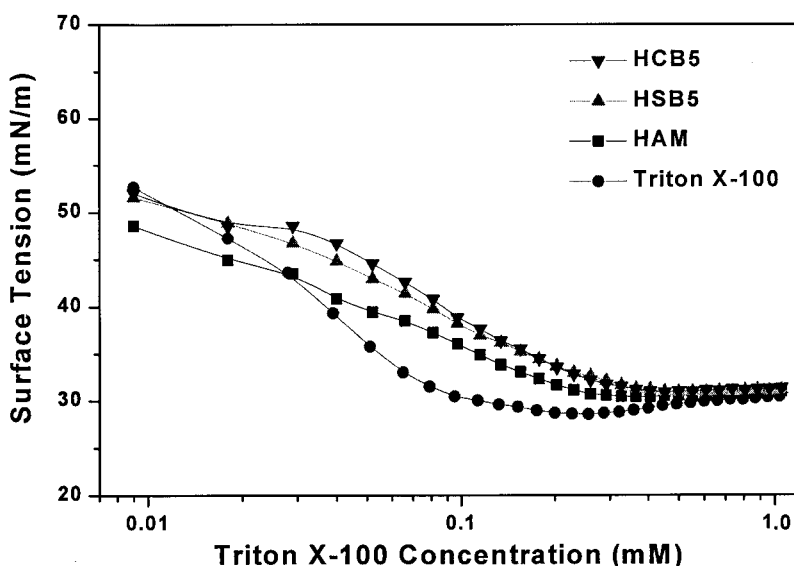
**Figure 7** Plots of surface tension as a function of Triton X-100 concentration in the absence and presence of PAM homopolymer. PAM concentration = 0.2 g/dL.

crosslinking, in accordance with Figure 2, Pathway 1. (Note that the high charge density HM polybetaines HCB25 and HSB25 were not included in any surface tension studies, as they did not demonstrate viscosity enhancement with any of the surfactants employed in the rheological studies.)

Effect of zwitterionic surfactant

The effect of the zwitterionic surfactant SB3–12 on the rheological behavior of HM polybetaines and control (co)polymers was also examined; the results are shown in Figures 9 and 10. HAM displays an initial

drop in viscosity at low concentrations of SB3–12. This may be attributed to disaggregation of the polymer by the surfactant. HSB5, HCB5, and HAM are the only polymers that exhibit maxima in the plot of apparent viscosity as a function of SB3–12 concentration; this viscosity enhancement appears to be consistent with the model shown in Figure 2, Pathway 1. HCB5 displays a greater maximum in viscosity than HSB5, as was the case for these polymers in the presence of Triton X-100. In the case of HCB25, SB3–12 addition causes a decrease in solution viscosity; this is likely due to the disruption of intermolecular associations by the surfactant and/or a polyelectrolyte effect (recall



**Figure 8** Plots of surface tension as a function of Triton X-100 concentration in the presence of low charge density HM polybetaines and the HAM control polymer. Polymer concentration = 0.2 g/dL.
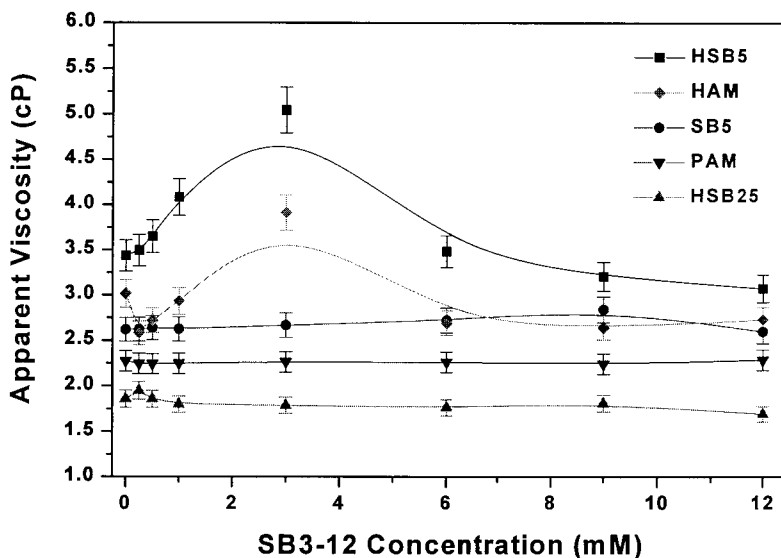
**Figure 9** Apparent viscosity of the HM sulfobetaine terpolymers and the control polymers as a function of SB3–12 concentration. Polymer concentration = 0.4 g/dL.

that HCB25 possess significant polycationic character at ambient pH, with $pK_a = 7.2$).

Data from surface tension analysis of these polymer–surfactant systems indicated a lack of interaction between non-HM polymers and SB3–12 (data not shown).[30] As determined by the surface tension plots in Figure 11, all HM polymers show indications of association with SB3–12. Two important conclusions can be drawn from the data in Figure 11: First, the lower surface tension values of SB3–12 in the presence of the HM polymers indicate that there is additive adsorption of polymer and surfactant at the air–water interface. Second, above the crossover concentrations ($C_1$ in Fig. 4), the

polymer–surfactant systems display characteristic comicellization/complex formation of polymer and surfactant. The maxima in the viscosity curves correspond to the polymer–surfactant interaction region found in the surface tension profiles. For SB3–12, the viscosity values plateau at the concentration that corresponds to $C_2$ in the surface tension plot. This is consistent with the mechanism depicted in Figure 2, Pathway 1.
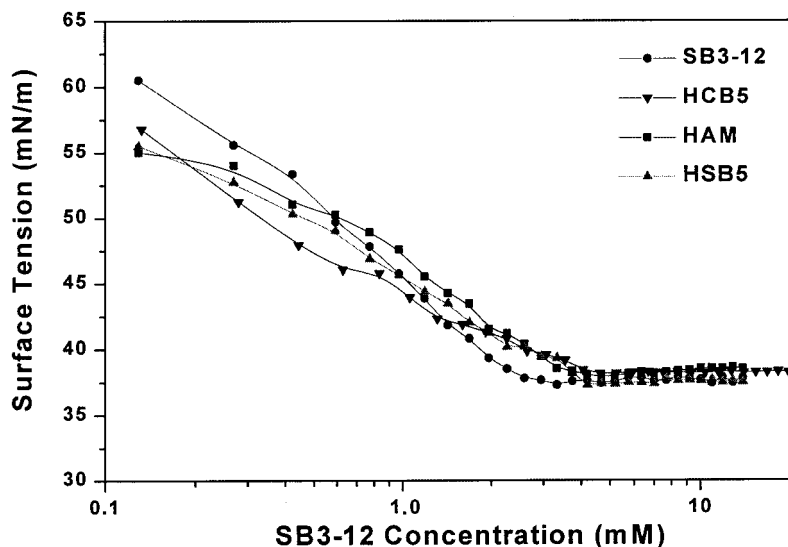
### Effect of anionic surfactant

Of all the surfactants examined in this study, SDS has the most profound effect on solution viscosity and
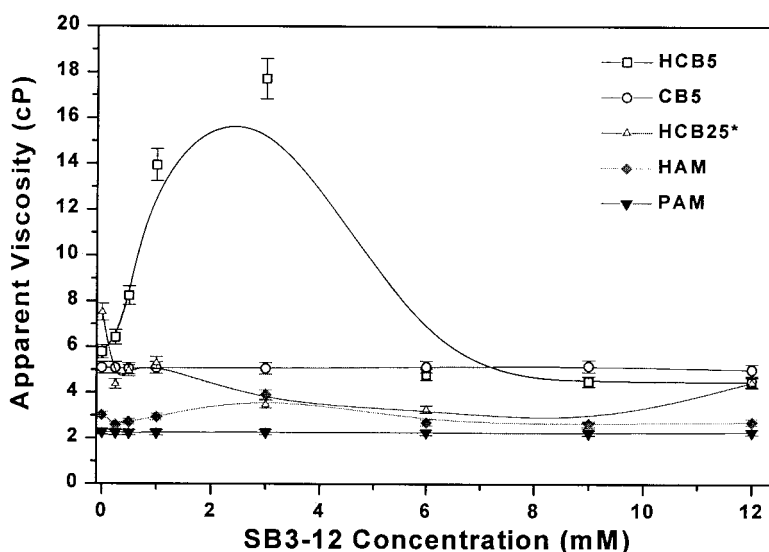


**Figure 10** Apparent viscosity of the HM carboxybetaine terpolymers and the control polymers as a function of SB3–12 concentration. Polymer concentration = 0.4 g/dL, except HCB25, polymer concentration = 0.1 g/dL.

**Figure 11** Plots of surface tension as a function of SB3–12 concentration in the presence of low charge density HM polybetaines and the HAM control polymer. Polymer concentration = 0.2 g/dL.

yields the greatest viscosity enhancements. The viscosity responses of the HM polysulfobetaines and HM polycarboxybetaines to the addition of SDS are shown in Figures 12 and 13, respectively. Again, the HM polymers (HSB5, HCB5, and HAM) are the only samples that display viscosity maxima in the presence of SDS, with HCB5 exhibiting the greatest enhancement in viscosity upon SDS addition. Given the highly cationic nature of the HM polycarboxybetaines at ambient pH (due to higher $pK_a$ of HM polycarboxybetaines),[29] the polymer–surfactant interactions are probably hydrophobic and electrostatic in nature, es-

pecially in the case of HCB25 where precipitation is observed. This insolubility is consistent with data previously reported by Goddard and coworkers.[36,37]

Data from surface tension experiments conducted to investigate the interaction between the HM polymers and SDS are shown in Figure 14. As in the previous cases, HAM, HBS5, and HCB5 show the characteristic features of polymer–surfactant interaction, while PAM, SB5, and CB5 do not (data not shown).[30] Comparison of the surface tension data with the viscosity data clearly indicate that the viscosity buildup begins at concentrations below $C_1$. This is consistent with the
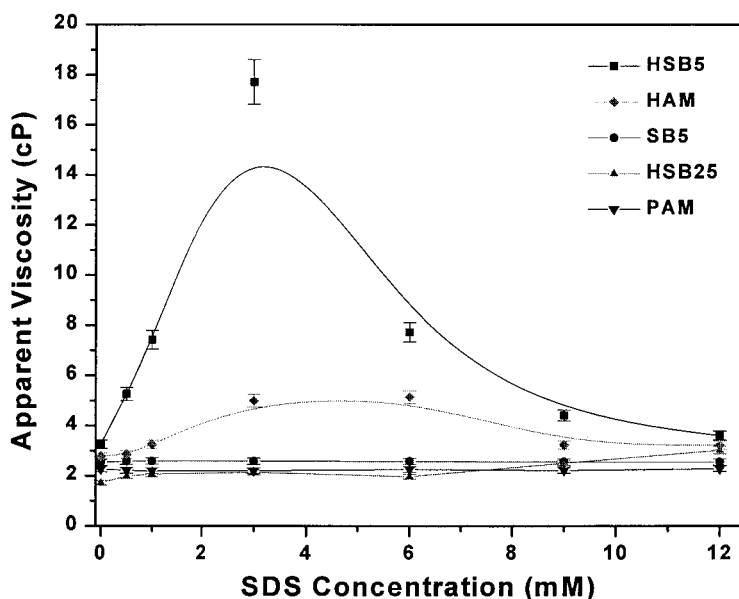


**Figure 12** Apparent viscosity of the HM sulfobetaine terpolymers and the control polymers as a function of SDS concentration. Polymer concentration = 0.4 g/dL.
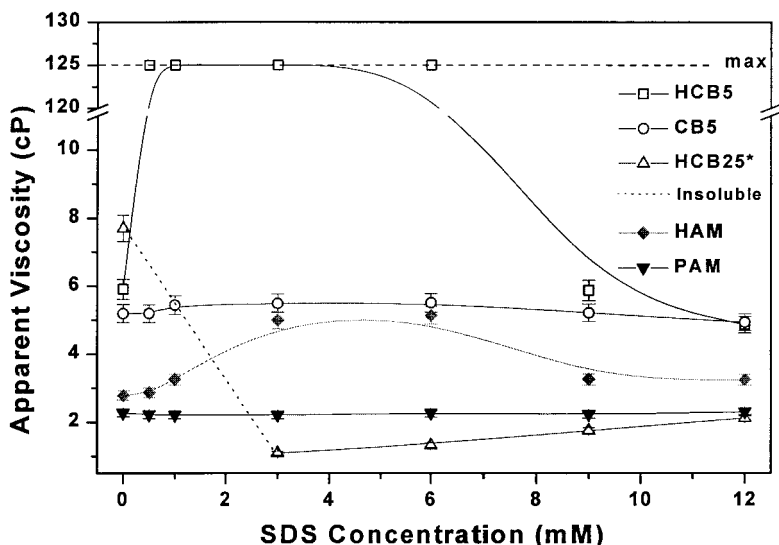
**Figure 13** Apparent viscosity of the HM carboxybetaine terpolymers and the control polymers as a function of SDS concentration. Polymer concentration = 0.4 g/dL, except HCB25, polymer concentration = 0.1 g/dL.

formation of hemimicelles along the polymer backbone at concentrations well below the surfactant *cmc*.[41] The viscosity reaches its plateau value at the onset of the formation of regular micelles. This is consistent with polymer–surfactant complex formation according to Figure 2, Pathway 1.

Effect of cationic surfactant

The solution behavior of the HM polybetaines and control (co)polymers was also investigated as a function of DTAB concentration, as shown in Figures 15 and 16. Consistent with the observed trend, HSB5,

HCB5, and HAM all demonstrate viscosity maxima at an intermediate DTAB concentration, with HCB5 showing the greatest viscosity enhancement. It should be noted that significantly higher concentrations of DTAB are required to elicit viscosity enhancement compared to the polymer–surfactant solutions containing Triton X-100, SB3–12, or SDS. This is most likely due to the lower surface activity of this surfactant (for example at 25°C, $cmc_{DTAB}$ = 15.6 mM versus $cmc_{SDS}$ = 8.3 mM).[42]

The results of surface tension measurements conducted with DTAB and the polymers in this study are similar to those obtained from oppositely charged
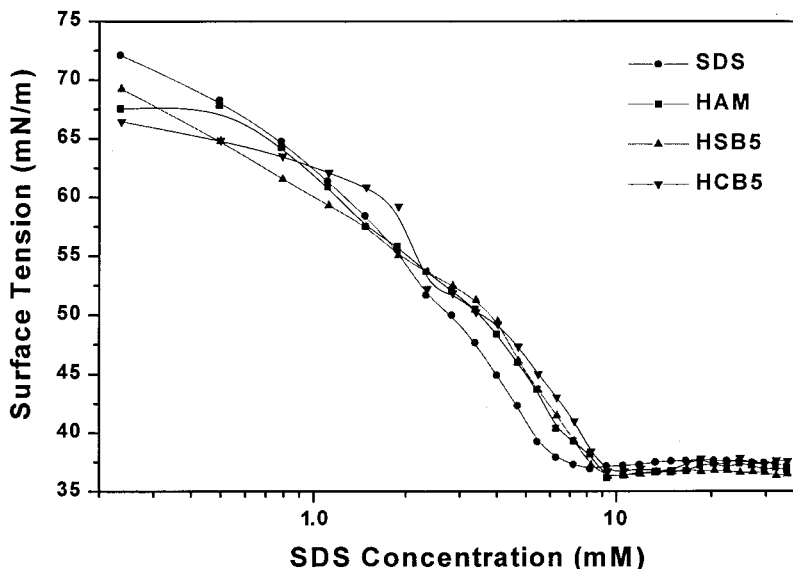


**Figure 14** Plots of surface tension as a function of SDS concentration in the presence of low charge density HM polybetaines and the HAM control polymer. Polymer concentration = 0.2 g/dL.
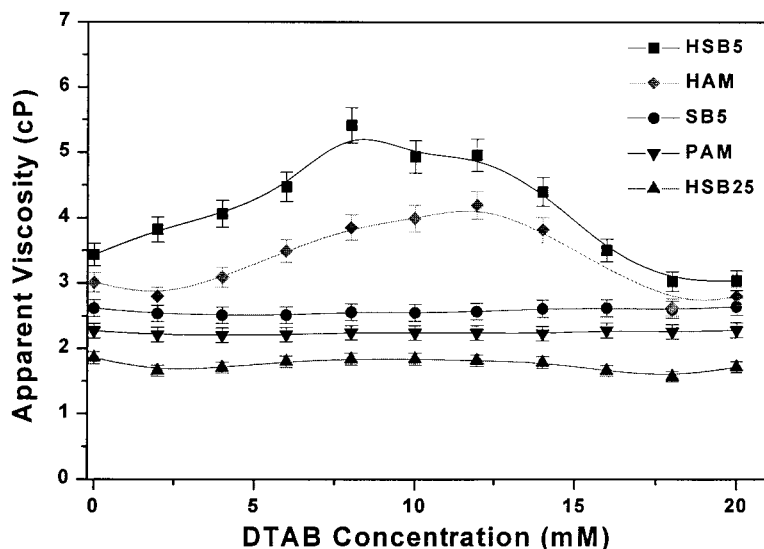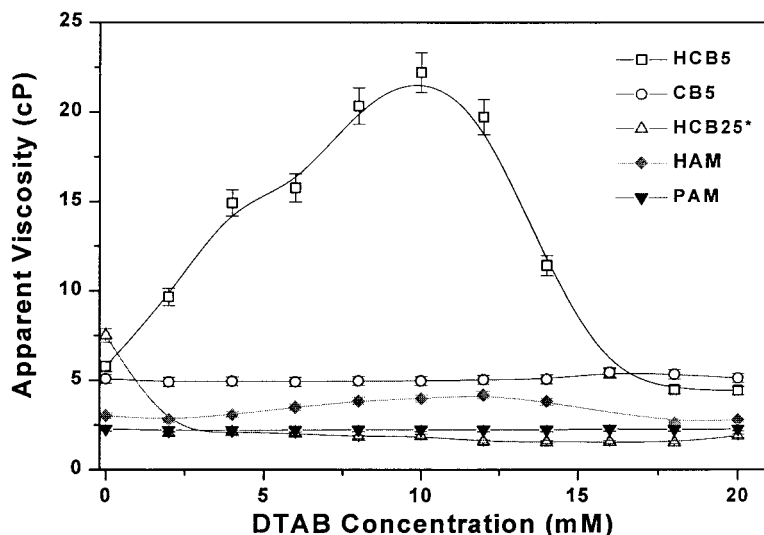
**Figure 15** Apparent viscosity of the HM sulfobetaine terpolymers and the control polymers as a function of DTAB concentration. Polymer concentration = 0.4 g/dL.

polymer–surfactant systems.[20,25,38,43] The interaction of PAM with DTAB (Fig. 17) was unexpected, as there is no apparent basis for interaction between PAM and DTAB, as was the case with PAM and Triton X-100 (Fig. 7). PAM homopolymer is known to be nonsurface active[44] and has very little tendency to interact with surfactants.[36] We postulate that hydrolysis of the pendant amide groups may have occurred in the polymer samples to an extent not detected by NMR spectroscopy or potentiometry. It is reasonable to expect trace amounts of PAM hydrolysis during polymer synthesis, purification, and solution preparation/aging.[45] Interaction between the cationic ammonium headgroup of DTAB and the anionic carboxylate moi-

eties along a partially hydrolyzed PAM chain may effectively bind hydrophobic groups to the chain, thus yielding a surface active complex. Due to the uncertainty introduced by the polymer hydrolysis issue, no quantitative information was obtained from the surface tension profiles in the presence of DTAB, as the exact mode of polymer–surfactant interaction could not be readily attributed to comicellization.

Overall, SDS induces the largest changes in polymer solution viscosity, followed by DTAB and SB3–12, which have similar effects. Addition of Triton X-100 to polymer solutions results in minimal or no viscosity enhancement. The effect of surfactant headgroup on chain expansion and bridging is believed to be largely



**Figure 16** Apparent viscosity of the HM carboxybetaine terpolymers and the control polymers as a function of DTAB concentration. Polymer concentration = 0.4 g/dL, except HCB25, polymer concentration = 0.1 g/dL.
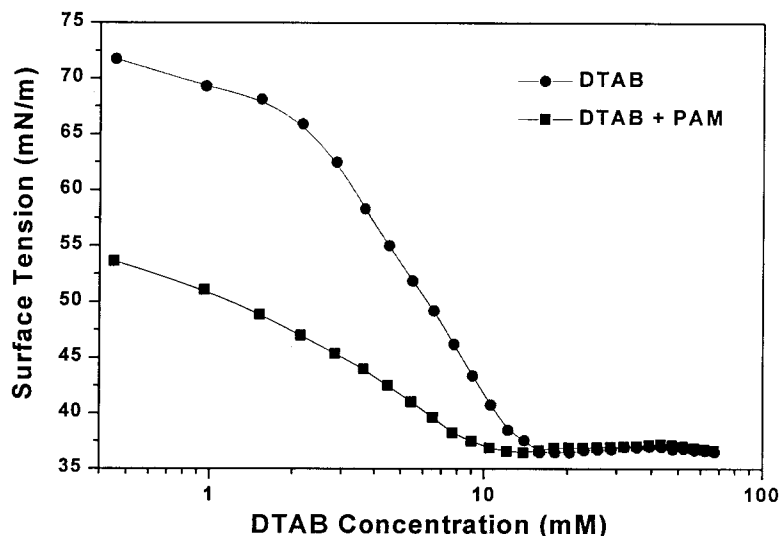
**Figure 17** Plots of surface tension as a function of DTAB concentration in the absence and presence of PAM homopolymer. PAM concentration = 0.2 g/dL, pH 7.5 ± 0.5.

responsible for this trend. It is postulated that the microblocky architecture of the HM polymers promotes hemimicelle formation along the polymer backbone, resulting in chain expansion. This increased hydrodynamic volume allows coil overlap and thus hydrophobe exchange and insertion, resulting in bridged networks (Fig. 2, Pathway 1). SDS apparently forms more effective networks with all of the HM polymers, followed by SB3–12, DTAB, and Triton X-100. The differences in the corona of mixed micelles from each of the surfactant types are likely to be significant, with headgroup charge and solvation playing major roles in intrachain conformation and interchain capture of hydrophobic units.

The nature of the interactions between HCB25 and most surfactants are such that viscosification mechanisms of this HM polycarboxybetaine (intermolecular hydrophobic and electrostatic association) are effectively inhibited. Unlike the other polymers, the addition of surfactant generally induces significant viscosity reduction in HCB25 solutions (Figs. 6, 10, and 16), and precipitation is observed when small amounts of SDS are added to HCB25 solutions (Fig. 13). The initial insolubility of HCB25, followed by its subsequent dissolution as additional SDS is added to the solution, is typical of oppositely charged polymer–surfactant interactions.[36,37] As stated previously, the p$K_a$ of HCB25 is rather high (p$K_a$ = 7.2) and the polymer is predominately cationic at ambient pH; thus, SDS is strongly attracted to HCB25 due to combined electrostatic and hydrophobic interactions.

**Polymer-bound surfactant**

The onset of polymer-surfactant interaction is taken as the crossover point $C_1$ indicated in Figure 4. The point

at which surfactant micelle formation commences is called the saturation point, $C_2$. From $C_2$ and the *cmc* of the surfactant ($cmc_{surf}$), the number of bound surfactant molecules per polymer hydrophobe, $m$, can be calculated utilizing Equation (1), where [H] is the concentration of polymer-bound hydrophobes in mol/L.

$$ m = \frac{C_2 - cmc_{surf}}{[H]} \tag{1} $$

Values of $m$ were calculated ulitizing Equation (1) in cases in which experimental $C_1$ and $C_2$ values could be obtained. Due to the uncertainty in the nature of the polymer–DTAB interactions, data analysis was not performed on those surface tension profiles. Table II contains the values of $C_1$, $C_2$, and $m$ obtained from the surface tension profiles. The parameter $m$ tends to be higher for ionic surfactants. Values of $m$ for Triton

**TABLE II**
**Values of $C_1$, $C_2$, $m$, and $A$ Derived from Surface Tension Analysis**

| Sample ID | $C_1$ (mM) | $C_2$ (mM) | $m$ | $A$(Å²/molecule) |
|---|---|---|---|---|
| Triton X-100 | — | — | — | 3.3 |
| +HAM | 0.018 | 0.73 | 3 | 8.9 |
| +HSB5 | 0.011 | 0.74 | 2.2 | 9.1 |
| +HCB5 | 0.011 | 0.67 | 2.5 | 8.9 |
| +SB3–12 | — | — | — | 68 |
| +HAM | 0.59 | 4.2 | 5.7 | 100 |
| +HSB5 | 1.3 | 4.4 | 5.1 | 104 |
| +HCB5 | 0.92 | 4.2 | 5.5 | 137 |
| +SDS | — | — | — | 185 |
| +HAM | 0.5 | 9.4 | 8 | 228 |
| +HSB5 | 1.9 | 8.3 | 9.3 | 253 |
| +HCB5 | 1.1 | 9.4 | 8 | 266 |

X-100 ranged from 2.2 to 3.0, and the range of $m$ was observed to increase to 5.1–5.7 for SB3–12 and 8.0–9.3 for SDS. The lower values of $m$ for Triton X-100 are expected, due to the greater size and irregular shape of this surfactant. Fewer Triton X-100 molecules are able to bind per hydrophobe as a result of the steric bulk of the ethoxylated headgroup and the nonstraight chain hydrophobe.

The area per surfactant molecule adsorbed at the surface ($A$) was also estimated from the surface tension data. The surface adsorption, $\Gamma$, was calculated using the Gibbs equation [Eq. (2)],

$$\Gamma = -\frac{1}{nRT} \times \frac{d\gamma}{d\ln C} \qquad (2)$$

where $R$ is the universal gas constant in J $K^{-1}$ $mol^{-1}$, $T$ is the absolute temperature in K, and $d\gamma/d\ln C$ is the slope of the plot of surface tension versus the logarithm of the surfactant concentration.[46] For nonionic surfactants, $n = 1$, however, the counterions associated with ionic surfactants for the surface to be electrically neutral must be accounted for, thus $n = 2$ for ionic surfactants in the absence of excess salt. By assuming monolayer adsorption at the surface, $A$ may be calculated from the following relationship:

$$A = \frac{1}{N_A \times \Gamma} \qquad (3)$$

where $N_A$ is Avogadro's number.

Table II lists values of $A$ for Triton X-100, SB3–12, and SDS in the absence and in the presence of the HM polymers. In all cases, the area per molecule of surfactant increases in the presence of the polymers. This indicates that the polymers or polymer–surfactant complexes are surface active and effectively compete with the surfactants for the air–water interface.

## CONCLUSION

Low charge density HM polybetaines and the nonionic HAM copolymer were shown to interact and comicellize with nonionic, anionic, cationic, and zwitterionic surfactants, as demonstrated by rheological and surface tension analyses. Changes in polymer solution viscosity upon addition of surfactant are consistent with the conceptual model shown in Figure 2, Pathway 1, although the degree of surfactant-induced viscosity enhancement is widely varied depending on surfactant type. SDS causes the most profound viscosity enhancement, followed by SB3–12, DTAB, and Triton X-100. The observed trends can be attributed to surfactant structure and the nature of the surfactant headgroup. Surface tension experiments generally support the evidence of polymer–surfactant interac-

tions derived from rheological analysis, although the surface tension profiles of polymer–DTAB interactions are anomalous (presumably due to multiple modes of interaction between the polymers and DTAB) and require further investigation. The HM polycarboxybetaine containing a high betaine comonomer incorporation (HCB25) possesses unusual solution behavior compared to the other polymers in this study. The collapse of hydrodynamic dimensions with the addition of surfactants is presumably due to surfactant-induced intramolecular comicellization (Fig. 2, Pathway 2). The aqueous solution behavior of HCB25 shown here and in Part I of this study is due to a complex interplay of hydrophobic, hydrogen bonding, and electrostatic interactions that is easily perturbed upon surfactant addition.

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