Macromolecules **1994,** *27,* 2145–2150

Water-Soluble Copolymers. 50. Effect of Surfactant Addition on the Solution Properties of Amphiphilic Copolymers of Acrylamide and Dimethyldodecyl(2-acrylamidoethyl)ammonium Bromide

Yihua Chang, Robert Y. Lochhead, and Charles L. McCormick*

Department of Polymer Science, University of Southern Mississippi, Southern Station Box 10076, Hattiesburg, Mississippi 39406-0076

Received July 22, 1993; Revised Manuscript Received January 12, 1994®

ABSTRACT: The interactions of surfactants sodium dodecyl sulfate (SDS), trimethyltetradecylammonium bromide (TTAB), and Triton X-100 with amphiphilic copolymers of acrylamide and dimethyldodecyl(2-acrylamidoethyl)ammonium bromide (DAMAB) have been investigated in aqueous solutions. The rheological properties of a copolymer/surfactant system are affected by both the microstructure of the copolymer and the nature of the surfactant. Addition of the nonionic surfactant, Triton X-100, resulted in a large increase in the reduced viscosity for the microblocky copolymers with 5 mol % DAMAB, while a random copolymer with the same composition exhibited a collapsed conformation in the presence of the cationic surfactant, TTAB. A strong viscosity enhancement was observed when SDS was added to the solution of a copolymer containing 0.32 mol % DAMAB. Evidence of mixed micelles formed by surfactant molecules and the hydrophobic groups of the copolymers was obtained utilizing surface tension, pyrene probe fluorescence, and viscometry.

Introduction

The solution properties of aqueous media can be dramatically changed by utilizing combinations of amphiphilic copolymers and simple surfactants.[1] However, there is presently an inadequate understanding of the mechanism of the interactions between macromolecules and surfactants.[2] Aqueous solutions comprised of polymers and surfactants have been studied by a variety of experimental techniques including viscometry, surface tension, dialysis equilibrium, NMR, ESR, neutron scattering, and fluorescence. In general, the surfactant molecules form micelle-like clusters associated with the polymer chains. The behavior of these systems can be described by two critical surfactant concentrations, namely, the critical aggregation concentration (C_1) and the apparent critical micelle concentration (C_2). C_1 is defined as the surfactant concentration required to induce surfactant binding to the polymer, and C_2 is the concentration at which all the polymer sites available for interaction with surfactant are saturated; further increase in surfactant concentration will lead to the formation of classical micelles.[3,4] C_1 and C_2 are always located, respectively, below and above the critical micelle concentration (cmc) of the corresponding surfactant in pure water solution. C_1 is largely independent of the polymer concentration, while the maximum amount of polymer-bound surfactant in the system increases linearly with the total polymer concentration in the solution.[5]

Interactions between polyelectrolytes and charged surfactants in aqueous solution are governed primarily by Coulombic forces and dipole–ion interactions. For example, polyelectrolytes interact strongly with oppositely charged surfactants which can lead either to a large increase in solution viscosity[6,7] or in some cases to phase separation.[8] Often the associations between polyelectrolytes and surfactants are quite weak or absent mainly because of the unfavorable electrostatic repulsions.[2b,9] When polyelectrolytes are hydrophobically modified, the situation becomes more complicated. In addition to the forces operating in simple polyelectrolyte/surfactant systems, hydrophobic interactions between the amphiphilic groups on the polymer chains and the surfactant molecules also play important roles. For instance, a C_{12}-grafted hydroxyethyl cellulose[10] exhibits strong association with SDS while its parent polymer, [11] hydroxyethyl cellulose, interacts only weakly with SDS.

Another major consideration affecting amphiphilic polymer/surfactant interactions is the chemical microstructure of the polymer, particularly the "mer" distribution resulting from the method of polymerization.[12,29,30] Change in the compositional distribution can dramatically alter the association of surfactant with the polymer. Addition of SDS to an aqueous solution of hydrophobically modified poly(sodium acrylate) has been shown to cause a marked viscosity enhancement.[13] The viscosity passes through a pronounced maximum in the region of the critical micelle concentration. This viscosity increase is observed only when the polymer concentration is in the semidilute regime and it is attributed to mixed micelle liasons between the hydrophobic elements of the chains. The decrease in viscosity above the cmc arises from stoichiometry, since the mixed micelles eventually will contain, on average, only one polymer alkyl chain per micelle, and cross-linking will be lost because there is no longer any stoichiometric requirement for the polymer hydrophobes to share micelles. Similarly, studies for hydrophobically modified acrylamide copolymers in the presence of SDS suggest that the surfactant disrupts intermolecular association of the hydrophobic groups, causing a decrease in solution viscosity.[14,15] In viscometric studies, Goddard et al.[6] investigated the effect of the polymer structure on the interactions of cationic polymers and an anionic surfactant system. Their studies indicated that addition of SDS to a cationically modified cellulosic terpolymer leads to intermolecular association between polymer chains via bound surfactant at high polymer concentrations (1% by weight) but intramolecular association at low concentration (0.1%). A similar investigation of the interaction of SDS with poly(acrylamide–*co*–(β-methacryloxyethyl)trimethylammonium chloride) showed no detectable change in viscosity over the same SDS concentration range, and it was concluded that the latter polymer maintained a constant conformation during binding of the surfactant.[17,29] In an analogous study, Hayakawa et al.[16] investigated the

---

® Abstract published in *Advance ACS Abstracts,* March 1, 1994.

0024-9297/94/2227-2145$04.50/0

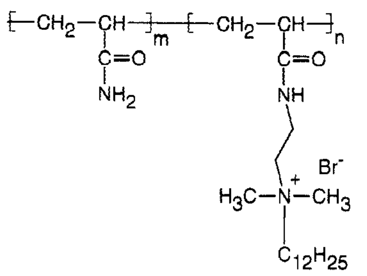

Figure 1. Structure of AM/DAMAB copolymers.

interaction of trimethyldodecylammonium bromide with poly(styrenesulfonate) and dextran sulfate. The equilibrium binding constant is higher for poly(styrenesulfonate) than for dextran sulfate, but, surprisingly, the cooperativity of the binding is higher for the more hydrophilic dextran sulfate. Thus higher hydrophobicity in a polymer does not necessarily result in enhanced micellar clustering of surfactant on the polymer; other factors such as linear charge density and flexibility of the polymer must also be taken into account.

In previous work, we described the synthesis and solution properties of copolymers of acrylamide and dimethyldodecyl(2-acrylamidoethyl)ammonium bromide (Figure 1).[17,29] These copolymers contain various amounts (up to 10 mol %) of dodecyl groups and show very interesting hydrophobic associative properties in aqueous solutions. Associative behavior of the copolymers is affected to a large degree by the arrangement of the hydrophobic groups along the copolymer chain. When the hydrophobic groups in such copolymers are arranged in a blocklike fashion, the hydrophobic interactions promote intermolecular association when the copolymer concentration is above C^*. A random copolymer with the same composition exhibits intramolecular associative behavior and reaches C^* at much higher concentration. The intermolecular interactions can be enhanced by increasing the length of the hydrophobic blocks and/or the number of blocks in the copolymer.

In this paper we report studies of the effects of sodium dodecyl sulfate, trimethyltetradecylammonium bromide, and Triton X-100 on the solution properties of copolymers of acrylamide with dimethyldodecyl(2-acrylamidoethyl)ammonium bromide. Surfactant concentrations were chosen to span a range from below to above the cmc of the surfactants in pure water. Rheological behavior as a function of the type of surfactant and the distribution of the hydrophobic groups is investigated. Complementary data obtained by surface tension and pyrene probe fluorescence are also presented.

Experimental Section

Materials. Deionized water used in this study has a resistivity of 18 MΩ and a surface tension of 70.8 mN/m. All surfactants were purchased from Aldrich (purity: SDS, 98%; TTAB, 99%; Triton X-100, containing <3% poly(ethylene glycol)). The syntheses of the copolymers have been described elsewhere.[17,29] Microblocky copolymers were prepared by free-radical polymerization in aqueous solution with the surfactant monomer concentration above cmc (BS-C12-4.3, B-C12-4.7). Two random copolymers were synthesized via solution polymerization techniques: one in *tert*-butyl alcohol (R-C12-5.1) and the other in water with the surfactant monomer concentration below the cmc (R-C12-1). The compositions of the copolymers are summarized in Table 1. The DAMAB content was determined by elemental analysis, and the weight-average molecular weights of the copolymers were measured with a Chromatix KMX-6 low-angle laser light scattering spectrophotometer in methanol/water mixture (50/50 by volume).

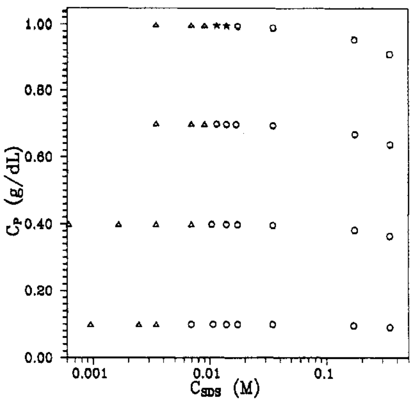

Figure 2. Solubility diagram of R-C12-1/SDS: two phases (△); clear solution (○); gel (★).

Table 1. Composition of Copolymers

copolymer	DAMAB content (mol %)	$M_w \times 10^{-6}$
PAM	0	1.12
R-C12-1	0.32	0.74
BS-C12-4.3	4.3	0.95
B-C12-4.7	4.7	1.04
R-C12-5.1	5.1	0.47
B-C12-10.5	10.5	1.12

Methods. Surface tension measurements were performed with a Kruss Processor Tensiometer K12 instrument at 25 °C using a Pt DeNouy ring. Viscosity measurements were conducted on a Contraves LS-30 low-shear rheometer at 25 °C and a shear rate of 6 s^{-1}. Elemental analyses were conducted by MHW Laboratories of Phoenix, AZ. Steady-state fluorescence spectra were obtained with a Spex Fluorolog 2 fluorescence spectrophotometer equipped with a DM3000F data system. Classical light scattering studies were performed with a Chromatix KMX-6 low-angle laser light scattering spectrophotometer with a 2-mW He-Ne laser operating at 633 nm. Refractive index increments for classical studies were obtained on a Chromatix KMX-16 laser differential refractometer. A Spectra-Physics 127 laser operating at 632.8 nm was used for dynamic light scattering studies. Data were collected using a Brookhaven Instruments Model BI-2000SM automatic goniometer interfaced with a Brookhaven Instruments personal computer. Studies were performed at 90°, and the signals were processed with a Brookhaven Instruments Model BI-2030AT autocorrelator. Data were analyzed using the algorithm CONTIN and associated software provided by the manufacturer. Polymer solutions of 2.0×10^{-4} g/mL in 0.5 M NaCl were filtered in a Tygon tubing filter loop using Millipore 0.45-μm filters to remove dust. Typical filtration times were 14-48 h. Multiple analyses were performed to ensure reproducibility.

Results and Discussion

Anionic Surfactant. Solubility. The solubility diagram for the copolymer R-C12-1/SDS system in deionized water is shown in Figure 2. At low polymer concentrations (C_p <1%), the system exhibits several distinguishable solubility zones. When SDS is initially added to the copolymer solution, turbid two-phase dispersions are observed. Continued addition of the surfactant results in macroscopic phase separation in which one clear phase is on top of the other clear phase. The precipitate is resolubilized in the presence of excess surfactant, and the resulting solutions are clear and fluid. This solubility behavior is similar to that reported by Goddard et al.[18] Note that the transition occurs at the cmc of SDS. Initial precipitation of the copolymer in this case is caused by interaction of SDS with the copolymer by opposite ion charge interaction between surfactant and polymer ions, and this simultaneously increases hydrophobicity of the copolymer. At higher surfactant con-

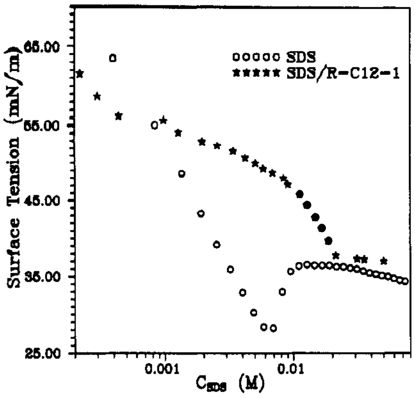

Figure 3. Surface tension measurements of SDS in the presence and absence of R–C12–1 copolymer (C_p = 0.33 g/dL).

centrations, however, it is likely that the SDS forms micelle-like clusters around hydrophobic groups attached to the polymer, and the copolymer is resolublized.

When copolymer concentrations are above 1%, a gel phase is observed at the surfactant concentrations between the precipitating zone and the resolubilizing zone. Apparently, liaisons result in a physical cross-linking network requiring association between SDS and the copolymer; no such gel formation is observed in the pure copolymer solutions.[19]

Phase separation occurs when SDS is mixed with B–C12–4.3, B–C12–4.7, and R–C12–5.1 copolymer solutions throughout the copolymer concentration range. Dubin et al.[20] have shown that the degree of ion pairing between high charge density polyelectrolytes and oppositely charged micelles is very extensive so that complexation leads to the rapid and irreversible formation of an amorphous solid, much as the mixing of oppositely charged strong polyelectrolytes produces water-insoluble "polyelectrolyte complexes".[21] In our study, precipitation of the copolymers upon addition of SDS may be caused by this strong ion-pair interaction. Because of solubility limits, studies of the interaction of SDS and copolymers were focused on SDS/R–C12–1 systems.

Surface Tension. Surface tension measurements show a classical "crossover" of the "with- and without-polymer" surface tension curves for the SDS solutions[22] (Figure 3). The surface tension of the SDS solution in the absence of the copolymer displays a pronounced minimum in the region of the cmc. This has been previously reported as a result of the presence of a lauryl alcohol impurity in the surfactant.[23]

The concentration, C_1, at which the surfactant begins to interact with the polymer and the concentration, C_2, at which the normal micelles begin to form are conspicuous in Figure 3. It is interesting to note that in the presence of the copolymer the surface tension curve shows no minimum. It can be inferred from the shape of the curve that lauryl alcohol is comicellized in the polymer–surfactant complex in preference to being adsorbed at the air–liquid interface. When regular micelles form, the measured surface tensions are slightly higher in the presence of copolymer. This may be an artifact of the DeNouy method, arising from viscoelastic recoil of the solubilized copolymer. The lower value of the copolymer curve at surfactant concentrations below C_1 can be explained by the surface activity of the copolymer. Adsorption of copolymer at the surface would necessarily compress the area available for surfactant adsorption, which would, in turn, increase the surface excess surfactant concentration and, consequently, cause a lowering of the surface tension. The higher surface tension at a surfactant concentration around the cmc clearly demonstrates binding of the surfactant to the copolymer and concomitant depletion of surfactant from the air–water interface. C_1 in this case is 4.5 × 10^{-4} M. The surfactant adsorption on the polymer reaches a limit at a surfactant concentration of 9.7 × 10^{-3} M, corresponding to 60 SDS molecules per DAMAB monomer. This agrees well with the value of 50–60 surfactant molecules per micelle cluster reported in previous literature.[24]

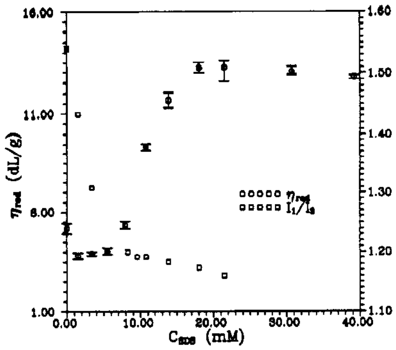

Figure 4. η_{red} and I_1/I_3 as a function of SDS concentration for R–C12–1 copolymer at a concentration of 0.33 g/dL (C_{pyr} = 10^{-6} M).

Viscosity and Fluorescence Measurements. Figure 4 illustrates the dependence of the reduced viscosity of R–C12–1 copolymer on the SDS concentration. Initial addition of SDS causes a slight decrease in the viscosity, presumably due to the loss of the copolymer from the solution which could arise from mixed micelle formation within each single amphiphilic copolymer molecule in solution. On the other hand, I_1/I_3 decreases in the region until a constant value is reached at a surfactant concentration of 5.1 × 10^{-3} M, a concentration significantly lower than the cmc of SDS (8.3 × 10^{-3}). It is noteworthy that I_1/I_3 decreases gradually with increasing SDS concentration over a large surfactant concentration range, indicating that the binding of charged surfactant occurs by a noncooperative mechanism.[25] It is likely that surfactant molecules first adsorb on DAMAB monomer units at low surfactant concentrations to form hydrophobic clusters. Continuous addition of the surfactant results in an increase in cluster size; a hydrophobic microdomain is formed at a critical concentration of 5.1 × 10^{-3} M. The ratio of SDS molecules to DAMAB monomers in each microdomain is 34 as estimated from fluorescence data in Figure 4. This value is lower than that determined from surface tensiometry but is reasonable. It appears that not all of the polymer hydrophobes are comicellized at C_1. The transition point of the curve corresponds to the surfactant concentration at which the precipitate begins to resolubilize. This clearly implies that micelle type aggregates are responsible for redissolution of the precipitate.

At the cmc of SDS, further addition of surfactant dramatically enhances the solution viscosity. The curve reaches a plateau value at 18 mM SDS. This viscosity behavior differs from that observed by Leung and Goddard[6] for a cationic cellulose ether and SDS. In the latter case, the highest viscosity was observed in the precipitation zone, and viscosity dropped sharply in the resolubilization zone. In our system the increase in viscosity may be ascribed to association of surfactants and DAMAB of the copolymer in mixed hydrophobic microdomains. It is reasonable to assume that adjacent hydrophobic microdomains combine with increasing SDS concentration. Larger clusters then form which may contain DAMAB units belonging to two or more distinct polymer chains. Taking into account that the copolymer concentration

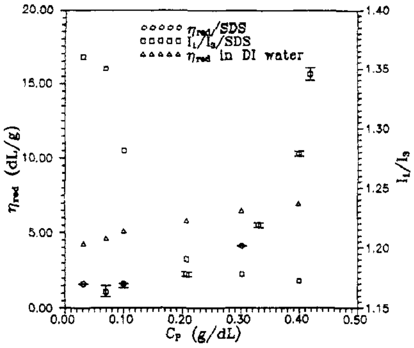

Figure 5. η_{red} and I_1/I_3 as a function of concentration of R–C12-1 copolymer in deionized water and 8.32 mM SDS aqueous solution.

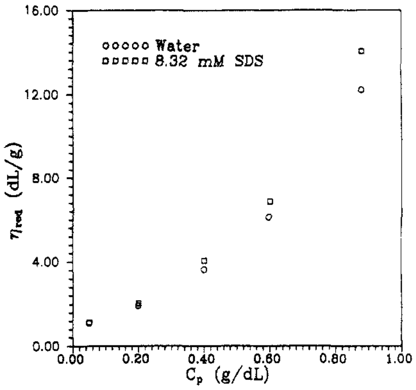

Figure 6. Effect of SDS on the η_{red} of homopolyacrylamide.

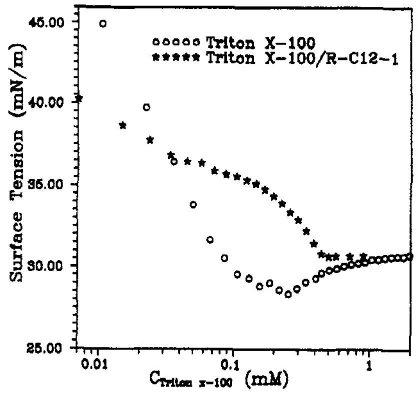

Figure 7. Surface tension measurements of Triton X-100 in the presence and absence of R–C12-1 copolymer (C_p = 0.33 g/dL).

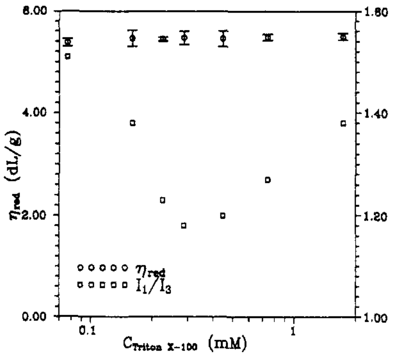

Figure 8. η_{red} and I_1/I_3 as a function of Triton X-100 concentration for R-C12-1 copolymer at concentration of 0.33 g/DL (C_{pyr} = 10^{-6} M).

studied is in the semidilute regime, these microdomain clusters serve as sites where hydrophobic groups from adjacent polymer chains associate intermolecularly.

Formation of intermolecular association in this system can be seen more clearly by studying the viscosity behavior at fixed surfactant concentrations. As shown in Figure 5, a sharp upturn in the viscosity occurs within a narrow concentration range in the system containing 8.32 mM SDS, typical of intermolecular association. Such viscosity enhancement is not observed for polyacrylamide (Figure 6). Obviously, this interchain association is facilitated by interactions between SDS and DAMAB. It is interesting to note that the viscosity upturn occurs at the concentration where a constant limiting value of I_1/I_3 is reached. This value is very close to the one in Figure 4, suggesting that pyrene molecules locate in similar mixed micelles.

Clearly, two effects promote DAMAB association with SDS, hydrophobic and ionic associations. Hydrophobic associations reduce the contacts of the hydrophobic groups of the copolymer with water and consequently lower the free energy of the system.[26] Ionic attractions between SDS molecules and the cationic groups of the copolymer also contribute to the formation of mixed micelles. Each micelle apparently contains two or more DAMAB moieties belonging to different polymer chains.

Nonionic Surfactant. Surface Tension. It has been shown that, in a system composed of a nonionic surfactant and a polymer having long hydrocarbon pendent groups, surfactant molecules form micelle-like clusters adsorbed to each hydrocarbon chain.[2a,14,27,28] Such associations also occur when Triton X-100 is added to the R–C12-1 copolymer solution (Figure 7). C_1 is 0.032 mM and C_2 is 0.40 mM.

Viscosity and Fluorescence Studies. The effects of nonionic surfactant on the viscosity of C12-1 copolymer solution are shown in Figure 8. Contrary to behavior in SDS, addition of Triton X-100 to R–C12-1 solutions results in no observable change in the reduced viscosity. The hydrodynamic size of the polymer oil remains nearly constant ($d_0 \approx$ 77–79 nm) over a range of added surfactant concentration from 0.2 to 0.8 mM. However, I_1/I_3 decreases with increasing surfactant concentration, passing through a minimum and then increasing (Figure 8). The surfactant concentration at which I_1/I_3 shows the lowest value is very close to C_2. The initial decrease in I_1/I_3 is due to the formation of hydrophobic microdomains through association between surfactant molecules and hydrophobic groups of the copolymer. It is necessary to emphasize that the decrease in I_1/I_3 does not result from adsorption of surfactant to the pyrene molecules since the surfactant solution in the absence of the copolymer at the cmc shows a much higher I_1/I_3 of 1.44. When the limit of adsorption of the surfactant molecules onto the polymer is reached, further increase in surfactant concentration will result in the formation of normal surfactant micelles. Apparent I_1/I_3 values in such a system depend on the partitioning of pyrene molecules into two hydrophobic regions. By knowing the cmc of Triton X-100 in the system to be 0.3 mM and the C_1 of 3.2×10^{-2} mM, the number of surfactant molecules around each DAMAB unit is calculated to be ~3. Since there are no interactions between hydrophobes in the absence of surfactant, condensation of the surfactant onto the R–C12-1 polymer does not alter the polymer conformation, and the viscosity of the polymer solution is essentially invariant throughout the surfactant concentration range.

The effect of a nonionic surfactant on the viscosity of the polymer solution with higher hydrophobic content was investigated using the microblocky copolymer B-C12-4.3 (Figure 9). The polymer shows a higher viscosity in the presence of 0.264 mM Triton X-100 than in the absence of the surfactant. Apparently, this surfactant promotes intermolecular associations.

Cationic Surfactant. Surface Tension. No definite

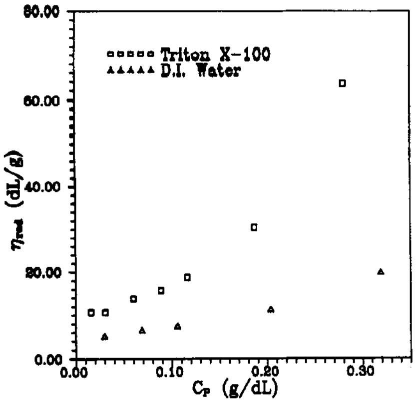

Figure 9. Viscosity behavior of B-C12-4.3 copolymer in 0.264 mM Triton X-100 aqueous solution and in deionized water.

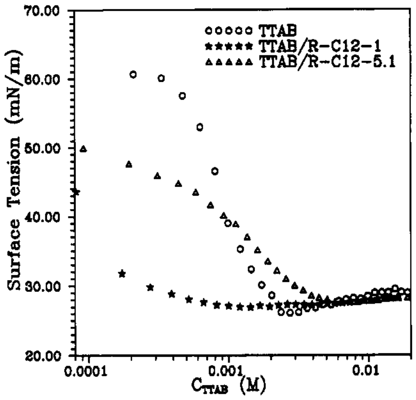

Figure 10. Surface tension behavior of TTAB in the presence of R-C12-1 and R-C12-5.1 copolymers (C_p = 0.33 g/dL).

crossover is observed for the R-C12-1/trimethyltetradecylammonium bromide (TTAB) mixture (Figure 10). However, the system shows much more pronounced surface activity at very low surfactant concentrations, and the curve levels off below the cmc. Apparently, hydrophobic interaction overcomes ionic repulsion between the DAMAB moiety and the TTAB surfactant molecules, resulting in the formation of a surface-active complex. The polymer/surfactant association is also observed in the R-C12-5.1/TTAB system. In this case, however, the complex is less surface-active as compared with R-C12-1/TTAB. This may be explained by the collapsed conformation of R-C12-5.1 upon addition of TTAB as discussed below. The dramatic decrease in the surface tension in both R-C12-1 and R-C12-5.1 solutions around the cmc of the surfactant is not due to the exclusion of the copolymers from solutions to the air-liquid interface as a result of increased ionic strength. This is verified by only a slight decrease in surface tensions in both systems with increasing NaBr concentration (Figure 11). Addition of TTAB to microblocky copolymer solutions (B-C12-4.3, B-C12-4.7, and B-C12-10.5) results in polymer precipitation, probably due to a "salting-out" effect.[24]

Viscosity and Fluorescence Studies. Addition of TTAB does not change the rheological properties of the R-C12-1 copolymer. However, a significant decrease in viscosity is observed when TTAB is mixed with the R-C12-5.1 copolymer (Figure 12). In this case, TTAB acts as a cosurfactant associating with the polymer coils which become much more compact. The hydrophobic effect is apparently too strong in this system for the polymer coil to expand; the reduced viscosity remains essentially unchanged upon dilution. In other words, the copolymer behaves like a highly collapsed coil.

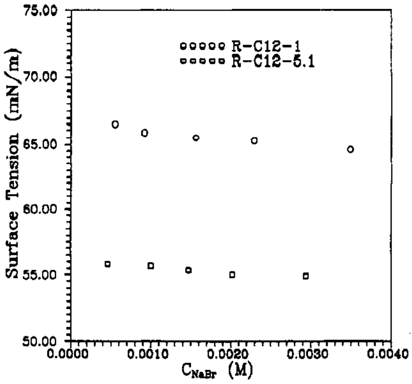

Figure 11. Effect of NaBr concentration on the surface tension of R-C12-1 and R-C12-5.1 solutions (C_p = 0.33 g/dL).

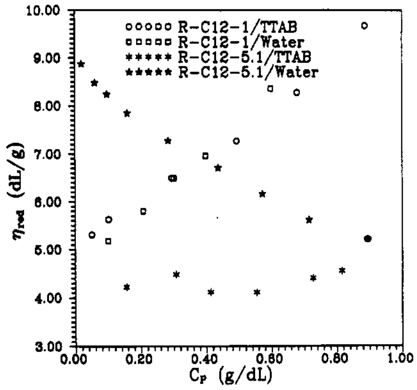

Figure 12. η_{red} as a function of polymer concentration in the presence and absence of TTAB.

Conclusions

Effects of small surfactants on the rheological properties of the copolymers depend on the type of surfactant and the nature of the hydrophobic association (intermolecular vs intramolecular). Addition of SDS results in a slight decrease in the solution viscosity of R-C12-1 at surfactant concentration below the cmc and then a rapid increase at the cmc. The curve reaches a plateau at 18 mM SDS. This viscosity behavior can be explained by the association of SDS around each hydrophobic group along the polymer chain to form mixed micelles and subsequent polymer chain extension due to the ionic repulsion between the mixed micelles. The copolymers with higher hydrophobic content precipitate from the solution in the presence of SDS. In contrast, no significant viscosity change has been observed when the nonionic surfactant is added to a solution of R-C12-1 although the surface tension measurements and fluorescence studies indicate that association of surfactant with the copolymer does occur. An initial decrese and then an increase in the I_1/I_3 value can be explained by the partitioning of pyrene molecules between the homomicelles of Triton X-100 and the mixed micelles formed by hydrophobic groups of the copolymer and Triton X-100. Addition of nonionic surfactant to the SB-C12-4.3 solutions results in a large increase in the viscosity. In the case of TTAB cationic surfactant, R-C12-5.1 exhibits a collapsed conformation while the viscosity of R-C12-1 is hardly affected. However, R-C12-1 forms a more surface-active complex with CTAB than does R-C12-5.1. Macrophase separation occurs for the microblocky copolymer solutions in the presence of this cationic surfactant.

Acknowledgment. We gratefully acknowledge the financial support of the Office of Naval Research, the Defense Advanced Research Projects Agency, and the U.S.

Department of Energy. We thank Dr. James P. Dickerson for assistance with dynamic light scattering measurements.

References and Notes

(1) For reviews, see: *Polymers in Aqueous Media*; Glass, J. E., Ed.; Advances in Chemistry Series 223; American Chemical Society: Washington, DC, 1989.

(2) For reviews, see: (a) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255. (b) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 301.

(3) Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36.

(4) Cabane, B.; Duplessix, R. *Colloids Surf.* **1985**, *13*, 19.

(5) Thalberg, K.; Lindman, B. *Langmuir* **1991**, *7*, 277.

(6) Leung, P. S.; Goddard, E. D. *Colloids Surf.* **1985**, *13*, 47.

(7) Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1983**, *87*, 506.

(8) Goddard, E. D.; Hannan, R. B. *J. Colloid Interface Sci.* **1976**, *55*, 73.

(9) Methemitis, C.; Morcellet, M.; Sabbadin, J.; Francois, J. *Eur. Polym. J.* **1986**, *22*, 619. C.

(10) Steiner, C. A. *J. Appl. Polym. Sci.* **1991**, *42*, 1493.

(11) Goddard, E. D.; Hannan, R. B. In *Micellization, Solubilization, and Microemulsions*; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 2; p 835.

(12) Biggs, S.; Selb, J.; Candau, F. *Langmuir* **1992**, *8*, 838.

(13) Iliopoulos, I.; Wang, T. K.; Audebert, R. *Langmuir* **1991**, *7*, 617.

(14) McCormick, C. L.; Nonaka, T.; Johnson, C. B. *Polymer* **1988**, *29*, 731. c

(15) Schulz, D. N.; Kaladas, J. J.; Maurer, J. J.; Bock, J.; Pace, S. J.; Schulz, W. W. *Polymer* **1987**, *28*, 2110.

(16) (a) Hayakawa, K.; Santerre, J. P.; Kwak, J. C. T. *Macromolecules* **1983**, *16*, 1642. (b) Hayakawa, K.; Santerre, J. P.; Kwak, J. C. T. *ACS Symp. Ser.* **1984**, *No. 253*, 225.

(17) Chang, Y.; McCormick, C. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (2), 202.

(18) Goddard, E. D.; Hannan, R. B. *J. Am. Oil Chem. Soc.* **1977**, *54* (12), 561.

(19) Goddard, E. D.; Leung, P. S.; Padmanabhan, K. P. A. *J. Soc. Cosmet. Chem.* **1991**, *42*, 19.

(20) Dubin, P. L.; Vea, M. E. Y.; Fallon, M. A.; The, S.S.; Rigsbee, D. R.; Gan, L. M. *Langmuir* **1990**, *6*, 1422.

(21) Smid, J.; Fish, D. In *Encyclopedia of Polymer Science and Technology*; Wiley-Interscience: New York, 1988; Vol. 11, p 720.

(22) Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36.

(23) Padmanabhan, K. P. A. In *Interaction of Surfactant with Polymers and Proteins*; Goddard, E. D., Padmanabhan, K. P. A., Ed.; CRC Press: Boca Raton, FL, 1993; p 14.

(24) Wennerstrom, H.; Lindman, B. *Phys. Rep.* **1979**, *52*, 1.

(25) Winnik, F. M.; Ringsdorf, H.; Venzmer, J. *Langmuir* **1991**, *7*, 905.

(26) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd ed.; John Wiley & Sons: New York, 1980.

(27) Cabane, B. J. *J. Phys. Chem.* **1977**, *81*, 1639.

(28) Holtzscherer, C.; Candau, F. *J. Colloid Interface Sci.* **1988**, *125* (1), 97.

(29) Ezzell, S. A.; McCormick, C. L. *Macromolecules* **1992**, *25* (7), 1881–1886.

(30) Ezzell, S. A.; McCormick, C. L.; Hoyle, C. E.; Creed, D. *Macromolecules* **1992**, *25* (7), 1887–1895.