Surfactant Interactions with P(AM–AA–BPAM) Hydrophobically Modified Polyelectrolytes

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ABSTRACT: The interactions of hydrophobically modified polyelectrolytes poly(acrylamide–sodium acrylic acid–N-(4-butyl)phenylacrylamide [P(AM-AA-BPAM)] with anionic (sodium dodecyl sulfate), cationic (cetyl trimethylammonium bromide), and nonionic (tetradecyldimethylaminoxid) surfactants were studied via solution rheology, surface tension, and atomic force microscopy measurements. Viscosity measurements indicated that the intermolecular association of the polymer was greatly enhanced by the interaction with the surfactants, especially the oppositely charged surfactants with both a hydrophobic association and an electrostatic attraction. The greatest viscosity increase was realized with the addition of such oppositely charged surfactants. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2664–2671, 2003

**Key words:** polyelectrolytes; surfactants; atomic force microscopy (AFM)

INTRODUCTION

The interactions of hydrophobically associating water-soluble polymers with small surfactant molecules have been the subject of much interest in recent years. Polymers contain a small amount of hydrophobic substituents as pendant chains, blocks, or terminal groups, and the association of the hydrophobic groups is reinforced by the formation of mixed micelles with surfactants, which act as crosslinks between the polymer molecules. For hydrophobically modified polyelectrolytes, the ion groups in the polymer chains make the polymer–surfactant interactions complicated. With oppositely charged systems, both favorable electrostatic and hydrophobic associations play a role. For nonionic systems, only hydrophobic associations are prevalent, whereas in similarly charged systems, favorable hydrophobic interactions are opposed by unfavorable electrostatic interactions. Because this kind of polymer–surfactant complex shows some extraordinary rheological properties, they are widely used in tertiary oil recovery, latex paint systems, drug delivery, cosmetic formulation, drag reduction, flocculation, biological/medical, purposes, and so on.[1–3]

In this study, we were interested in the investigation of the interactions of hydrophobically modified polyelectrolytes with surfactants, including similarly and oppositely charged surfactants and nonionic surfactants, by the measurement of surface tension and solution rheology. AFM was used to investigate the microstructures of the polymer–surfactant complexes.

EXPERIMENTAL

Materials and methods

The hydrophobically modified polyelectrolytes poly(acrylamide–sodium acrylic acid–N-(4-butyl)phenylacrylamide [P(AM–AA–BPAM)] were prepared by a procedure described previously. The molecular formula is as follows:
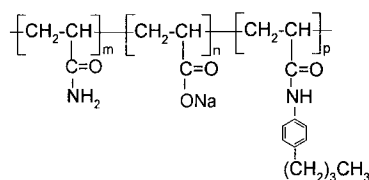
APA-n

TABLE I
Synthesis Parameters of the APA Terpolymers

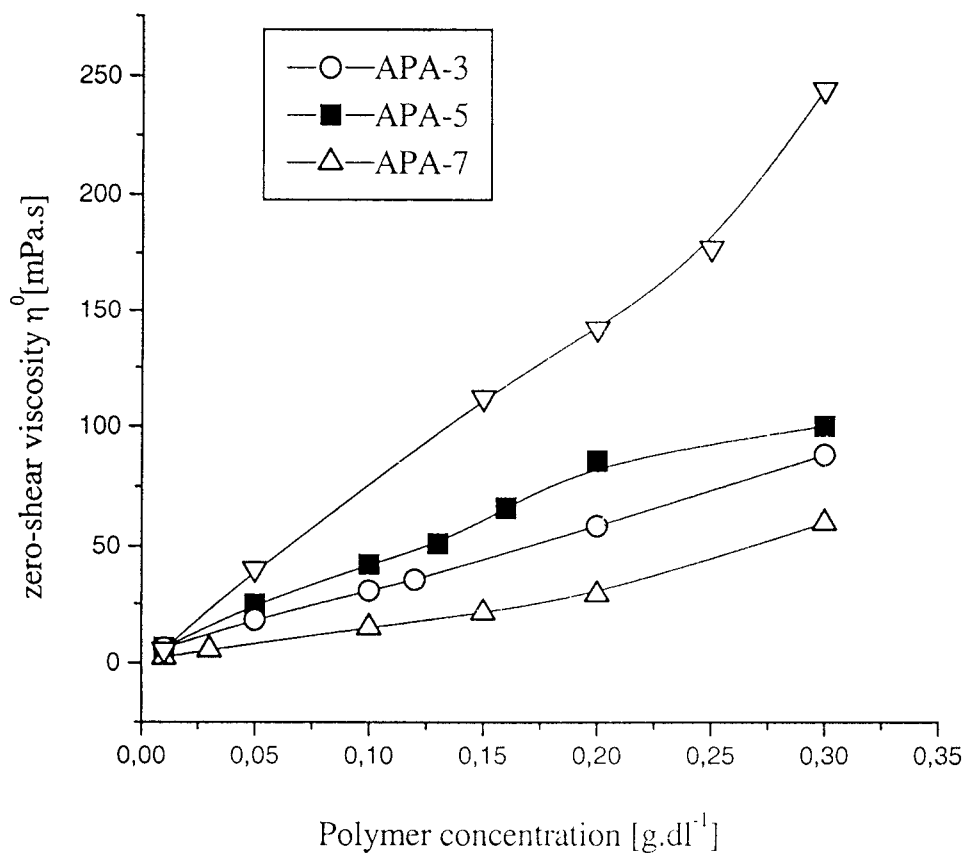| Sample	AM concentration (mol %)	AA concentration (mol %)	BPAM concentration (mol %)
APA-0	70.7	29.3	0
APA-3	72.8	26.6	0.61
APA-5	63.0	36.4	0.60
APA-7	83.7	15.8	0.56

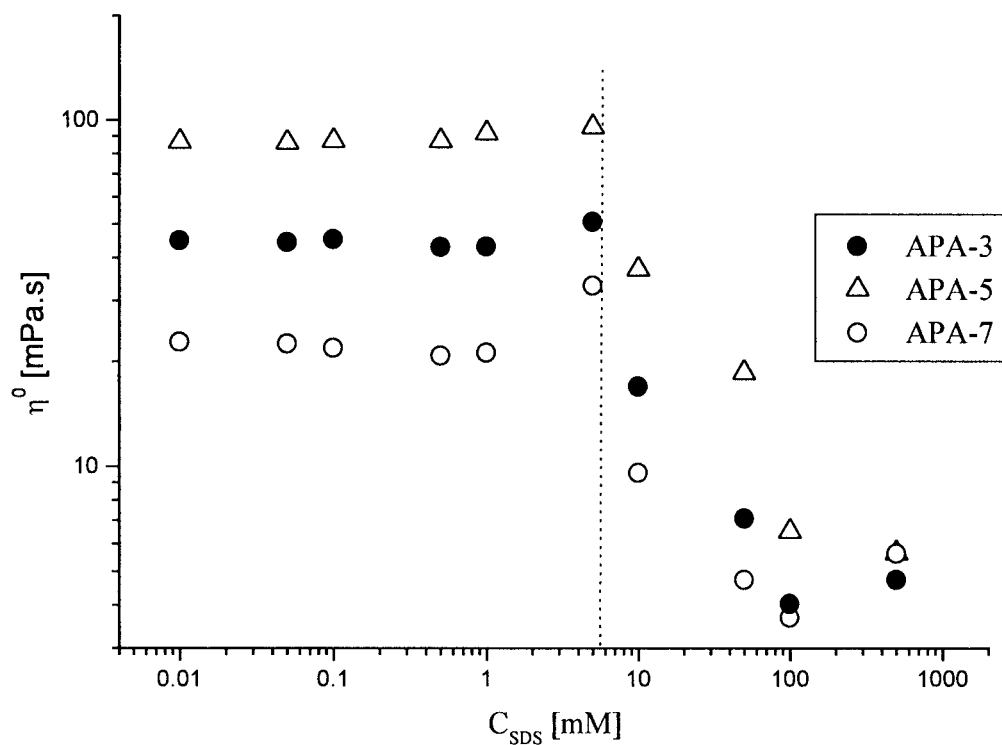**Figure 1** Zero-shear viscosity as a function of polymer concentration for the polymer solutions.

Figure 2 Effect of SDS concentration on the zero-shear viscosity of the polymer solution at 25°C (polymer concentrations: APA-3 = 0.15 g dL^{-1} and APA-5 and APA-7 = 0.2 g dL^{-1}).
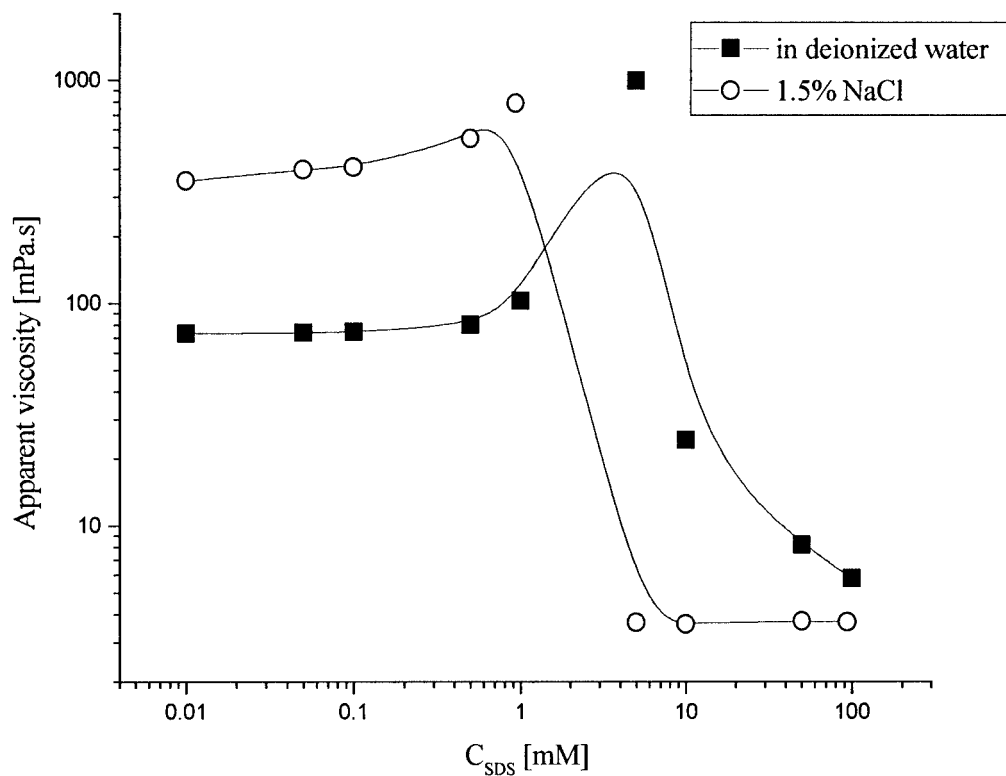
Figure 3 Effect of SDS concentration on the apparent viscosity of the APA-3 polymer solution at 6 s^{-1} and 25°C (polymer concentration = 0.2 g dL^{-1}).
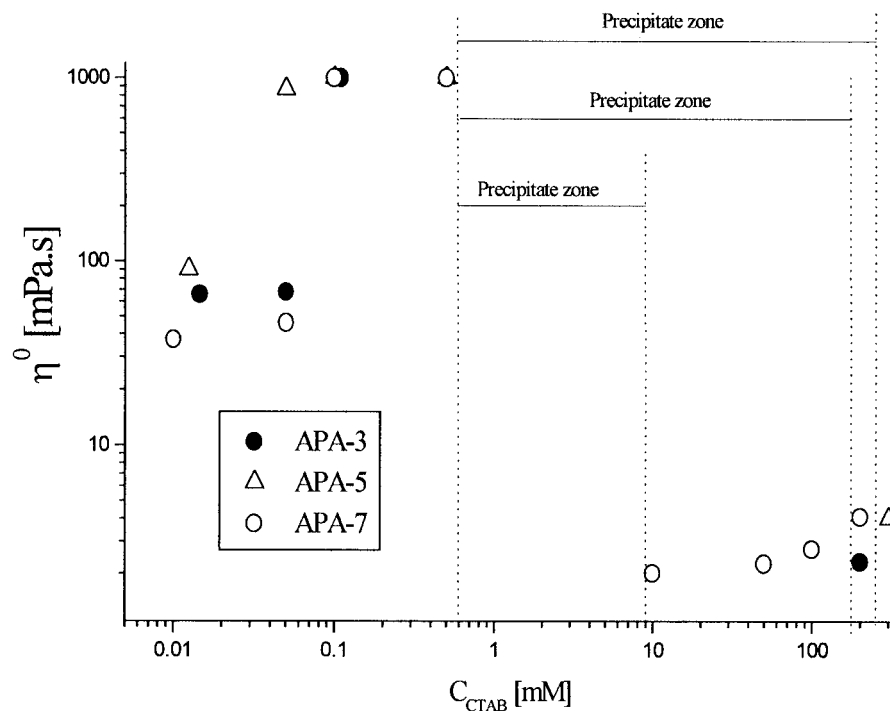

Figure 4 Effect of CTAB concentration on the zero-shear viscosity of the polymer solution at 25°C (polymer concentration = 0.2 g dL^{-1}).
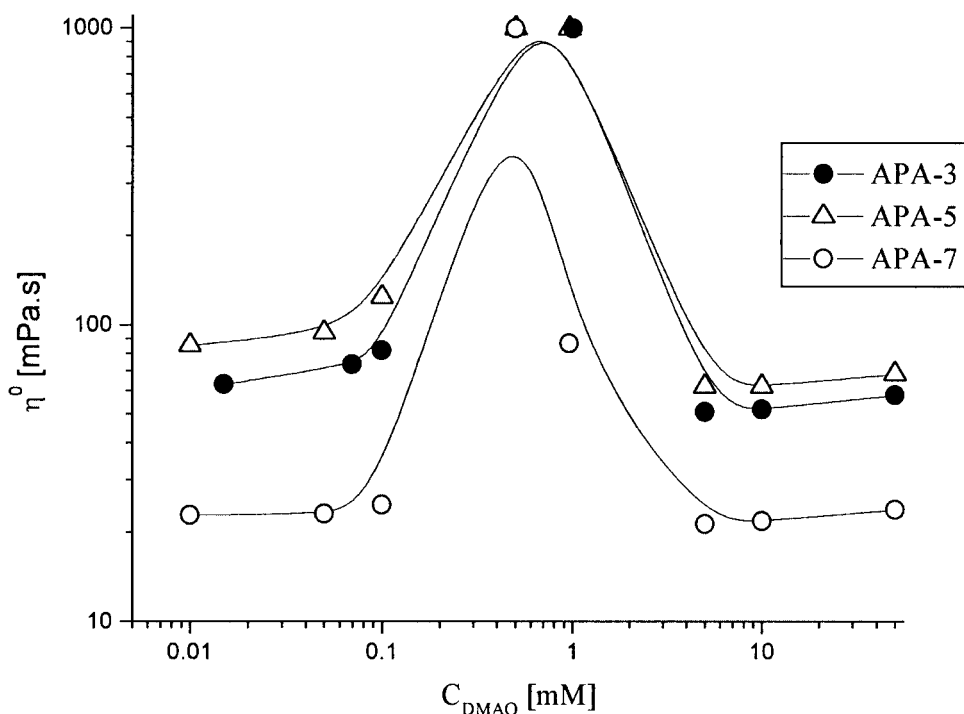
Figure 5 Effect of $C_{14}DMAO$ concentration on the zero-shear viscosity of the polymer solution at 25°C (polymer concentration = 0.2 g dL^{-1}).

The samples used in the study are listed in Table I. The surfactants used were sodium dodecyl sulfate (SDS; $C_{12}H_{25}SO_4Na$) from Serva, cetyl trimethylammonium bromide (CTAB; $C_{16}H_{33}N(CH_3)_3Br$) from Merck, and tetradecyldimethylaminoxid ($C_{14}DMAO$; $C_{14}H_{29}N(CH_3)_2O$) from Clariant and were crystallized twice from acetone. The samples were prepared from stock solutions by weight. All of them had polymer concentrations of 0.2 g dL^{-1}, which was above the critical association concentration and in the semidilute region of the polymer solution. Viscosity measurements and oscillatory rheological measurements were conducted on a Bohlin CS rheometer with a cone/plate or a double-gap concentric cylinder measuring geometry with a cone angle of 4° and a diameter of 40 mm. The double-gap device was applicable for low-viscous liquids. The zero-shear viscosity in dilute solution was measured with an oscillating capillary rheometer (Paar OCR-D). The measurement temperature was 25°C, and the shear rate was 6 s^{-1} unless otherwise indicated. The surface tension measurements were carried out on a Lauda tensionmeter at a constant temperature of 25°C. Atomic force microscopy (AFM) measurements were made with a Digital Instruments Nanoscope III controller with a Dimension 3100 microscope, and all measurements were performed in the tapping mode. Mica wafers were used as the substrate for the measurements, and the sample was prepared by dip-coating and drying up.

RESULTS AND DISCUSSION

Zero-shear viscosity of the polymer solutions

Figure 1 shows the concentration dependence of the solution zero-shear viscosity for the APA terpolymers. In deionized water, the polymers behaved as typical polyelectrolytes. The viscosities increased almost linearly with polymer concentration.

Addition of similarly charged surfactants

As shown in Figure 2, the initial addition of SDS resulted in a slight change in the solution viscosity, then reached a plateau at 5 mM SDS, and dropped sharply at high SDS concentrations. In this system, the increase in viscosity may have been due to the association of surfactants and hydrophobic tails of the polymer, which formed mixed hydrophobic micelles, leading to crosslinking between different polymer chains. However, the association was not so strong because of the repulsion of SDS and the polymer chain, which contained the same charge groups. Too many SDS micelles at high SDS concentrations may not have combined hydrophobic groups effectively and may have disrupted the intermolecular association of hydrophobic groups.[5]

Addition of NaCl to the polymer–SDS

As shown in Figure 3, the viscosities were enhanced by the addition of NaCl, and the viscosity maximum shifted to a lower SDS concentration. The NaCl salt screened the charges of the polymer molecules and
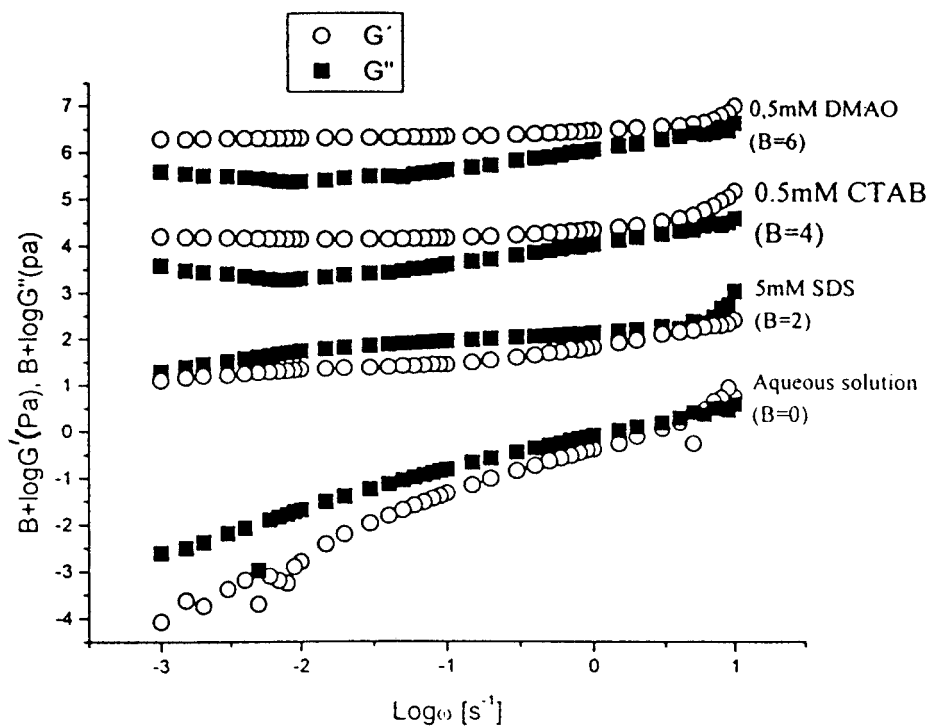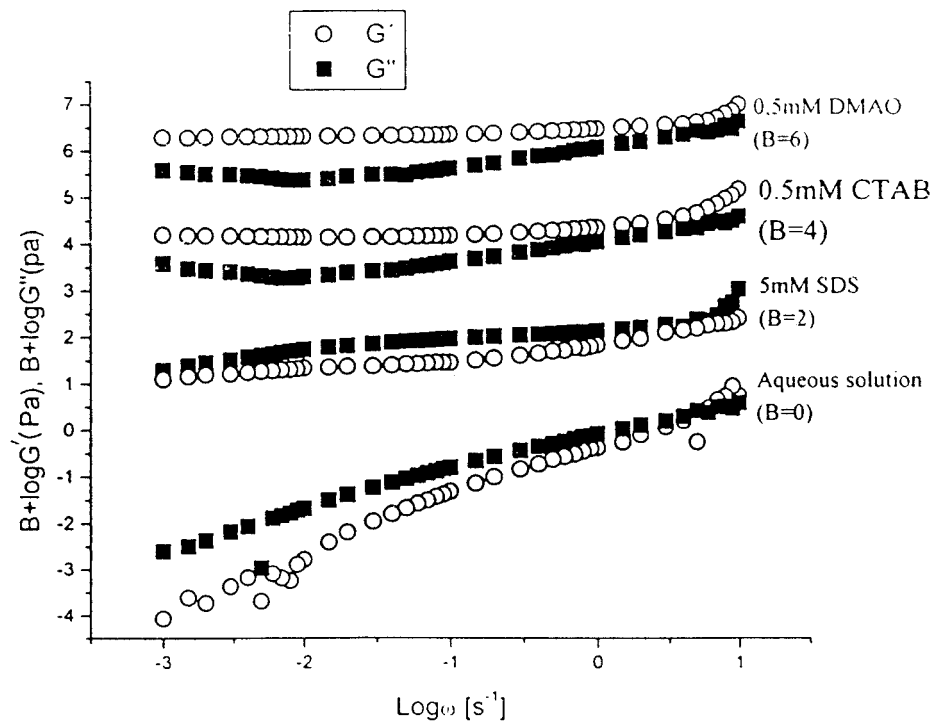
Figure 6 G' and G'' versus frequency measured for different surfactant interactions with the polymers (polymer concentration = 0.2 g dL^{-1}).
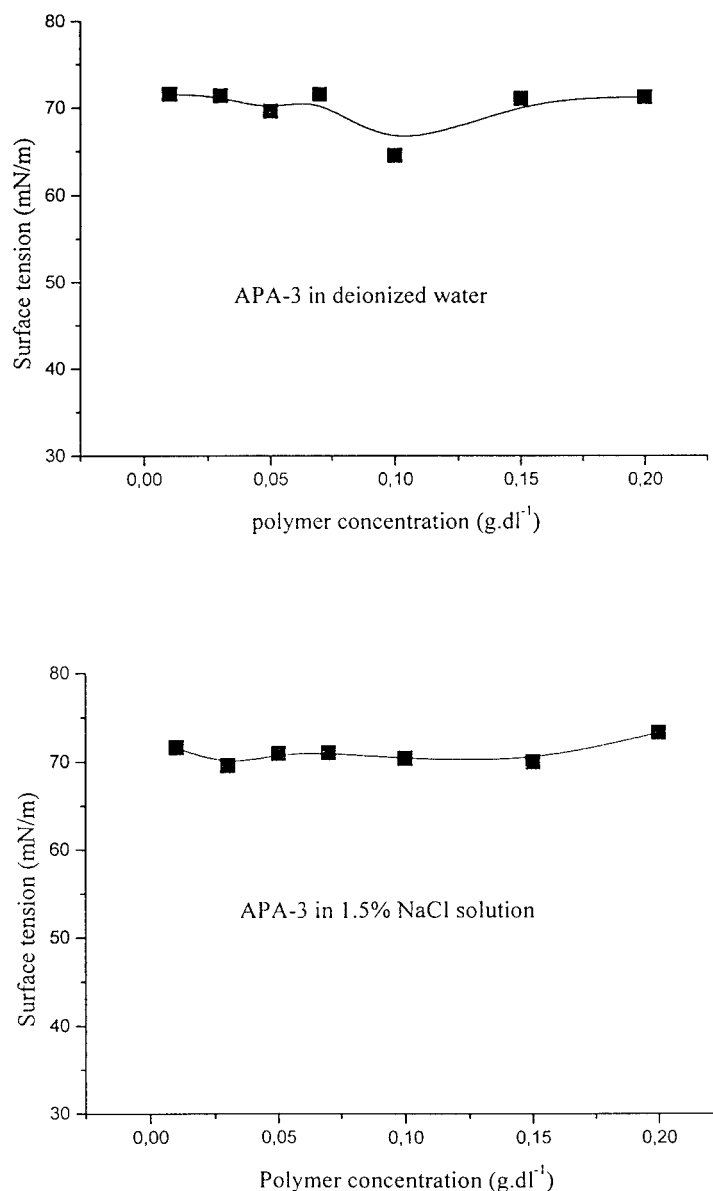
Figure 7 Surface tension of APA-3 in (top) deionized water and (bottom) 1.5% NaCl solution.

promoted associations between the polymer and surfactant by reduced electrostatic repulsion.

Addition of oppositely charged surfactants

As shown in Figure 4, the addition of CTAB dramatically enhanced the solution viscosity. A sharp upturn in the viscosity occurred at a CTAB concentration of 0.5 mM (a viscosity higher than 1000 mPas is considered to be 1000 mPas on the graph), and the gel-like solution could be formed at a polymer concentration of 0.2 g dL^{-1}. The copolymers precipitated from the solution at higher CTAB concentrations, and the viscosity dropped sharply in the resolubilization zone. With higher AA content, the polymer redissolved at higher CTAB concentrations. Two effects promoted the polymer hydrophobic group association with

CTAB: hydrophobic and ionic associations. Hydrophobic associations reduced the contacts of the hydrophobic groups of the polymer with water and, consequently, lowered the free energy of the system. Ionic attractions between CTAB molecules and anionic groups of the copolymer also contributed to the formation of the mixed micelles. Because the copolymer concentration was in the semidilute regime, these micelles clusters served as sites where hydrophobic groups from adjacent polymer chains associated intermolecularly. The micelle type aggregates were responsible for the redissolution of the precipitate.[6–8]

Addition of a nonionic surfactant

Figure 5 shows the viscosity versus the C_{14}DMAO concentration of the three samples. A dramatic in-
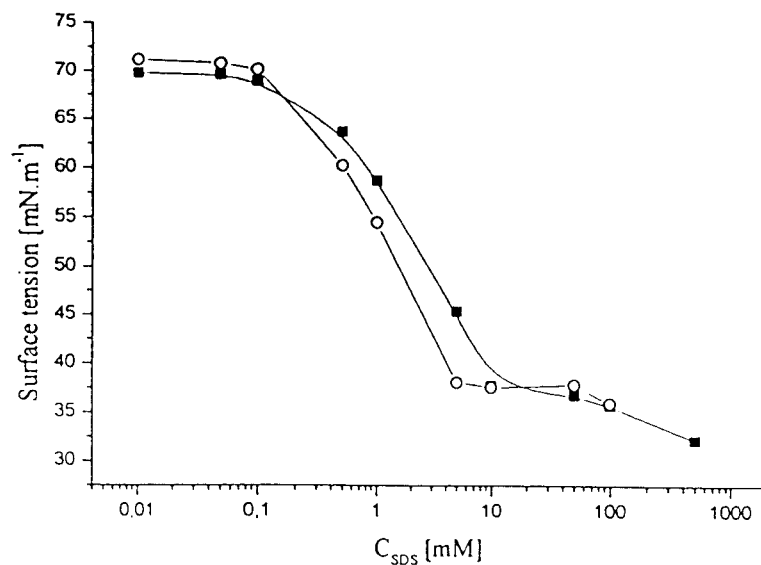
Polymer concentration:0.2g.dl⁻¹
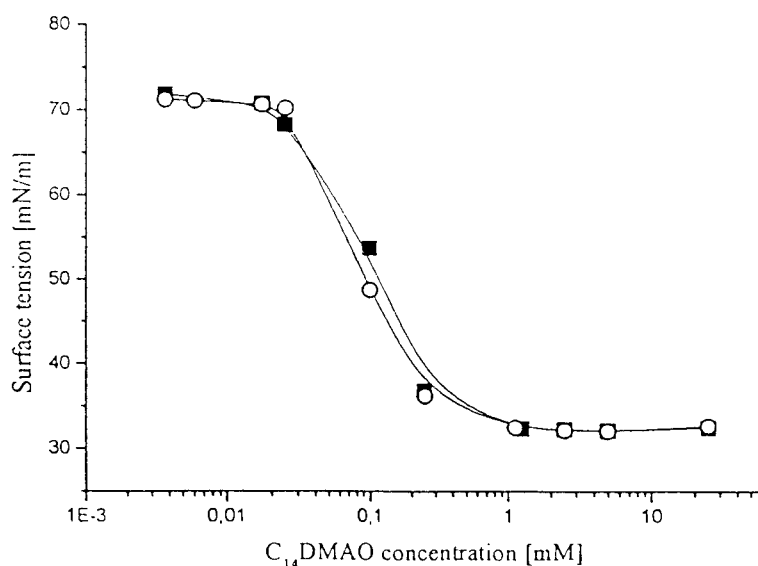
Polymer concentration:0.05g.dl⁻¹

Figure 8 Surface tension measurements for APA in the presence of (top) SDS and (bottom) C_{14}DMAO: (O) surfactant and (■) APA-3/surfactant system.

crease in the viscosity occurred at a concentration of 0.5–1mM C_{14}DMAO (a viscosity higher than 1000 mPas is considered to be 1000 mPas on the graph), where polymer molecules associated with surfactants. With further increasing C_{14} DMAO concentration, the viscosities decreased, and the solution became dilute. Only hydrophobe association predominated in this system.

Influence of added surfactants on the elastic properties of the polymer solution

A typical parameter for polymer network elasticity is the storage modulus (G'). As shown in Figure 6, the addition of surfactants made the polymer solution more elastic. For CTAB, with the opposite charges of the polymer molecules, two effects promoted the polymer molecule association with CTAB; hydrophobic
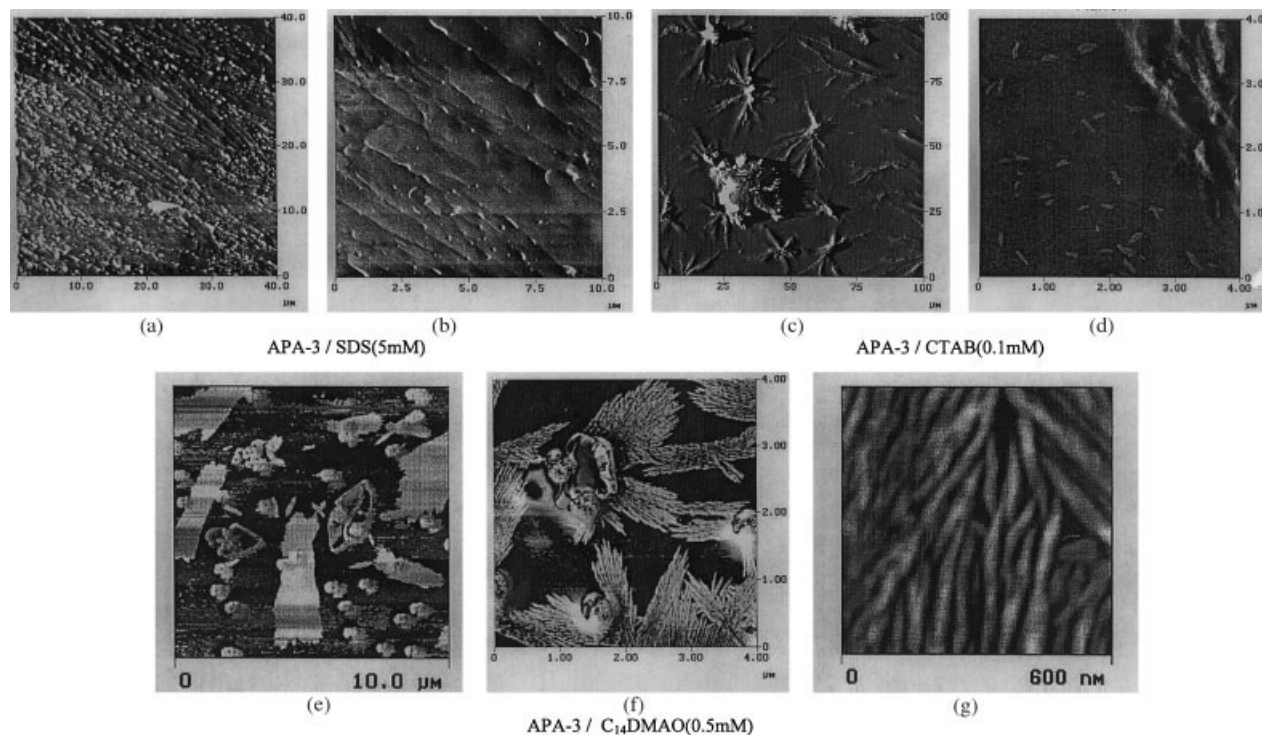
Figure 9 The supramolecular structure of APA-3 interaction with surfactants.

AFM measurement

The morphology of the polymer in surfactant solution was investigated by AFM. Figure 9 displays the supramolecular structure of the APA-3 interaction with the surfactant. For C_{14}DMAO [Fig. 9(e,f,g)], there were a lot of small string-like aggregations, and the diameter of the string was about 30–40 nm. The hydrophobic association between the polymer and the surfactant promoted the formation of the aggregations. For SDS [Fig. 9(a,b)], more large string-like aggregations were formed. The diameter of the string was about 1–2 um. For CTAB [Fig. 9(c,d)], there were a lot of flower-like aggregations, which may have been formed by the CTAB crystals and polymers. As shown in Figure 9(d), the polymer aggregations moved to the CTAB crystals because of the electrostatic attraction of the polymer and CTAB molecules.

and ionic associations. The polymer solutions were elastic ($G' < G''$). For SDS, with the same charges as the polymer molecules, the electrostatic repulsion caused the association to be weak, and the polymer solutions were less elastic ($G' < G''$). There only existed hydrophobic associations for C_{14}DMAO, and the association was still very strong at this concentration of DMAO.

Polymer surface tension measurements

Figure 7 displays the relationship of the surface tension and the polymer concentration of APA-3 in deionized water and 1.5% NaCl solution. Almost no change in the surface tension for the polymer solution suggested that the polymer micelles were formed in dilute solution, and the hydrophobic groups stuck inside the micelles. So, no surface activity of the polymer solution was observed.

Polymer/surfactant surface tension measurements

The surface tension curves for SDS and C_{14}DMAO in the presence and absence of the terpolymer are shown in Figure 8. For both the polymer–surfactant system and the surfactant alone, they showed the same trend for the surface tension–surfactant concentration relationship. The initial surface tension of APA-3 SDS was lower than that of the surfactant. This was especially true if the polymer was surface active.[2–9]

References

1. Jimenez-Regalado, F.; Selb, J.; Candau, F.; Langmuir 2000, 16, 8611.
2. Kästner, U.; Hoffmann, H.; Dönges, R.; Ehrler, R. Colloids Surf A 1994, 82, 279.
3. Tan, H.; Tam, K.C. Langmuir 2000, 16, 5600.
4. Ye, L.; Huang, R.; Wu, J.; Hoffmann, H. Colloid Polym Sci, in press.
5. Bromberg, L.; Temchenko, M.; Colby, R.H. Langmuir 2000, 16, 2609.
6. Zhang, K.; Xu, B.; Winnik, M.A.; Macdonald, P. M. J Phys Chem 1996, 100, 9834.
7. Nilsson, S.; Goldraich, M.; Lindman, B.; Talmon, Y. Langmuir 2000, 16, 6825.
8. Liu, T.; Xie, Y.; Liu, L.Z.; Chu, B. Langmuir 2000, 6, 7533.
9. Touhami, Y.; Rana, D.; Neale, G. H.; Hornof, V. Colloid Polym Sci 2001, 279, 297.