

# Hydrophobically Modified Polyelectrolytes: V. Interaction of Fluorocarbon Modified Poly(acrylic acid) with Various Added Surfactants

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The interactions between fluorocarbon-modified poly(sodium acrylate) and various kinds of added surfactants have been studied by means of viscometric measurement. Association behavior was found in both hydrogenated and fluorinated anionic, nonionic and cationic surfactants. Among them, the interactions between fluorocarbon-modified poly(sodium acrylate) and cationic surfactants are the strongest, owing to the cooperation of both electrostatic attractions and hydrophobic associations. The anionic surfactants have the weakest effects on the solution properties because of the existence of unfavorable electrostatic repulsion. The hydrophobic interactions between copolymers and fluorinated surfactants are much stronger than those between copolymers and hydrogenated surfactants.

**Keywords** Polyelectrolytes, interaction, surfactants, association, viscosity

## Introduction

Interactions between hydrophobically modified water-soluble polymers (HMWSP) and surfactants have received considerable attention in the last decades.<sup>1,2</sup> Bearing a small amount of hydrophobes on the hydrophilic backbone, these polymers form microdomains through inter- or intra-molecular hydrophobic association in aqueous media. When surfactants are added to the polymer solution, mixed micelle-like aggregates are usually formed by the absorption of the surfactant molecules onto the microdomains formed by aggregation of hy-

drophobes between the macromolecules. Thus the inter- or intra-molecular hydrophobic association can be enhanced or reduced upon addition of surfactant, which can be reflected by a significant viscosity enhancement or decrease. It is now generally accepted that the interaction between surfactants and hydrophobically modified polymers depends very much on the kinds and molecular structures of surfactants and polymers, the degree of hydrophobic modification, and the polymer concentration.

As one of the main kinds of the HMWSP, hydrophobically modified polyelectrolytes have invoked substantial interests due to their sensitivity to the pH value and the salt. Interactions between these polyelectrolytes and surfactants have also been studied widely. Although there have some researches on the interaction between cationic polyelectrolytes and anionic or cationic surfactants,<sup>3-15</sup> most of them were concerned on the interaction between anionic polyelectrolytes, such as poly(acrylic acid),<sup>6-8</sup> poly(maleic acid-co-alkylene) or poly(maleic acid-co-alkyl vinyl ether),<sup>10,11</sup> HASE,<sup>12,13</sup> (PEO-b-PPO-b-PEO)-g-PAA,<sup>14</sup> and anionic hydroxyethyl cellulose (HEC)<sup>15</sup>, with various kinds of anionic, nonionic and cationic surfactants. It is universally accepted that these polyelectrolytes interact strongly with oppositely charged surfactants due to the cooperation of both the electrostatic attractions and hydrophobic associations. Gel-like solutions are usually formed at certain ranges of surfactant concentrations. For the systems of

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polyelectrolytes and surfactants of the same charge, strong interactions can still be detected at a higher modification degree despite of the unfavorable electrostatic repulsion.

Till now, most studies have been devoted to the interactions between hydrocarbon-modified polyelectrolytes and conventional hydrogenated surfactants. However, only a few works have been reported on the interaction between fluorocarbon-modified water-soluble polymers and hydrogenated or fluorinated surfactants.<sup>3-5</sup> Since it is well known that fluorinated and hydrogenated surfactants do not mix ideally due to the mutual phobicity of fluorocarbon and hydrocarbon chains,<sup>16,17</sup> and the mixing of the two kinds of surfactants usually leads to a microphase separation with the coexistence of fluorocarbon rich and hydrocarbon rich micelles, the interaction between hydrogenated surfactants and fluorocarbon-modified polymers seems to be very interesting. Studies by Iliopoulos *et al.*<sup>5</sup> showed that highly modified poly(sodium acrylate) interacts with both fluorinated and hydrogenated surfactants, but the weakly modified polymers associate more selectively with surfactants of the same chemical nature. In this paper we extended the studies to the interactions of various kinds of surfactants (hydrogenated or fluorinated anionic, nonionic and cationic surfactants) on the solution viscosity of fluorocarbon modified hydrophobically modified poly(acrylic acid).

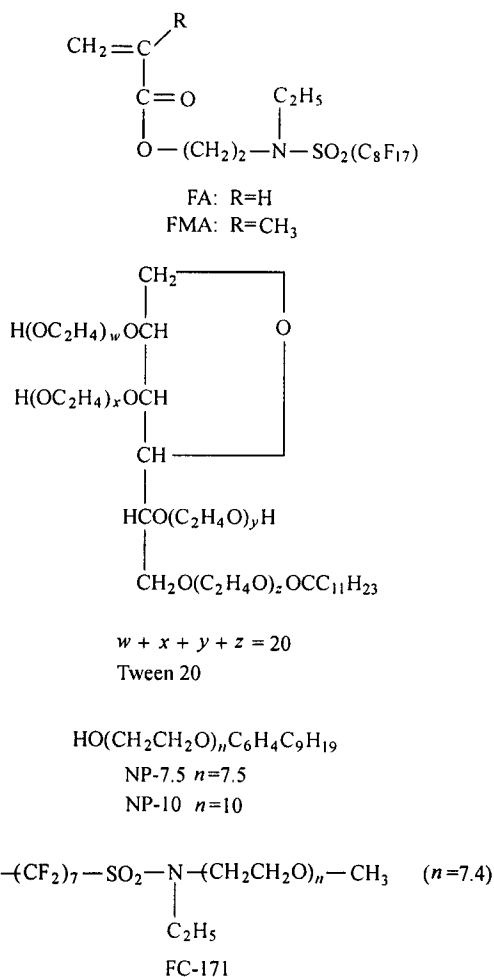
## Experimental

### Materials

The fluorocarbon-containing hydrophobically modified poly(acrylic acid) was synthesized via precipitation copolymerization of acrylic acid with hydrophobic comonomer (FA and FMA) (Scheme 1) in benzene, details of the synthesis of which was described previously.<sup>18</sup> The copolymers are represented as FA or FMA followed with a number, the one hundredth of which represents the mole feed of the hydrophobic comonomer. For example, FA-50 means FA was used as the hydrophobic comonomer, and its feed was 0.5 mol%. Sodium dodecyl sulfate (SDS) is obtained from Palekao, P. T. Cetyltrimethylammonium bromide (CTAB) is obtained from Chemical Research Institute of Jiling. FC-143 (Ammonium perfluorooctanoate) and FC-171 (noionic fluorocarbon-containing surfactant) are used as products

from 3M Co. Polyoxyethylene sorbitan monolaurate (Tween 20) and polyethylene glycol mono-*p*-nonylphenyl ether ( $n = 7.5$ ,  $n = 10$ ) are kindly donated by TCL Co. Molecular structures of these surfactants are also shown in Scheme 1.

**Scheme 1** Structures of perfluorocarbon comonomers and some surfactants



### Characterization

Viscometric measurements were performed on a Brookfield viscometer at 25°C. The copolymer-CTAB systems were prepared by mixing copolymer solutions with different CTAB concentrations. Mixtures of copolymers and other surfactants were obtained just by adding the surfactants into the copolymer solutions. All viscosity values reported in this paper are given for a shear rate of 0.4 s<sup>-1</sup> at 25°C.

## Results and discussion

### Effect of anionic surfactants

Fig. 1 shows the effect of SDS on the solution viscosity of the copolymers. It can be seen that both the polymer concentration and the degree of hydrophobic modification have influences on the solution viscosity of polymer-SDS systems. For the sample FA-200, the addition of SDS decreases the solution viscosity continuously at the concentration of 1.0 wt%, but a viscosity increase is observed at the concentration of 2.0 wt%. This result shows that a critical polymer concentration is needed to form efficient intermolecular associations. For the sample of low modification degree (FA-50), the viscosity decreases continuously at 2.0 wt% of the polymer concentration, which means that the sufficient intermolecular associations can not be formed due to the lack of hydrophobes. For the solution of 2.0 wt% FA-200, it can be seen that the viscosity reaches a maximum at the SDS concentration of ca. 0.1 wt%, which is  $0.4 \times CMC$  (the  $CMC$  of SDS is  $8.7 \times 10^{-3}$  mol/L, namely 0.25 wt%<sup>19</sup>). Similar result was reported by Iliopoulos *et al.*<sup>6</sup> on hydrocarbon modified poly(sodium acrylate), where the viscosity maximum appeared at the SDS concentration close to  $0.3 \times CMC$ . At this concentration range, sufficient SDS molecules were assembled around the fluorocarbon units and enhanced the intermolecular association and at the same time the co-micelles were not enough to dissociate the intermolecular association. As more surfactant was added, perfect micelle formed which "solve" the hydrophobic units and destroyed the inter-

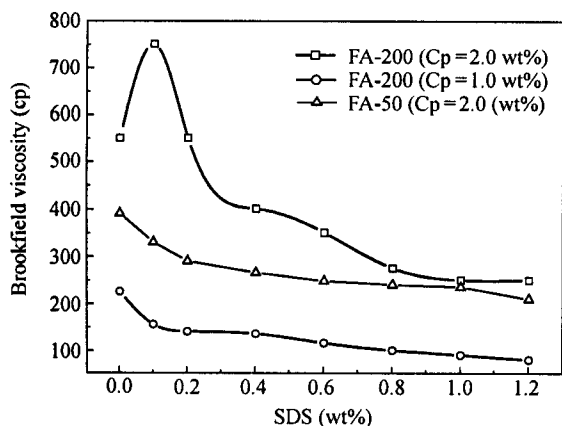


Fig. 1 Effect of SDS on the Brookfield viscosity of copolymers.

molecular association. Thus the viscosity decreased dramatically.

Fig. 2 presents the effect of FC-143 on the solution viscosity of fluorocarbon modified polymers with different modification degree. Compared to Fig. 1, it can be seen that both FC-143 and SDS have similar effects on the solution viscosity. However, since FC-143 is an anionic surfactant having a perfluorocarbon hydrophobic tail, it can be expected that the hydrophobic interactions of FC-143 with fluorocarbon modified copolymers are much stronger than those of SDS. For instance, the solution viscosity of 1.5 wt% FMA-100 increases from 220 cp to 3400 cp upon the FC-143 concentration increasing from 0.4 wt% to 0.6 wt%. And the solution viscosity of 1.0 wt% FA-200 reaches a maximum of 700 cp under FC143, but no viscosity enhancement is found under SDS (as shown in Fig. 1). Also similar to that of SDS system, the viscosity maximum appears at the FC-143 concentration range of  $(0.5-0.7) \times CMC$  (the  $CMC$  of FC-143 is 0.027 mol/L, namely 1.22 wt%<sup>20</sup>). The effect of FC-143 strongly relies on the polymer concentration and the degree of modification. As shown in Fig. 2, the addition of FC-143 decreases the solution viscosity continuously when the polymer concentration is low, and the polymer concentration needed for the enhancement in solution viscosity becomes lower as the degree of hydrophobic modification is increased.

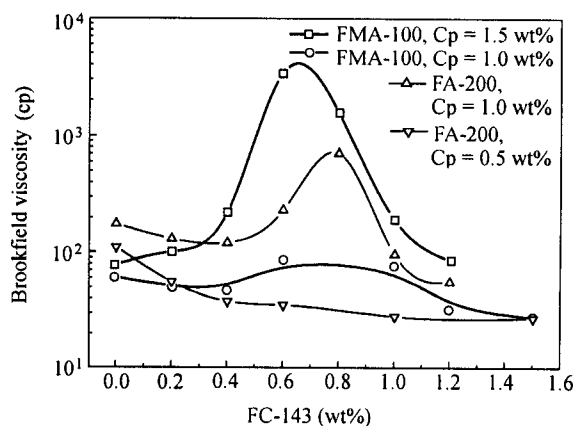


Fig. 2 Effect of FC-143 on the Brookfield viscosity of copolymers.

The following mechanism is generally represented and can be used to interpret the interaction between surfactant and hydrophobically modified polymers:<sup>21-23</sup> At surfactant concentration considerably lower than its criti-

cal micelle concentration ( $CMC$ ), the surfactant molecules absorb onto the polymer backbone due to the inducement of hydrophobic moieties along the polymeric chains. Mixed micelle-like clusters begin to form and associate with each other as more surfactant is added into the solution. At low polymer concentration, intramolecular associations dominate, which lead to the collapse of the polymer coils and therefore the decrease in solution viscosity. At high polymer concentration, however, intermolecular association tends to form a three-dimensional network, which results in the sharp increase in solution viscosity. At surfactant concentrations close to its  $CMC$  (for example  $0.4-0.7 \times CMC$ ), perfect micelles begin to form which "solubilize" the hydrophobic moieties attached on the polymer backbone. As a consequence, intermolecular hydrophobic associations are destroyed, resulting in a dramatically decrease in solution viscosity. With further addition of surfactant, only few changes in viscosity are detected.

#### Effect of nonionic surfactant

Two types of nonionic hydrogenated surfactants (Tween and NP) were added to the copolymer solution and their effects on the solution viscosity were studied (shown in Fig. 3 and Fig. 4). Interactions are found weak in copolymer-Tween systems, which may be related to the large hydrophilic groups in the molecules of Tween. Both NP-10 and NP-7.5 have stronger effects on the solution viscosity than Tween 20. Viscosity enhancement can be achieved at lower polymer concentration compared with copolymer-Tween system. Upon initially addition of NP-10 and NP-7.5, the solution viscosity increases sharply and then decreases. As more surfactants are added, different phenomenon appears: for the copolymer-NP-10 system, the viscosity decreases continuously to the starting value; however, the viscosity increases gradually again for NP-7.5. It should be noted that NP-7.5 has stronger effect on the solution viscosity than NP-10. This phenomenon is also observed in other reports<sup>7,9</sup> and is believed to be related with the size of the micelles and their dependence on surfactant concentration.<sup>7</sup>

Although FC-171 is a fluorocarbon containing nonionic surfactant, which has an ethoxylated number very similar to NP-7.5, it is a much better viscosifier to the copolymer solution studied. As shown in Fig. 5, the so-

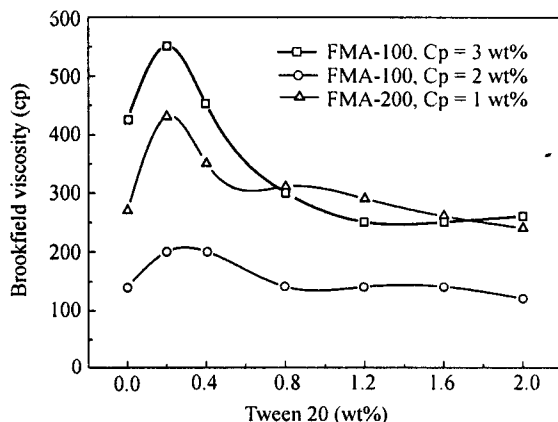


Fig. 3 Effect of Tween 20 on the Brookfield viscosity of copolymers.

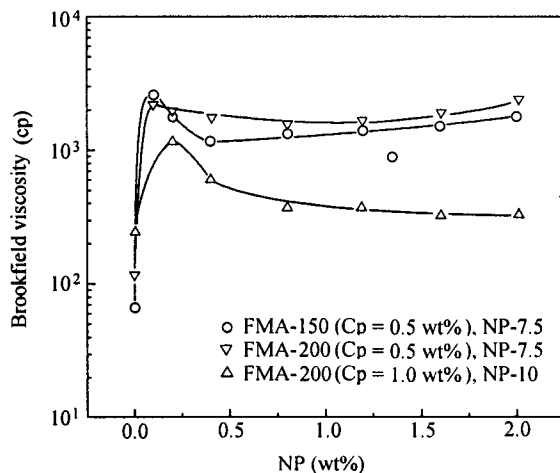


Fig. 4 Effect of NP on the solution viscosity of copolymers.

lution viscosity increases continuously with the addition of FC-171 to a very large value, and finally the solutions become gel-like solutions. Taking FMA-100 for example, the solution without any FC-171 has a viscosity of 45 cp, while in 1.2 wt% FC-171 solution the viscosity reaches 13200 cp. As the FC-171 concentration increases to 2.0 wt%, the solution viscosity is 18200 cp, which is around 400 times the starting value. The enhancement in viscosity can be ascribed to the strong interactions between FC-171 and fluorocarbon-containing polymers and the formation of three-dimensional networks. Upon imposing a shear force, the networks can be disrupted and thus reduce the solution viscosity sharply. As shown in Fig. 6, the FC-171-polymer sys-

tems show strong pseudoplastic behavior, which is in accordance with the assumption of the disruption of the networks. Unlike other surfactants, the viscosity of the FC-171-polymer systems does not show a maximum with increasing the concentration of FC-171. It seems to follow another mechanism that is different from the usual one.

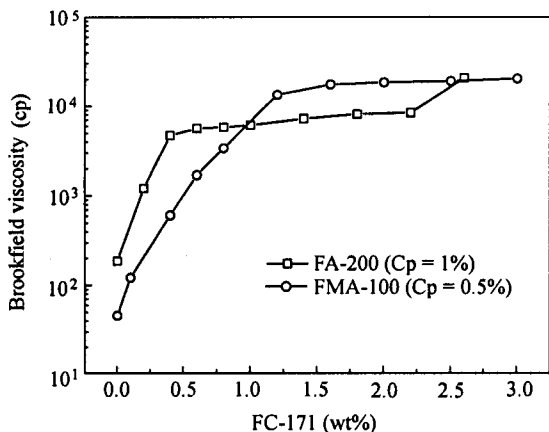


Fig. 5 Effect of FC-171 on the Brookfield viscosity of copolymers.

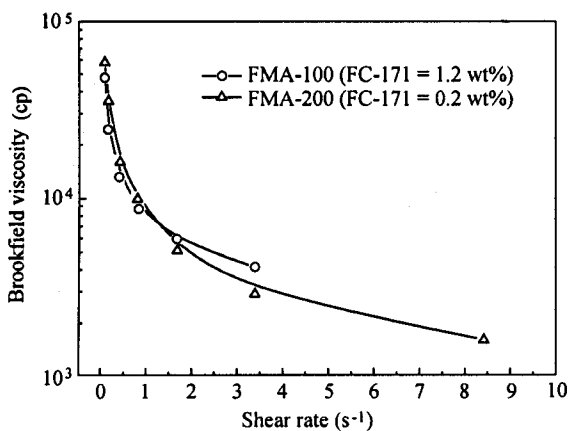


Fig. 6 Effect of shear rate on the Brookfield viscosity of copolymer at the polymer concentration of 0.5 wt%.

#### Effect of cationic surfactant

Besides the hydrophobic interactions, strong electrostatic attractions exist between cationic surfactant molecules and anionic polyelectrolytes. Thus, the addition of cationic surfactants can enhance the solution viscosity very sharply. As shown in Fig. 7, the solution viscosity starts to increase at the CTAB concentration of

$5 \times 10^{-4}$  mol/L, which is nearly one half of the CMC ( $9.2 \times 10^{-4}$  mol/L). After that, the viscosity increases dramatically until gel-like solution forms. Even small precipitates appear while mixing the polymer solution with high concentration of CTAB solution. As more CTAB is added, the viscosity drops sharply at the CTAB concentration of 0.12 mol/L. This result is quite similar to that of Iliopoulos *et al.*<sup>8</sup> on HMPA-DTAB system. But the surfactant concentration, at which the viscosity decreases, is almost one magnitude higher than that reported by Iliopoulos, which was about 0.025 mol/L. Since CTAB have a smaller CMC than DTAB, according to Iliopoulos,<sup>8</sup> this may be due to the poorer cooperativity of the binding process of CTAB to FMA-200.

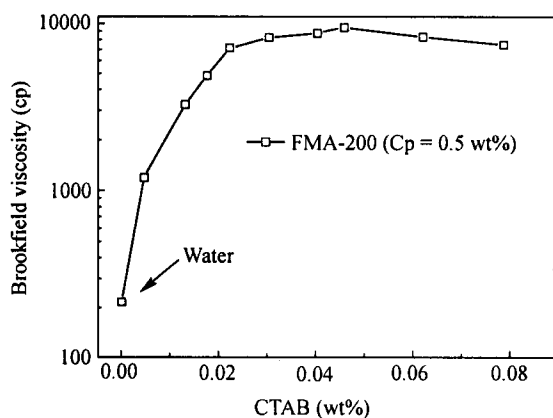


Fig. 7 Effect of CTAB on the solution viscosity of the copolymer.

#### Conclusions

The results mentioned above show that both hydrogenated and fluorinated surfactants form associations with fluorocarbon-modified poly(acrylic acid). The fluorinated surfactants have stronger interactions with copolymer than hydrogenated surfactants. Among all the surfactants studied, anionic surfactants have the weakest influences on the solution viscosity, depending on the polymer concentration. Intramolecular associations dominate at low polymer concentration, which reduce the solution viscosity. At higher polymer concentration, however, intermolecular associations play an important role in enhancing viscosity. Cationic surfactant has the strongest effect on the solution viscosity of copolymers because of the additional strong electrostatic attractions between carboxyl and ammonium groups. The effects of nonionic surfac-

tants are quite different from the other two kinds of surfactants, which are related to the volume of hydrophilic groups, the degree of ethoxylation ( $n$ ) and the type of hydrophobes.

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