Polymer–Surfactant Interactions in Graft Copolymer Solutions

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SYNOPSIS

Graft copolymers composed of water-soluble cellulosic backbones and > 0.4% (by weight) alkyl grafts are insoluble in water but soluble in surfactant solutions. Studies of the bulk viscosity and stability of polymer–surfactant solutions at 49°C indicate that the mechanism for solubilization of the polymer is the incorporation of the alkyl side chains into surfactant micelles. The tendency for side chains to combine with micelles appears to depend at least in part on the geometry of the surfactant tail group such that surfactants containing straight-chain tail groups solubilize alkyl side chains more readily than olefinic surfactants. The presence of small solutes near the surface of the micelle also inhibits incorporation of side chains from the polymer. Unsolubilized side chains remain in the aqueous phase of the solution, where they form thermally unstable intermolecular aggregates.

INTRODUCTION

Surface-active graft copolymers, that is, graft copolymers whose backbone and side-chain groups differ significantly with respect to their chemical structure and hydrophobicity, are of value as thickening agents and stabilizers for aqueous dispersions because of their ability to associate simultaneously with the dispersed and continuous phases. The specific interactions that occur depend on the structure of the polymer and the nature of the nonaqueous dispersed phase. For example, if the dispersed phase is a solid, such as latex particles, hydrophobic groups on the polymer will adsorb onto the surface of the solid, leaving the hydrophilic moiety solubilized in the continuous phase. If the dispersed phase is a liquid, however, such as emulsion droplets or surfactant micelles, the mechanism for interaction is less straightforward. It is known[1-4] that micelles adsorb onto the backbone of some water-soluble polymers. It has also been shown[5] that hydrophobic side chains provide a nucleation site for adsorption of micelles to polymers whose backbones do not interact with the surfactant. However, not all surfactants are equally compatible with surface-active graft copolymers.

Because of their ability to associate with a dispersed phase, surface-active graft copolymers are of interest as thickeners in applications such as shampoos and liquid detergents where high concentrations of surfactant are required. Therefore, it is important to understand the specific interactions that influence polymer–surfactant compatibility in these systems. The present study is a first effort toward that goal. We report the results of an investigation of the bulk solution properties of one type of surface-active graft copolymer in two different anionic surfactants and a zwitterionic surfactant under different conditions. Surfactant levels comparable to those found in commercial shampoo formulations were used, with polymer levels sufficient to bring the system viscosity within a practical range for these applications. The viscosity and viscosity stability of the solutions varied with solution composition. This was attributed to differences in the surfactant structure.

MATERIALS AND METHODS

The surface-active graft copolymer used in this study is hydrophobically modified hydroxyethyl cellulose (HMHEC) (trade name Natrosol Plus, Aqualon Co., Wilmington, DE). Its backbone is hydroxyethyl cellulose (HEC), a nonionic water-soluble cellulose ether. Alkyl side chains 12 or 16 carbons in length are grafted at random sites along the backbone, rendering the polymer insoluble in water.[6] Six different HMHECs, with the alkyl content ranging from 0.8 to 1.4% by weight, were studied. The control material was unmodified Natrosol 250HR hydroxyethyl cellulose (HEC) (Aqualon Co., Wilmington, DE). The HMHEC was used at two molecular weight levels: "low" (∼ 300,000 daltons) and "high" (∼ 400,000 daltons). The molecular weight of the control polymer was ∼ 400,000 daltons.

Ammonium lauryl sulfate (ALS) and sodium α-olefin sulfonate (AOS) (Stepan Chemical Co., Northfield IL), commercial names Stepanol AM and Bio Terge AS-40, respectively, were used as received at a level of 10% actives by weight. This level is two to three orders of magnitude greater than the critical micelle concentration of each surfactant and is comparable to that found in commercial shampoo formulations. The zwitterionic surfactant employed in this study was Miranol HS lauroamphopropyl-sulfonate (Miranol Chemical Co., South Brunswick (Dayton), NJ). It is a sulfonated imidazoline derivative containing both sulfonate and quarternary ammonium groups. It was used at a level of 20%

actives by weight. Organic salts and other additives were reagent grade.

The HMHEC–surfactant solutions were prepared by slowly stirring polymer into water containing the desired amount of surfactant and 0.05% w/w Dowicil 200 preservative (Dow Chemical Co., Midland, MI) and stirring at moderate speed for at least 12 h at room temperature. After this initial step the solutions were not stirred further. Solutions were covered and heat aged at 49°C in a forced convection oven, and the viscosity of each solution was measured at 1-week intervals. All viscosities were measured at room temperature. Polymer levels were selected to bring the viscosity into the range 200–5000 cP, a practical range for the applications of interest.

The bulk viscosity of polymer–surfactant solutions was measured using a Brookfield LVT-type viscometer. Size exclusion chromatography (SEC) was carried out using methanol–water as the carrier solution.[7]

RESULTS AND DISCUSSION

Typical viscosity-vs.-time profiles for 1% (w/w) HMHEC–surfactant solutions and HEC–water solutions during heat aging at 49°C are shown in Figure 1. The solutions exhibit a steep drop in viscosity during the first week of heat aging followed by a more gradual but still significant viscosity loss with time. The SEC and intrinsic viscosity measurements showed no change in molecular weight of either
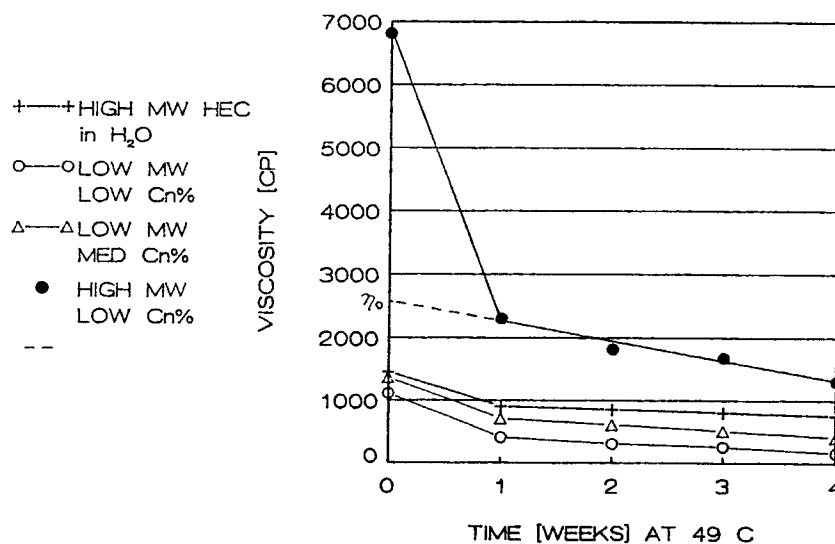

Figure 1 Typical viscosity profiles of 1% (w/w) HMHEC–surfactant solutions.

modified or unmodified HEC during heat aging. Thus the initial steep drop reflects a characteristic hydration time t_{hyd} of the cellulosic moiety common to both types of polymers, while the long-time decay of the viscosity may be attributed to rearrangement of the polymer chains and/or breakup of entanglements over time. Two parameters of the viscosity-vs.-time profile were used to characterize the behavior of polymer-surfactant solutions. These are the initial viscosity η_0, defined as the extrapolated intercept of the function viscosity vs. time measured at long times (> 1 week), and the viscosity stability S, defined as the decay rate of the viscosity (in centipoises per week) at long times normalized by η_0.

The results on the anionic and zwitterionic surfactants will be presented separately. The former demonstrate the effect of the surfactant tail group structure on HMHEC-surfactant interactions, while the latter showed the effect of small solutes solubilized near the surface of the micelle.

Anionic Surfactant Studies: Effect of Surfactant Tail Group Structure on HMHEC–Surfactant Interactions

Figures 2 and 3 show the effect of polymer concentration on η_0 for ALS and AOS solutions, respectively. Closed symbols represent high MW polymers and open symbols represent low MW polymers, while the different shaped symbols in each group correspond to polymers with different levels or length of side chains. As expected, the initial viscosity of HMHEC-surfactant solutions goes up with molecular weight of the polymer, side chain content for a given molecular weight, and total polymer concentration. This is true in all of the surfactants studied. However, the initial viscosity of HMHEC solutions is 2.9 ± 0.9 times higher in AOS than in ALS, while the reverse trend is seen with HEC solutions, which are 1.5 times more viscous in ALS than in AOS. Also note that high molecular weight HEC has initial viscosities η_0 comparable to those of high molecular weight HMHEC in ALS (Fig. 2) but low molecular weight HMHEC in AOS (Fig. 3). This suggests that the polymer side chains play a significant role in viscosity building of HMHEC–AOS solutions while in ALS the hydrophobes are inactive. The stability of HMHEC in both surfactants ranged from 4 to 10% viscosity loss per week. The control polymer stability depended strongly on surfactant: 1% (w/w) solutions of HEC in AOS exhibited an average viscosity loss of 20% per week, pointing to poor compatibility of the backbone with the surfactant, while 1% (w/w) HEC in ALS decayed only an average of 4% per week, which is comparable to the viscosity loss of HEC in water. The initial viscosity of 1% HEC solutions was 2900, 1900, and 1000 cP in ALS, AOS, and water, respectively.

The addition of 2% (w/w) ethanol to these solutions affects the initial viscosity, as summarized in Table I. Averages are given for the six different HMHECs studied. In AOS, ethanol has no effect on HEC solution viscosity while HMHEC solution viscosities decrease by an average of 31%. In contrast, the effect of 2% ethanol on ALS solutions was to increase the solution viscosity by an average of 133%
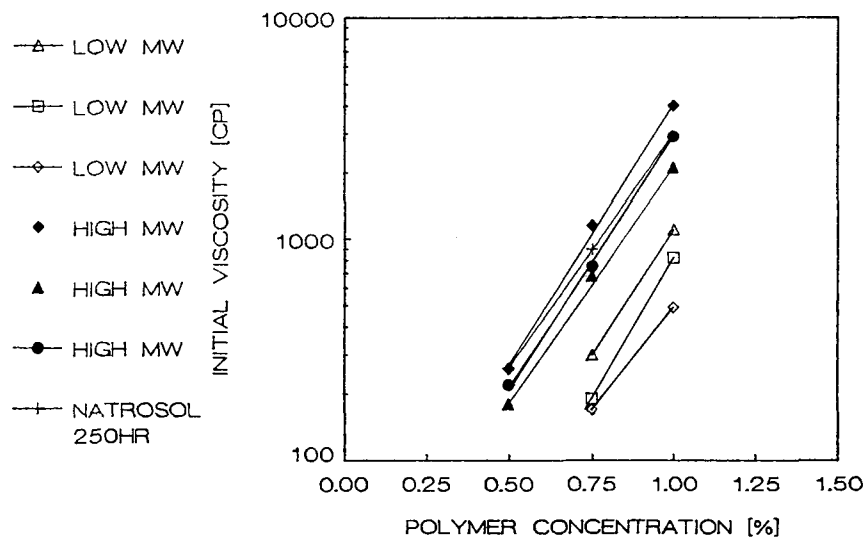
Figure 2 Effect of polymer structure and concentration on HMHEC solution initial viscosity in 10% ALS.
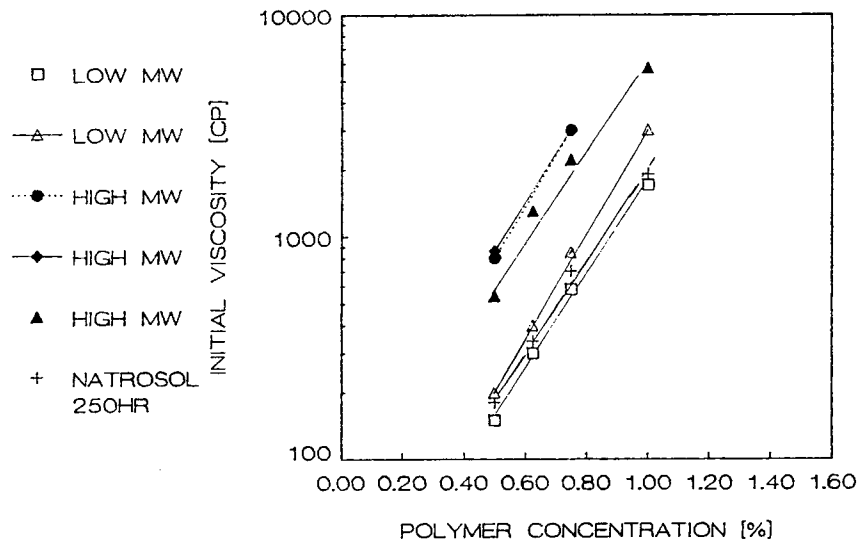
Figure 3 Effect of polymer structure and concentration on HMHEC solution initial viscosity in AOS.

(after elimination of one spurious point in which the viscosity increased by only 10%). Moreover, the control polymer also exhibited a 22% increase in viscosity in ALS with ethanol. Ethanol had no effect on the viscosity of 1% HEC solutions in water.

These results may be explained in terms of interactions involving the polymer side chains in the solutions as follows. The hydrophobic side chains on HMHEC are incompatible with water and hence will be driven to aggregate with other nonhydrogen bonding components in the solution. There are three types of hydrophobic interactions that may result. These are intermolecular hydrophobic interactions [Fig. 4(a)], where side chains from more than one polymer molecule associate into aggregates; intramolecular hydrophobic interactions [Fig. 4(b)], involving more than one side chain from the same polymer molecule; and polymer–micelle interactions [Fig. 4(c)], in which side chains become incorporated into surfactant micelles or micellelike aggregates. Each of these interactions has a distinct effect on the viscosity and viscosity stability of HMHEC–surfactant solutions. Intermolecular hydrophobic interactions will give rise to solutions with a rela-

Table I Effect of 2% Ethanol on Viscosity of Polymer–Surfactant Solutions

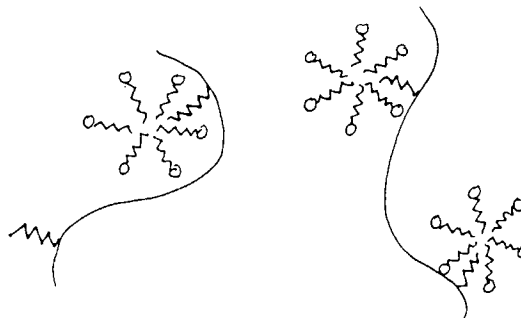| Polymer	ALS	AOS
HEC	+22%	−2%
HMHEC	+133 ± 33% (N = 5)	−31 ± 16% (N = 5)

TYPES OF HYDROPHOBIC INTERACTIONS

I. INTERMOLECULAR

II. INTRAMOLECULAR
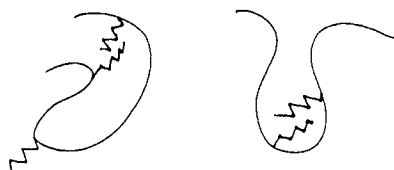
III. POLYMER-SURFACTANT

Figure 4 Types of hydrophobic interactions: (a) intermolecular, (b) intramolecular, and (c) polymer–surfactant.

tively high viscosity by acting act as pseudocrosslinks between polymer chains. However, these interactions are expected to be unstable to the thermal motion of the polymer chains during heat aging. Intramolecular interactions can form only when the backbone of the polymer assumes a highly coiled configuration, bringing the side chains close together. This gives rise to a relatively low-bulk viscosity because of the associated low radius of gyration of the polymer. Polymer–micelle interactions involving HMHEC allow the polymer to behave like HEC in aqueous solution because the contribution of aqueous phase hydrophobes to the solution viscosity is eliminated. These interactions should be stable to heat aging due to the relative stability of the micelles themselves, provided that the complexes do not involve side chains from more than one polymer molecule. The extent to which the straight-chain side chains can penetrate the micelle, or in other words, the proportion of side chains that actually do become involved in these complexes, depends on the structure of the surfactant. We can now examine the data presented in the preceding in light of this picture.

All of the HMHEC polymers studied here are insoluble in water but form clear, macroscopically homogeneous solutions in all the surfactants studied. Thus it is clear that some polymer–micelle complexes form in all cases. However, HMHEC behaves like the control polymer in ALS but produces much higher viscosities than controls in AOS. We conclude that in ALS the high viscosity of the polymer solutions can be attributed primarily to the contribution of the HEC backbone of the polymer, which is water soluble. In AOS, the water-insoluble side chains on the polymer also contribute to the bulk viscosity of the solution via intermolecular hydrophobic interactions in the aqueous phase. Such interactions have also been documented in poly-(methacrylic acid)[8] and were shown to be broken down by ethanol.[9] Ethanol disrupts aqueous phase hydrophobic interactions, which accounts for the observed decrease in the viscosity of HMHEC–AOS solutions on addition of ethanol. It is also clear that the observed increase in viscosity of HMHEC–ALS solutions with ethanol must be due to some effect of the ethanol on the surfactant rather than the polymer, since the HMHEC contributes to high viscosity via intermolecular hydrophobic interactions that cannot persist in the presence of EtOH. Ethanol at high concentrations such as that used here is known to increase the critical micelle concentration of surfactants by "breaking" the structure of water,

thereby increasing the solubility of non-hydrogen-bonding material.[10] This creates a relatively oily aqueous phase with the expected higher viscosity. Of the two surfactants discussed here, ALS is the less hydrophobic and would therefore be more soluble in the aqueous ethanol than AOS.

These results indicate that the tendency for straight-chain alkyl side chains on the HMHEC to become incorporated into surfactant micelles depends at least in part on the structure of the surfactant tail group. The ALS has a linear tail group, and the linear polymer side chains are highly soluble in ALS micelles. On the other hand, AOS has a double bond in the tail group near the micellar surface. This "kink" appears to restrict the passage of straight-chain polymer side chains into the center of the micelles, forcing a greater proportion of them to remain in the aqueous phase, where they interact intermolecularly to form a high-viscosity solution that may be broken down by ethanol.

Zwitterionic Surfactant Studies: Effect of Small Solutes on HMHEC–Surfactant Interactions

The effects of monomeric solutes on HMHEC–surfactant interactions were investigated using a zwitterionic surfactant and the experimental techniques described in the preceding. The specific solutes investigated were the pH 7 sodium salts of tartaric, citric, and fumaric acids. All three are dibasic at pH 7 but have different solubilities in water due to the differences in their structure. The water solubilities of the salts, in mmoles per gram of water, are 9.33, 3.07, and 0.0543 for sodium tartrate, sodium citrate, and sodium fumarate, respectively.[11] The salts will partition into the micelles to a degree that is inversely proportional to their solubility in water and will remain near the surface of the micelles due to their charge. The isoelectric point (P_I) of the surfactant was determined by simultaneous conductimetric and potentiometric titration to be pH 5.45, the point of minimum conductance of the solution. This is in very good agreement with the calculated value of 5.57 determined by averaging the pK_a's of all the charged species on the molecule.

Solutions for this part of the study were composed of 20% surfactant and 1% (w/w) high molecular weight water-insoluble HMHEC, adjusted to pH 7 with HCl. The organic salts used here have no effect on the water solubility of the HMHEC. The HEC is not soluble in this surfactant. The initial viscosity of the HMHEC–Miranol HS solutions was 1200 ± 100 cP and exhibited no clear trend with organic
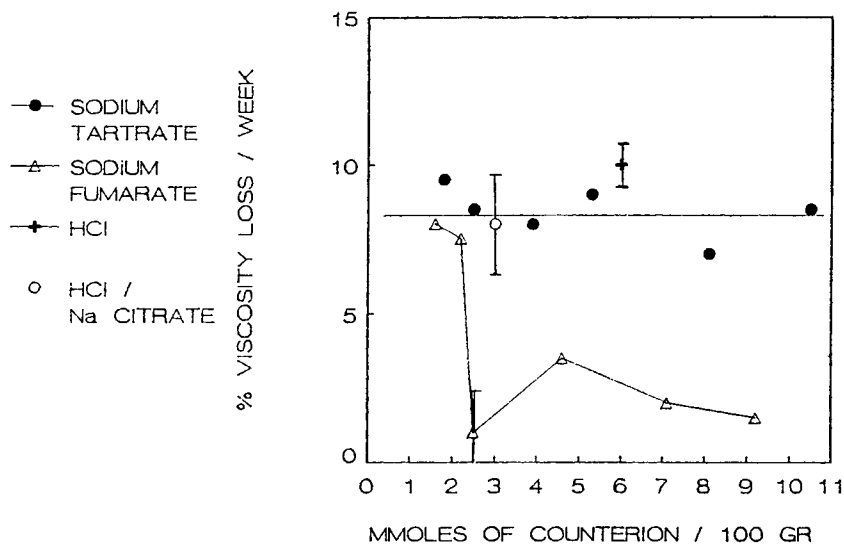
Figure 5   Effect of solute on viscosity stability of 1% (w/w) HMHEC–Miranol HS solutions.

salt concentration. However, the stability results are very solute dependent.

The effect of tartrate and fumarate ion on the viscosity stability of 1% (w/w) HMHEC–surfactant solutions is shown in Figure 5. Over the range 0.018–0.15 M added tartrate, the solution viscosities drop $\sim$ 8% per week on the average. This stability value was also observed with no tartrate (adjusted to pH 7 with 0.06 M HCl) and with solutions adjusted to pH 7 using citric acid (corresponding to 0.03 M solute). With fumarate, on the other hand, increasing the solute concentration above its saturation level in water results in the solution viscosity becoming more stable, eventually reaching a level of only 1% viscosity loss per week.

Based on our assumption that the most stable of the interactions shown in Figure 4 are the side chain–micelle complexes, these results indicate that the presence of small hydrophobic solutes solubilized near the surface of the surfactant micelle enhances complex formation. This may occur in two possible ways. First, the solute itself can act as a spacer between surfactant molecules in the micelle, facilitating passage of the polymer side chains into the micelle center. Second, the carboxylate ions will repel the neighboring sulfate ions, driving the head groups apart. Again, this widens the channels through which the side chains must pass to become incorporated into the micelle. Both of these effects appear likely to contribute. Preliminary results with dodecanol as a cosurfactant suggest that a spacer between surfactant molecules does enhance side chain

solubility. We have also shown[12] that the stability of HMHEC solutions in this zwitterionic surfactant is strongly pH dependent, indicating that a high micelle charge density promotes complex formation. Additional experiments with small nonionic hydrophobic solutes would permit the estimation of the relative importance of these two effects on polymer–micelle interactions.

CONCLUSIONS

The bulk viscosity and viscosity stability of HMHEC–surfactant solutions may be manipulated by the appropriate choice of surfactant. Surfactants with linear tail groups permit penetration of the alkyl polymer side chains into the micelle, giving rise to a relatively low initial viscosity. Polymer–surfactant compatibility is also promoted by the presence of small solutes near the surface of the micelle, which have the effect of separating the head groups, thereby opening channels through which alkyl side chains may enter the interior of the micelle. This property may be used to optimize the stability of HMHEC–surfactant solutions.

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