Interactions between Hydrophobically Modified Polymers and Surfactants: A Fluorescence Study

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Interactions between hydrophobically modified polymers (hm-polymers) and surfactants were investigated by steady-state fluorescence as well as rheological experiments. Hydrophobically modified hydroxyethylcellulose (hmHEC) with C_{16} hydrophobe grafts of 0.9% mole along with tetradecyltrimethylammonium bromide and cetyltrimethylammonium bromide were studied. The presence of C_{16}HEC induced the aggregation of surfactant micelles in aqueous solution at concentrations about one-half times lower than the critical micelle concentration. As surfactant is added, the viscosity of hm-polymer solution first increases due to the bridging of hydrophobe clusters by surfactant micelles to form mixed micelles and later decreases due to the masking of hydrophobes individually by excess micelles. Fluorescence quenching experiments showed that the number of hydrophobes (N_H) in a mixed micelle decreases steadily with increasing surfactant concentration due to hydrophobe dilution by the surfactant. N_H declines from greater than two with no surfactant to around two at the concentration where the viscosity reaches a maximum and eventually falls to one or below when hydrophobes are masked. The observations were explained in terms of the effective associating junctions and are consistent with the picture of interactions between hm-polymers and surfactants for polymers with stiff backbones and no intramolecular association.

Introduction

Interactions between water-soluble polymers and surfactants have been extensively studied as they are relevant in many industrial applications.[1] In aqueous solution, surfactant molecules aggregate to form spherical micelles at the critical micelle concentration (cmc).[2−4] The presence of polymers, whose backbones contain some degree of hydrophobicity, induce the aggregation of surfactant micelles onto the polymer chains at a concentration below the cmc, called the critical aggregation concentration (cac).[5−8]

Recently, intensive work has been focused on interactions between hydrophobically modified polymers and surfactants.[9−21] These systems are of great interest as viscosity modifiers in various applications, such as enhanced oil recovery and coatings.[22,24] Hydrophobically modified polymers (hm-polymers) are polymers which contain hydrophobic groups, or hydrophobes, which are attached either as grafts along the backbone or as end-groups.[22−24,26] The viscosity of an aqueous hm-polymer solution is increased through hydrophobic associations between hydrophobes from different polymer chains, forming micelle-like hydrophobe clusters and transient cross-links between the chains.[22−24] For hm-polymers in

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surfactant solutions, the hydrophobes induce a specific aggregation of surfactant micelles around the hydrophobe clusters to form mixed micelles at concentrations lower than the cac of unmodified polymers.[10,13,14,19,27−30] The bridging of hydrophobe clusters by spherical micelles leads to an increase in viscosity as surfactant is added.[9,11−13,15−20] However, at high surfactant concentrations, the hydrophobes are individually solubilized, or masked, by excess spherical micelles, resulting in the disruption of associations and a decrease in viscosity.[9,13,15,19]

Thus, the general picture of the interactions between hm-polymers and surfactants as a function of surfactant concentration is well accepted. The number of *intermolecular* associating sites between polymers controls the viscosity of the fluid. The addition of surfactant creates additional mixed micelles and redistributes the polymers' hydrophobes from *intramolecular* aggregates to *intermolecular* network-forming associating sites. Therefore, while the number of hydrophobes per mixed micelle decreases monotonically with the addition of surfactant, the viscosity increases.[19] At even higher surfactant concentrations, the number of micelles equals or exceeds the number of hydrophobes, and *intermolecular* associations are prevented by repulsive interactions between the micelles. Consequently, the viscosity decreases.

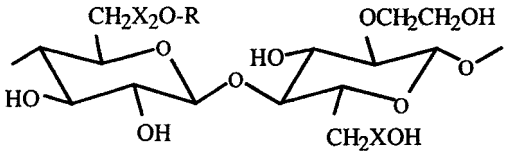
In this study, we looked at systems of hm-cellulosic polymers with a stiff backbone, in which intramolecular associations are minimized.[15] First, we measured the cac of surfactants with hm-polymers by performing steady-state fluorescence experiments and compared the results with those previously reported.[31,32] Then, we carried out quenching experiments to determine the aggregation numbers of hydrophobes and surfactants in a mixed micelle at various surfactant concentrations. These values were then correlated with rheological data to provide a more general picture of the interactions between hm-polymers and surfactants. They provide the first quantitative picture of the relationship between the stoichiometry of the hydrophobe/micelle interaction and rheology. For this system, the viscosity maximum occurs when the number of hydrophobes per mixed micelle is approximately two. This corresponds to the ideal network structure in which each junction point is an effective cross-link between two chains. The relatively high stiffness of the cellulosic backbone prevents significant *intramolecular* associations in contrast to more flexible polymer backbones such as acrylate backbones. In the previous study of hm-poly(sodium acrylate), Magny et al.[19] found on the order of 25 hydrophobes per micelle in the absence of surfactant and on the order of 12 hydrophobes per micelle at the viscosity maximum with added surfactant. For the flexible polymer chain, most hydrophobe interactions are elastically ineffective and form only *intramolecular* associations. This shows the important role of polymer backbone stiffness on the efficiency of hydrophobe utilization.

Experimental Section

Materials. Hydrophobically modified hydroxyethylcellulose (hmHEC) samples, along with a control unmodified HEC, were provided by Aqualon, Inc. (Wilmington, DE). The hydrophobe units are C_{16} linear alkanes at a substitution level of 0.9% mole, as shown below. The molecular weight of the unfunctionalized polymer is approximately 250,000, with an overlap concentration, c^*, of 0.2 wt %[33] and $[\eta] = 9.53 \times 10^{-3} M_w$ 0.87 mL/g.[34] The hydroxyethyl substitution level, "X", is about 2.5.[35]

R = H for HEC X = OCH_2CH_2

= $C_{16}H_{33}O$ for C_{16}HEC



Tetradecyltrimethylammonium bromide (TTAB) and cetyltrimethylammonium bromide (CTAB), both 99% pure, were obtained from Aldrich and recrystallized twice from 80:20 (v/v) acetone:methanol. Pyrene, 99% pure, and cetylpyridinium chloride (CPyCl), 98% pure, were purchased from Aldrich and recrystallized twice in ethanol and 50:50 (v/v) ethanol:ethyl acetate, respectively. CPyCl was used as a quencher for the pyrene probe, as previously used in EHEC and C_nTAB systems.[36]

The following stock solutions were made with deionized water: 1 wt % HEC, 1 wt % C_{16}HEC, 0.02 M TTAB, and 0.02 M CTAB. Solutions of 0.5 wt % C_{16}HEC (or HEC) and various surfactant concentrations (about 5−6 mL) were prepared from equal-weight dilutions of stock solutions. The mixtures were shaken gently and left standing for a few days to equilibrate. Solutions of 1.2×10^{-4} M pyrene in ethanol and 0.01 M CPyCl in water were prepared. In fluorescence experiments, about 10 μL of pyrene solution were added to 2000 μL of polymer/surfactant solution to yield a pyrene concentration of 6×10^{-7} M. For quenching experiments, about 3 to 8 μL of CPyCl solution, with the volume depending on the concentration of the pre-diluted solution, were added in series for three to five times to the sample. CPyCl concentrations were adjusted to be 0.5 to 2.5 times the micelle concentration, which was estimated by dividing the surfactant concentration by the aggregation number of free micelles (70 for TTAB and 90 for CTAB).[2]

Methods. *Fluorescence.* Steady-state fluorescence experiments were performed on an SPEX Fluorolog 1680 0.22 m double spectrometer. The excitation wavelength was 334 nm; the band-passes were set at ten and 1−2 nm for excitation and emission, respectively. About 2 mL of surfactant/polymer solution were placed in a 4-mL quartz cell, which was temperature-controlled at 30 °C. The pyrene spectrum was scanned at wavelengths from 350 to 400 nm, at an increment of 0.5 nm/s. Intensities, I_1 and I_3, were taken from the emission intensities at 373 and 384 nm, respectively. I_1 was also used to determine the aggregation numbers in quenching experiments.

Rheology. Viscosity measurements were made with the Rheometrics Fluid Spectrometer II (RFS2) from Rheometric Scientific, Inc. (Piscataway, NJ). A Couette ge-

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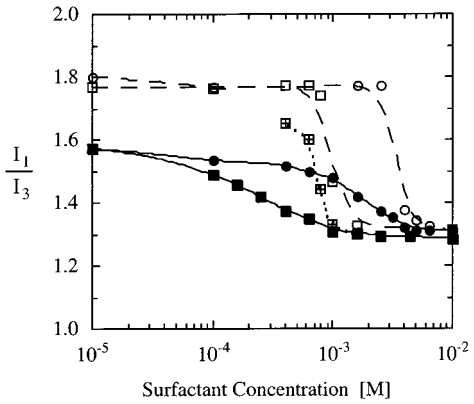

Figure 1. I_1/I_3 as a function of surfactant concentration for TTAB and CTAB solutions with no polymer (○, □; *dashed line*), 0.5 wt % HEC (none, ⊞; *dotted line*), and 0.5 wt % C_{16}HEC (●, ■; *solid line*) at 30 °C ($c_{pyrene} = 6 \times 10^{-7}$ M).

ometry was used for steady-shear testings, performed at 30 °C. The radii of the bob and cup were 16 and 17 mm (1-mm gap), and the length was 33.3 mm. The zero-shear viscosity readings were taken from the constant-viscosity (Newtonian) region at shear rates below 1 to 100 s^{-1}, depending on the surfactant concentration and type.[37]

Results and Discussion

Steady-state fluorescence measurements were performed to determine the cac of surfactants with hm-polymers, and fluorescence quenching was used to determine the numbers of hydrophobes and surfactants in each mixed micelle.

Critical Aggregation Concentration. Steady-state fluorescence is commonly performed to determine the onset of surfactant aggregation. The technique involves the use of a fluorescent probe, which prefers to be solubilized in hydrophobic domains.[31,32,38] For pyrene, the ratio of the intensities of the first and third vibrational peaks in the emission spectrum (I_1/I_3) can provide information about the solvent polarity.[39] This ratio shows a transition from around 1.8 in an aqueous environment to about 1.3 in a hydrophobic (micellar) environment in C_nTAB solution.[30] The onset of this transition has been used to determine the cmc of surfactants and the cac of polymer and surfactant systems.[31,38]

In Figure 1, I_1/I_3 values of TTAB and CTAB solutions, as a function of concentration are shown. The I_1/I_3 curves show a sharp transition at the cmc, which is around 4 mM for TTAB and 1 mM for CTAB, decreasing from 1.8 to 1.3 with increasing concentration. The steepness of the profiles indicates that the micellization process of pure surfactant is highly cooperative.[2]

The effect of unmodified HEC on the cmc of CTAB is given in Figure 1. With HEC, the I_1/I_3 profile of CTAB is shifted slightly to lower concentrations, with the new cac being slightly lower than the cmc, by about one-fifth. The depression of the cmc, which is seen in the shift in the transition along the surfactant concentration axis, is merely due to the decrease in the solvent polarity with the addition of HEC. This can be inferred from the lower I_1/I_3 values at low CTAB concentrations, rather than polymer-induced aggregation.[1] The transition at the cac remains steep and narrow, indicating that there is no interaction between HEC and CTAB, which was also evident in the viscosity data.[40] At high concentrations, the I_1/I_3 values of CTAB with HEC converge to those of pure CTAB as the probe resides in the same hydrophobic environment.

In Figure 1, I_1/I_3 values of TTAB and CTAB solutions as a function of concentration with semidilute C_{16}HEC are shown. For both surfactants, the I_1/I_3 profiles are shifted significantly to lower concentrations and become much broader than those of surfactants without hm-polymers. The presence of hydrophobes induces surfactant aggregation at a much lower concentration (cac) than the cmc. The transition also becomes more gradual and less cooperative, taking place over two concentration decades, as the micelles are nucleated on hydrophobes, which have a lower activation energy than nucleation of the micelle in solution.[19,30] For both surfactants, the I_1/I_3 values at low concentrations decrease considerably with the addition of hmHEC as the solvent becomes less polar. The I_1/I_3 values at high concentrations remain unchanged since pyrene is imbedded in the same micellar domain. The extent of cac reduction and the degree of cooperativity depend on the strength of interactions between surfactants and hm-polymers, which is a function of surfactant tail length.[15,20] A proportionately greater reduction in the cac from the cmc, by about one-half for TTAB and three-fifth for CTAB, is seen as the surfactant tail length is increased because of increasing hydrophobicity. This is analogous to the decrease in the cac observed with increasing hydrophobe length and content.[19] Likewise, the profiles become slightly less cooperative as the surfactant length and strength of interactions are increased.

Numbers of Hydrophobes and Surfactants in a Mixed Micelle. Steady-state fluorescence quenching experiments were used to determine the aggregation number of surfactant micelles. The technique involves the use of a quencher which inhibits the emission of a probe, such as *n*-alkylpyridinium chloride for pyrene.[31,38] Quenching occurs when quenchers randomly partition into the micelles containing the probes. The number of quenchers per micelle is small, about 0.5 to 2.5, and should not lead to a mixed-micelle effect.[2] By measuring the probe's emission intensity as a function of quencher concentration, [Q], the micelle concentration, [*M*], can be determined from the following equation by performing a linear regression

$$\ln\left(\frac{I_0}{I}\right) = \frac{[Q]}{[M]} \tag{1}$$

where I and I_0 are the intensities with and without a quencher, respectively.[41] The number of surfactants in a micelle, N_s, can be calculated from

$$N_S = \frac{[S] - cac}{[M]} \tag{2}$$

where [S] is the surfactant concentration.[31,38] This method is frequently used to determine the aggregation number of micelles in polymer and surfactant systems.[1,31,38] For hm-polymer and surfactant solutions, the number of hydrophobes per mixed micelle, N_H, can be determined from

$$N_H = \frac{[H]}{[M]} \tag{3}$$

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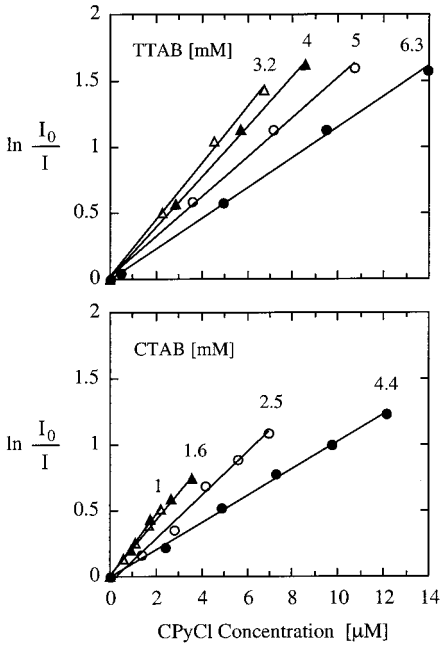

Figure 2. ln(I_0/I) as a function CPyCl concentration for TTAB (*top*) and CTAB (*bottom*) solutions of various surfactant concentrations with 0.5 wt % C_{16}HEC at 30 °C ($c_{pyrene} = 6 \times 10^{-7}$ M).

Table 1. Values for TTAB and CTAB Solutions with 0.5 wt % C_{16}HEC at 30 °C

[S][a] [mM]	[*M*] [b] [μM]	N_H [c]	N_S [d]
	[H][e] = 90 μM		
	TTAB (cac ~ 1.8 mM; cmc ≈ 4 mM)		
3.2	47	1.9	29
4	53	1.7	42
5	67	1.4	48
6.3	87	1.0	52
	CTAB (cac ~ 0.4 mM; cmc ≈ 1 mM)		
1	43	2.1	14
1.6	47	1.9	25
2.5	61	1.5	34
4.4	97	0.9	41

[a] Surfactant concentration. [b] Micelle concentration. [c] Number of hydrophobes in a mixed micelle. [d] Number of surfactants in a mixed micelle. [e] The molar concentration of hydrophobes is [H] = 90 μM.

where [H] is the hydrophobe concentration, assuming that all hydrophobes take part in intermolecular associations.[19,42]

In Figure 2, ln(I_0/I) is plotted versus CPyCl concentration for TTAB and CTAB solutions with C_{16}HEC at various surfactant concentrations. Viscosity data showed that the addition of CPyCl does not affect the associations between CTAB and C_{16}HEC.[37] At all surfactant concentrations, the quenching data are linear in CPyCl concentration. The slope that is obtained from least-squares fitting was used to calculate the micelle concentration, which is just the inverse of the slope (eq 1). The numbers of hydrophobes and surfactants per mixed micelle were calculated from the micelle concentration by using eqs 3 and 2, respectively. In Table 1, [*M*], N_H, and N_S are tabulated as a function of [S] at different TTAB and CTAB concentrations.

In Figure 3, N_H is plotted versus surfactant concentration for TTAB and CTAB in C_{16}HEC solutions. For both surfactants, the number of hydrophobes in a mixed micelle decreases roughly linearly, from around two to one, as the surfactant concentration is increased. Essentially, the decrease in N_H is due to the dilution of hydrophobes in each micelle by the added surfactant. The number of hydrophobes decreases faster with CTAB than with TTAB because of CTAB's lower cac. N_S is more difficult to determine than N_H because the cac is less well defined for the broad transition in I_1/I_3, which occurs around 1.8 mM for TTAB and 0.4 mM for CTAB, as shown in Figure 1. The cac is estimated to be at the onset of the viscosity increase (see Figure 4), as suggested by an earlier work.[19] With increasing surfactant concentration, the number of surfactants in each mixed micelle increases steadily from 30 to 50 for TTAB and from 15 to 40 for CTAB. These numbers are lower than the aggregation numbers of their respective free micelles, 70 for TTAB and 90 for CTAB.[2] It is possible that interactions with C_{16}HEC depress the number of surfactants in a mixed micelle, as seen in interactions between polymers and surfactants.[31] These results are similar to those reported for hydrogels of C_{12}-HEC and SDS, in which N_H gradually decreases from around eight to four and N_S increases from 50 to 70 with increasing SDS concentration.[42]

Furthermore, the plots for TTAB and CTAB can be extrapolated to their cac to estimate the number of hydrophobes per mixed micelle, N_H, for C_{16}HEC in the absence of surfactant. The number is difficult to determine experimentally for small hydrophobe clusters of lightly

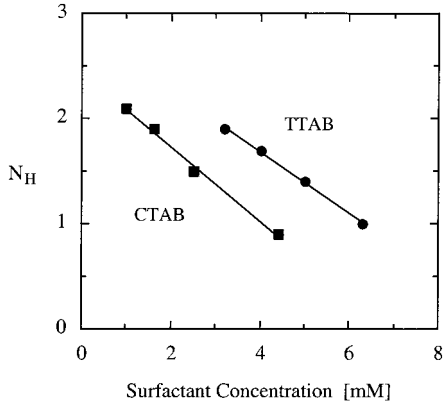

Figure 3. Number of hydrophobes in a mixed micelle, N_H, in 0.5wt % C_{16}HEC solutions as a function of surfactant concentration for TTAB (●) and CTAB (■) at 30 °C; the dotted line is extrapolated to each surfactant's cac.

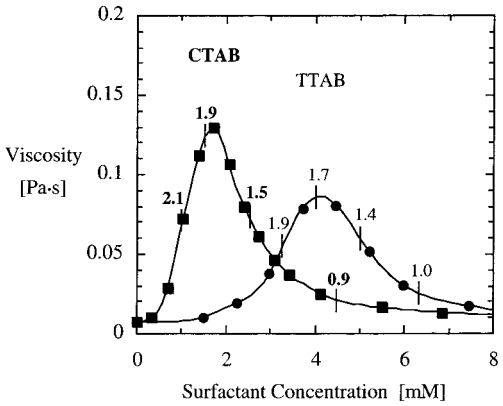

Figure 4. Viscosity of 0.5wt % C_{16}HEC solutions as a function of surfactant concentration for TTAB (●) and CTAB (■) at 30 °C. The number of hydrophobes in a mixed micelle at each surfactant concentration (indicated by a vertical line) is indicated along the profile.

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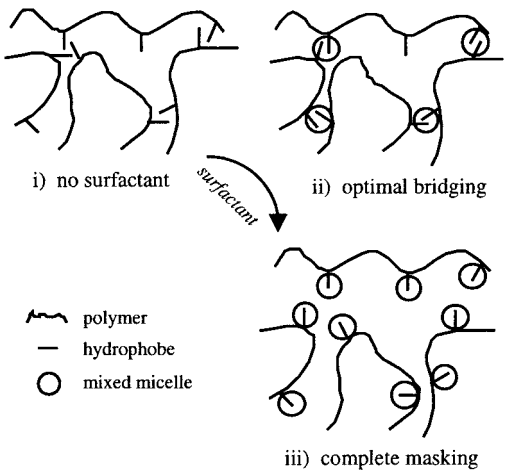

Figure 5. Schematic diagram of interactions between hmHEC and spherical micelles in different surfactant concentration regimes.

substituted and stiff C_{16}HEC chains (about five hydrophobes per chain), which are not hydrophobic enough to solubilize the probe and quencher. The value obtained is around 2.3 for both surfactants, implying that there are two or three hydrophobes in each hydrophobe cluster, which is consistent with the viscosity data. It is high enough, greater than two, to explain the increase in viscosity over that of unmodified HEC and low enough to account for the small extent of viscosity increase, which is by only about one-third.[40] Again, this number is in sharp contrast to the aggregation numbers on the order of 20−30 found for very flexible hm-poly(sodium acrylate).[19]

The number of hydrophobes in a mixed micelle at each surfactant concentration is correlated with the viscosity profiles of C_{16}HEC solutions with TTAB and CTAB in Figure 4. As the surfactant concentration is increased, the number of hydrophobes falls below two, beyond the viscosity maximum of C_{16}HEC with both TTAB and CTAB, which marks the transition from the bridging ($N_H > 2$) to masking ($N_H < 2$) concentration regions. This is consistent with the picture of interactions between hm-polymers and spherical micelles. The viscosity is proportional to the number of effective associating junctions. With increasing surfactant concentration, the viscosity initially increases as surfactants and "diluted" hydrophobes form additional micellar junctions but eventually decreases as the associating junctions are broken up when the number of hydrophobes falls below two, as observed in various hmHEC and surfactant systems.[14,15,18] At higher surfactant concentrations, the number of hydrophobes eventually decreases to one in the masking region. However, for both TTAB and CTAB, N_H is around one at the concentration where the viscosity decrease and, therefore, hydrophobe masking is not complete yet. This is because whereas on average $N_H \approx 1$, there is still a large population of mixed micelles with $N_H = 2$ because the partitioning follows a Poisson distribution.

Therefore, we were able to show that the number of intermolecular associating hydrophobes in a mixed micelle of stiff C_{16}HEC chains is somewhat greater than two with no surfactant, is around two at the viscosity maximum, and drops below one in the masking region. The picture of interactions between hm-polymers, with a stiff backbone and no intramolecular associating hydrophobe, and surfactants is illustrated in Figure 5. Although work on poly(sodium acrylate) also showed that the number of hydrophobes in a mixed micelle decreases with increasing DTAC concentration, the number reflects both *intramolecular* and *intermolecular* associations, which are inherent in flexible hm-polymer systems. N_H is about 30 with no surfactant, around 12 at the viscosity maximum, and six in the masking region.[19] Nevertheless, both findings are qualitatively similar in that the total number of hydrophobes at the viscosity maximum is twice that in the masking region.

Summary

The interactions between hydrophobically modified polymers and surfactants were studied by steady-state fluorescence and rheology. In aqueous solution, the presence of C_{16}HEC induced micellar aggregation around the hydrophobes at concentrations (cac) about one-half times lower than the cmc for TTAB and CTAB. Fluorescence quenching experiments showed that the number of hydrophobes in a mixed micelle (N_H) decreases gradually with increasing surfactant concentration due to dilution of the hydrophobes by the surfactant. The results were correlated with rheological data, which showed that N_H declines from greater than two with no surfactant to around two at the viscosity maximum and falls to one in the masking region. The findings were explained in terms of the effective associating junctions and are consistent with the picture of interactions between hm-polymers, with stiff backbones and no intramolecular association, and surfactants.

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