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Interaction of Hydrophobically Modified (Hydroxyethyl)cellulose with Various Added Surfactants

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ABSTRACT: The effects of the addition of various anionic and nonionic surfactants on the rheological properties of aqueous solutions of hydrophobically modified (hydroxyethyl)cellulose (HMHEC) have been investigated using oscillatory measurements. Significant polymer/surfactant interaction was observed in the vast majority of systems at surfactant concentrations considerably lower than the critical micelle concentration of the free surfactant in water. For any individual surfactant, the observed rheological effects were found to be strongly dependent upon the level of surfactant addition, with at first an increase and then a decrease in the storage and loss moduli of the HMHEC/surfactant system occurring with increasing surfactant concentrations due to the enhancement and then subsequent breakdown of the network structure. At high surfactant concentrations, complete disruption of the polymer network was evident, with the HMHEC/surfactant systems exhibiting rheological characteristics typical of a dilute polysaccharide solution. The magnitude of the observed rheological effects was also found to be dependent upon both the alkyl chain length and the nature of the hydrophilic head group of the added surfactant. The interaction of HMHEC with the anionic surfactant sodium dodecyl sulfate (SDS) has been studied in greater detail using rheological and electrochemical techniques. From this, and previously reported spectroscopic data, a mechanism for the HMHEC/SDS interaction at various levels of surfactant addition is proposed.

Introduction

Hydrophobically associating water-soluble polymers are a relatively new class of industrially important macromolecules which are gaining increasing industrial use due to their ability to impart improved rheological behavior to particulate dispersions.[1-5] Essentially, these polymers consist of a long-chain hydrophilic backbone, but they also possess a small number of hydrophobic side chains or terminal groups, usually in the range of 8–40 carbon atoms in composition. While the nature of their backbone usually renders the polymer soluble in aqueous media, intermolecular association of the hydrophobic groups leads to the formation of reversible three-dimensional network structures.[1,2]

The regions of intermolecular hydrophobic association represent areas of high affinity for surfactant interaction, and consequently, the addition of surfactants has been found to have a dramatic effect on the rheological properties of solutions containing hydrophobically associating polymers.[6-12] However, the observed rheological effects have often been found to be strongly dependent upon the actual levels of surfactant addition. Thus, it is evident that the explanation of such complex rheological phenomena is dependent upon a detailed understanding of the behavior of the surfactant in the system, and, consequently, mechanisms for polymer/surfactant interaction have now been proposed for a number of different systems.[8-16]

In this paper, we report the effects of the addition of various anionic and nonionic surfactants on the rheological properties of a hydrophobically associating water-soluble polymer, hydrophobically modified (hydroxyethyl)cellulose (HMHEC) and propose a mechanism for the interaction of HMHEC with the anionic surfactant sodium dodecyl sulfate, based on rheological, electrochemical, and previously reported spectroscopic data.[7]

Materials

(Hydroxyethyl)cellulose (HEC) and hydrophobically modified (hydroxyethyl)cellulose (HMHEC) were kindly supplied by Aqualon (U.K.) Ltd. under the trade names Natrosol 250 GR and Natrosol Plus Grade 330, respectively. The polymers are both water-soluble at room temperature, and the manufacturer reports them to be of comparable molecular mass (~250 000) and to have molar substitutions of 2.5 and 3.3, respectively. In addition, HMHEC contains approximately 1% w/w of chemically grafted C_{12}–C_{18} alkyl side chains.[17]

For the electrochemical investigations, the polymers were purified by extensive dialysis against distilled water and then freeze-dried.

The anionic surfactants sodium hexanoate, sodium octanoate, sodium decanoate, and sodium dodecanoate were obtained from Sigma Chemicals Ltd. and were used without further purification. Sodium dodecyl sulfate (specially pure grade) and sodium decyl sulfate were obtained from BDH Chemicals Ltd. and Lancaster Synthesis Ltd., respectively, and were used as supplied.

The nonionic, alkylpoly(oxyethylene) ether-type surfactants $C_{11}E_8$ and $C_{13}E_8$ were kindly supplied by Hoechst U.K. Ltd. under the trade names Genapol UD 080 and Genapol X 080, respectively, and were used without further purification.

Methods

(i) Rheological Measurements. Equal amounts of various aqueous surfactant solutions of known concentration were added to approximately 5 g of aqueous solutions of known concentration of HMHEC. The mixtures were then tumbled overnight to ensure complete homogeneity. The storage modulus (G'), loss modulus (G''), and dynamic viscosity (η^*) of the various solutions were measured over the frequency range 0.01–10 Hz at a fixed amplitude of 6×10^{-3} rad using a Carri-Med CS100 controlled stress rheometer (Carri-Med Ltd., U.K.) fitted with either a 4-cm 2° or a 2-cm 2° cone-and-plate measuring system.

(ii) Electrochemical Measurements. (a) Determination of Critical Micelle Concentration. The critical micelle concentrations (cmc) of the various anionic surfactants in water at 20 °C were determined from the position of the change of gradient of a plot of solution conductivity against added surfactant concentration which occurs as a result of counterion condensation. Measurements were made using a Jenway 4010 conductivity meter.

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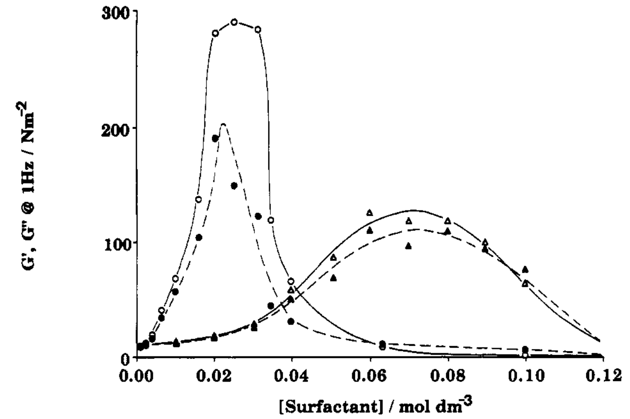

Figure 1. Effect of the addition of (△,▲) sodium decanoate and (○,●) sodium dodecanoate on the storage (*G'*; open symbols) and loss (*G''*; closed symbols) moduli (ω = 1 Hz) of 2% aqueous solutions of HMHEC.

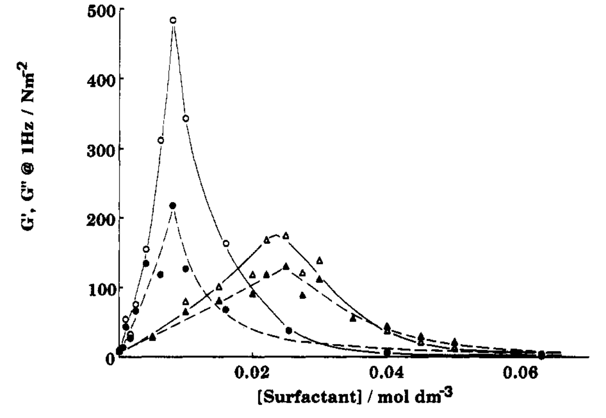

Figure 2. Effect of the addition of (△,▲) sodium decyl sulfate and (○,●) sodium dodecyl sulfate on the storage (*G'*; open symbols) and loss (*G''*; closed symbols) moduli (ω = 1 Hz) of 2% aqueous solutions of HMHEC.

(b) Specific Ion Electrode Investigation of HMHEC/SDS Interaction. Since HMHEC is a nonionic polymer, electrochemical investigations of the HMHEC/SDS system are selective to the anionic surfactant molecules. Consequently, the occurrence of counterion condensation as a result of surfactant aggregation can be detected using a selective ion electrode.

The activities of the sodium ions in aqueous solutions containing varying amounts of SDS in the absence and the presence of either 0.5% HMHEC or 0.5% HEC were determined at 25 °C using an Orion Na$^+$ selective ion electrode in conjunction with an EIL 7050 pH meter using a saturated KCl/calomel electrode as reference. Calibration curves were constructed immediately before taking measurements, using standard sodium chloride solutions.

The fraction, θ, of condensed sodium ions in each polymer/surfactant system was calculated from comparison of the measured sodium ion activities with the known amount of sodium dodecyl sulfate present in the system.

Results

The effects of the addition of the anionic surfactants sodium decanoate and sodium dodecanoate on the storage modulus (*G'*) and loss modulus (*G''*) of 2% aqueous solutions of HMHEC at a frequency of 1 Hz are given in Figure 1. The corresponding curves for the addition of the anionic surfactants sodium decyl sulfate and sodium dodecyl sulfate are given in Figure 2. All the curves given in Figures 1 and 2 exhibit the same general trends, with both moduli at first increasing with increasing surfactant concentration up to a maximum value at least 1 order of magnitude greater than that observed for the HMHEC solution in the absence of surfactant. At this "optimum" concentration of added surfactant, the originally viscous fluids exhibited distinctly gel-like characteristics, with *G'* being greater than *G''*. For each of the systems illustrated in Figures 1 and 2, the surfactant concentration ($[S]_{max}$) at which the maximum in storage modulus (G'_{max}) was observed also, within the bounds of experimental error, corresponded to the attainment of the maximum loss modulus (G''_{max}). Although the value of $[S]_{max}$ varied for each surfactant, further additions of surfactant above the level of $[S]_{max}$ produced, in all cases, a marked decrease in both moduli. At sufficiently high concentrations of added surfactant, the samples became fluid-like again, with *G''* being greater than *G'* in all instances. The actual magnitudes of both moduli at such high surfactant additions were significantly less than in the absence of surfactant.

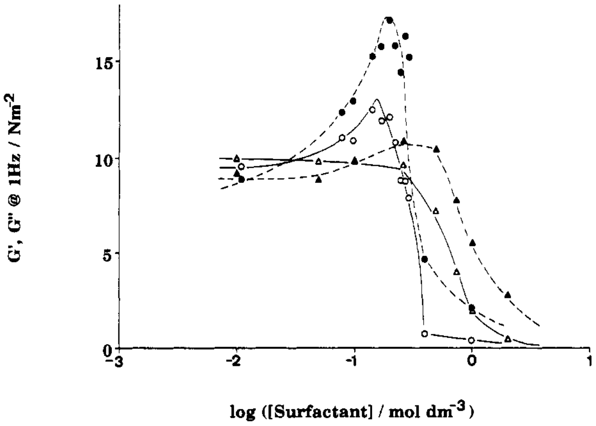

Figure 3. Effect of the addition of (○,●) sodium octanoate and (△,▲) sodium hexanoate on the storage (*G'*; open symbols) and loss (*G''*; closed symbols) moduli (ω = 1 Hz) of 2% aqueous solutions of HMHEC.

The effects of the addition of sodium hexanoate and sodium octanoate on *G'* and *G''* of a 2% aqueous solution of HMHEC at a frequency of 1 Hz are given in Figure 3. The various curves are of the same general shape as those obtained with the other anionic surfactants described above but, in these instances, the addition of the surfactants was found to have a greater effect on *G''* of the HMHEC solutions compared to *G'*. The observed increases in *G'* and *G''* illustrated in Figure 3 are considerably smaller than those observed for the anionic surfactants illustrated previously in Figures 1 and 2.

The effects of the addition of the nonionic surfactants $C_{11}E_8$ and $C_{13}E_8$ on *G'* and *G''* of a 2% aqueous solution of HMHEC at a frequency of 1 Hz are given in Figure 4. Both surfactants produced the same general trend of at first a small increase and then a decrease in *G'* and *G''* with increasing surfactant concentration, with the greater effect being observed with *G''*. The maximum increases in the rheological moduli are of similar magnitude to those obtained for sodium octanoate, but much less than those observed for the anionic surfactants featured in Figures 1 and 2.

The values of G'_{max}, G''_{max}, and $[S]_{max}$ for the various added surfactants are given in Table I, together with the cmc of the free anionic surfactants in water at 20 °C, as determined conductimetrically. The observed values for the various cmc's are in good agreement with the available literature.[18-20] For a given hydrophilic head group, it can be seen that G'_{max} increases with increasing alkyl chain length of the surfactant. For the anionic surfactants, plots of G'_{max} and G''_{max} as a function of the effective alkyl chain length of the added surfactant, which, for the carboxylated surfactants, is one less than the actual number of

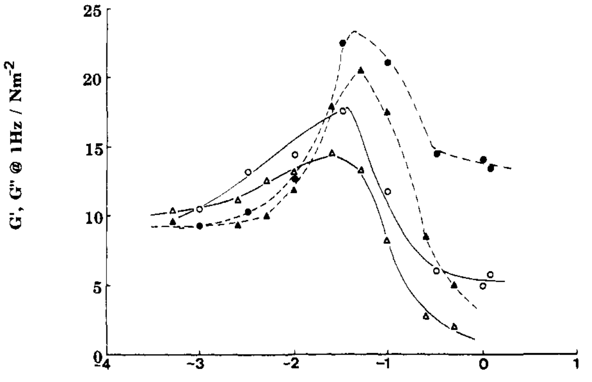

Figure 4. Effect of various alkylpoly(oxyethylene) ether-type nonionic surfactants on the storage (G'; open symbols) and loss (G''; closed symbols) moduli (ω = 1 Hz) of 2% aqueous solutions of HMHEC: (△,▲) $C_{11}E_8$; (○,●) $C_{13}E_8$.

carbon atoms in the molecule since the terminal carboxyl carbon atom is incorporated in the hydrophilic head group, are given in Figure 5. The data show that, above an apparently limiting alkyl chain length of approximately C_6, both moduli increased exponentially with increasing effective alkyl chain length of the added surfactant, with the effect being more pronounced for G'_{max}. Interestingly the values of both moduli for the carboxylated and sulfated surfactants fall on the same respective curves, indicating that, for these two series of surfactants, the nature of the head group is of secondary importance to the alkyl chain length of the added surfactant in determining the overall HMHEC/surfactant interaction.

The variations of G' and G'' over the frequency range 0.01–10 Hz for 2% solutions of HMHEC containing varying amounts of SDS, sodium decanoate, and the nonionic surfactant $C_{11}E_8$ are given in Figure 6a–c, respectively. The data (i) in the absence of surfactant, (ii) in the presence of surfactant concentration corresponding to $[S]_{max}$, and (iii) in the presence of a relatively high (excess) surfactant concentration indicate that G' and G'' become less frequency dependent and that $G' > G''$ over a greater frequency range when the added surfactant concentration is increased up to $[S]_{max}$. This is indicative of a change to more gel-like characteristics.[21] At higher surfactant concentrations, G' and G'' show increased frequency dependence, and $G'' > G'$ over the entire frequency range studied, which is more characteristic of a low-viscosity solution. The dynamic viscosities, η^*, of the same polymer/surfactant systems are given in Figures 7a–c. Again the results indicate that the polymer solutions become more viscoelastic with increased frequency dependence, typical for polymer network systems containing entangled chain networks, as the added surfactant concentration is increased up to $[S]_{max}$. At higher surfactant concentrations, the frequency dependence of η^* is considerably reduced, and the systems displayed rheological characteristics typical of dilute polymer solutions with little molecular entanglement.[21] No evidence of the shear-thickening behavior reported[22,23] for other associative thickeners was observed in any of the systems investigated in this study.

The effects of SDS on G' of a 2% HMHEC solution in the presence of varying amounts of added sodium chloride are given in Figure 8. The addition of increasing amounts of electrolyte would appear to cause a slight decrease in the values of both G'_{max} and $[S]_{max}$. The effects of added SDS on G' of aqueous solutions of varying concentrations of HMHEC are given in Figure 9. Increasing the polymer concentration over the range 0.5–2% would appear to cause a slight increase in the value of $[S]_{max}$.

Plots of the fraction of condensed sodium ions, θ, as a function of the concentration of added SDS, both in the absence and in the presence, of either 0.5% HEC or 0.5% HMHEC are given in Figure 10. In the absence of polymer, counterion condensation is first observed at an SDS concentration of approximately 8×10^{-3} mol dm^{-3}, which corresponds to the cmc of SDS in water. In the presence of 0.5% HEC, an essentially identical curve is obtained, with counterion condensation once again being first observed at an SDS concentration of approximately 8×10^{-3} mol dm^{-3}. This indicates that HEC has little or no effect on the micellization behavior of the surfactant in the system. In contrast, for SDS in the presence of 0.5% HMHEC, counterion condensation is first observed at a critical SDS concentration of approximately 10^{-4} mol dm^{-3}. The value of θ then increases with increasing surfactant concentration up to a value of 0.38 at an SDS concentration of approximately 8×10^{-3} mol dm^{-3}. Above this concentration of SDS, θ increases rapidly with increasing surfactant concentration, presumably as a consequence of the formation of free SDS micelles in solution.

Discussion

From the rheological data given in Figures 1–4, it is evident that the interaction of surfactants with HMHEC is relatively complex, since, generally, there is first an increase, then a decrease, and finally a complete disruption of the network structure with increasing surfactant addition. Among the points requiring elucidation are details such as identification of the nature of the interaction between the polymer and surfactant molecules, the critical concentrations of each component which mark the onset of the polymer/surfactant interaction, and the significance of the surfactant concentration, $[S]_{max}$, at which the maximum storage and loss moduli of the HMHEC/surfactant system are observed.

The dramatically different rheological behavior of unmodified HEC and HMHEC in the presence of added surfactant[7-12] means that it is now generally accepted that the interaction of HMHEC with added surfactant occurs via the bound hydrophobe of HMHEC and the hydrophobic alkyl chains of the added surfactant, thereby increasing intermolecular associations through a "bridging-type" mechanism. However, it should be noted that, following viscometric studies which indicated only a relatively small increase in the coil dimensions of HMHEC due to its interaction with SDS, Sivadasan and Somasundaran[11] recently suggested that the SDS binding on HMHEC was through its polar head group and that the exposed nonpolar groups aggregated along with alkyl groups of HMHEC, thereby enhancing the overall hydrophobicity and possibly the interpolymer association. It should, however, be pointed out that the HMHEC used in their studies, which had a molar substitution (MS) of ethylene oxide groups of 2.5 compared to 3.3 for the sample used in our studies, precipitated at added SDS concentrations of between 5×10^{-5} and 5×10^{-3} mol dm^{-3}, which was not the case for our sample.

In his study of the interaction of HMHEC (MS 2.5) with the anionic surfactant sodium oleate, Gelman[8] found that enhancement of the viscosity of HMHEC/sodium oleate solutions was first observed at surfactant concentrations only slightly less than its expected cmc. This led Gelman to suggest that, at such a surfactant concentration, the bound hydrophobes were present in sufficient quantities as to act as effective substitutes for sodium oleate molecules, thereby permitting the formation of mixed bound hydrophobe/surfactant "micelles". The formation

Table I
Critical Micelle Concentrations of Various Anionic and Nonionic Surfactants in Water at 20 °C and Characteristics of the Maximum Value of the Storage and Loss Moduli (at 1 Hz) Achievable through Their Addition to a 2% Aqueous Solution of HMHEC

surfactant	solvent	G'_{max}, N m^{-2}	G''_{max}, N m^{-2}	$[S]_{max}$, mol dm^{-3}	cmc, mol dm^{-3}
sodium hexanoate	water	10 ± 1	11 ± 1	0.40 ± 0.05	
sodium octanoate	water	12 ± 1	16 ± 1	0.19 ± 0.01	0.40
sodium decanoate	water	122 ± 6	105 ± 5	0.075 ± 0.003	0.098
sodium dodecanoate	water	290 ± 10	200 ± 10	0.023 ± 0.003	0.026
sodium decyl sulfate	water	185 ± 15	125 ± 10	0.025 ● 0.002	0.033
sodium dodecyl sulfate	water	485 ± 20	290 ± 15	(8.0 ± 0.4) × 10^{-3}	8.2 × 10^{-3}
sodium dodecyl sulfate	0.01 mol dm^{-3} NaCl	440 ± 20	180 ± 10	(7.3 ± 0.4) × 10^{-3}	5.6 × 10^{-3}
sodium dodecyl sulfate	0.10 mol dm^{-3} NaCl	405 ± 20	160 ± 10	(7.0 ± 0.4) × 10^{-3}	1.5 × 10^{-3}
$C_{11}E_8$	water	15 ± 1	20 ± 1	(3.1 ± 0.7) × 10^{-3}	3.5 × 10^{-4}
$C_{13}E_8$	water	18 ± 1	23 ± 1	(4.0 ± 0.8) × 10^{-3}	2.8 × 10^{-5}

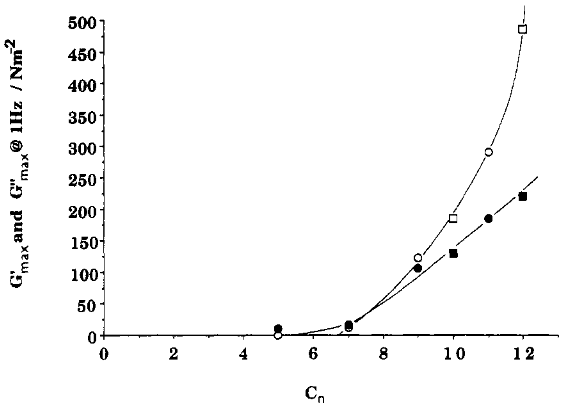

Figure 5. Variation of G'_{max} (open symbols) and G''_{max} (closed symbols) of 2% aqueous solutions of HMHEC with effective alkyl chain length, C_n, of added anionic surfactants: (●,○) sodium alkanoates (C_n–COO$^-$Na$^+$); (■,□) sodium alkyl sulfates (C_n–OSO$_3^-$ Na$^+$).

of such mixed "micelles" effectively increased the degree of interpolymer association and, consequently, the solution viscosity. Gelman also postulated that the micellization of the added surfactant must occur for viscosity enhancement to be observed.

If one considers the effects of the various added surfactants on the storage and loss moduli of the aqueous HMHEC solutions, as illustrated in Figures 1–4, it is evident that, with the exception of sodium hexanoate and, possibly, the nonionic surfactants $C_{11}E_8$ and $C_{13}E_8$, enhancement of G' and G'' was evident at surfactant concentrations considerably lower than the value of their cmc, as given in Table I. This is indicative of significant "premicellar" polymer/surfactant interaction. A similar conclusion may be drawn for the HMHEC/SDS system from both the counterion condensation data given in Figure 10 and previous electron spin resonance spin probe investigations.[7] Such "premicellar" association has also been observed by a number of workers for various other cellulosic polymer/SDS systems.[10–16]

The increasing degree of counterion condensation occurring within the HMHEC/SDS system over the range of surfactant addition from 10^{-4} to 8 × 10^{-3} mol dm^{-3}, as evident from Figure 10, suggests the HMHEC/SDS aggregates are continually growing in number and/or size over this region. This is consistent with the observations of Dualeh and Steiner,[12] who, using a steady-state fluorescence probe technique, found that the mean aggregation number of mixed HMHEC-bound hydrophobe/SDS aggregates increased with increasing surfactant concentration. Through application of their observations on the mixed micellization behavior of SDS and poly(oxyethylene) lauryl ether (the free surfactant corresponding to the bound hydrophobe in the HMHEC studied), Dualeh and Steiner[12] also concluded that the mean number of SDS molecules per mixed bound hydrophobe/SDS aggregate increased from approximately 50 to 75 upon increasing

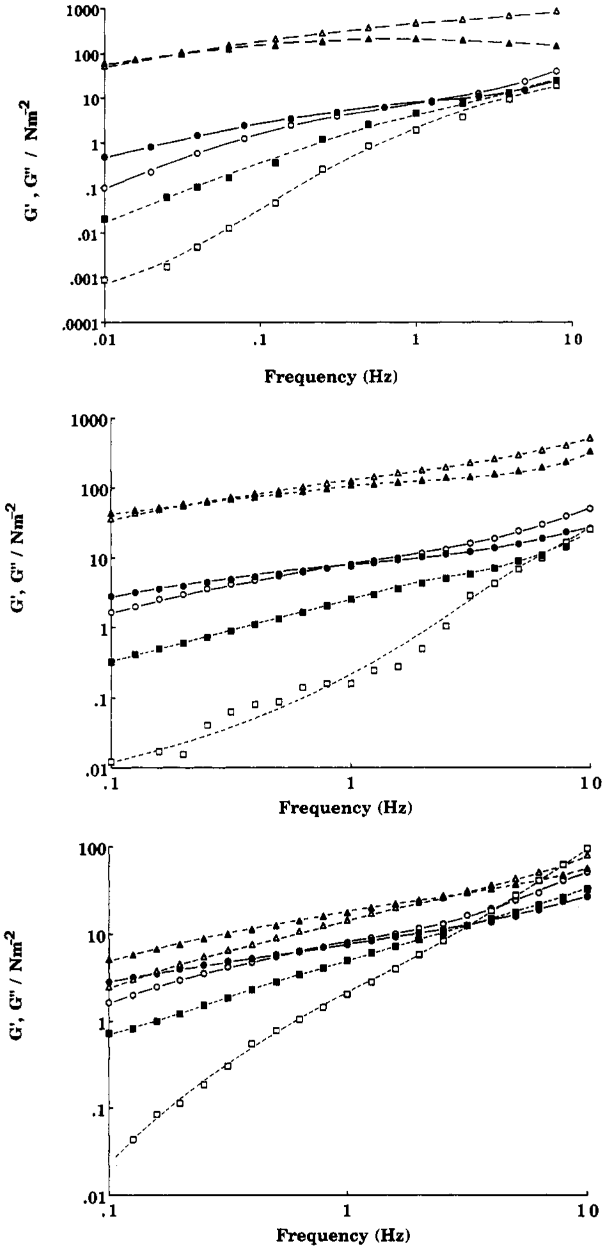

Figure 6. Double logarithmic scale plots of the effect of the frequency of oscillation on the storage moduli, G' (open symbols), and loss moduli, G'' (closed symbols), of 2% aqueous solutions of HMHEC in the presence of (i) (○,●) no added surfactant, (ii) (△,▲) $[S]_{max}$, and (iii) (□,■) excess surfactant for (a, top) sodium dodecyl sulfate, (b, middle) sodium decanoate, and (c, bottom) $C_{11}E_8$.

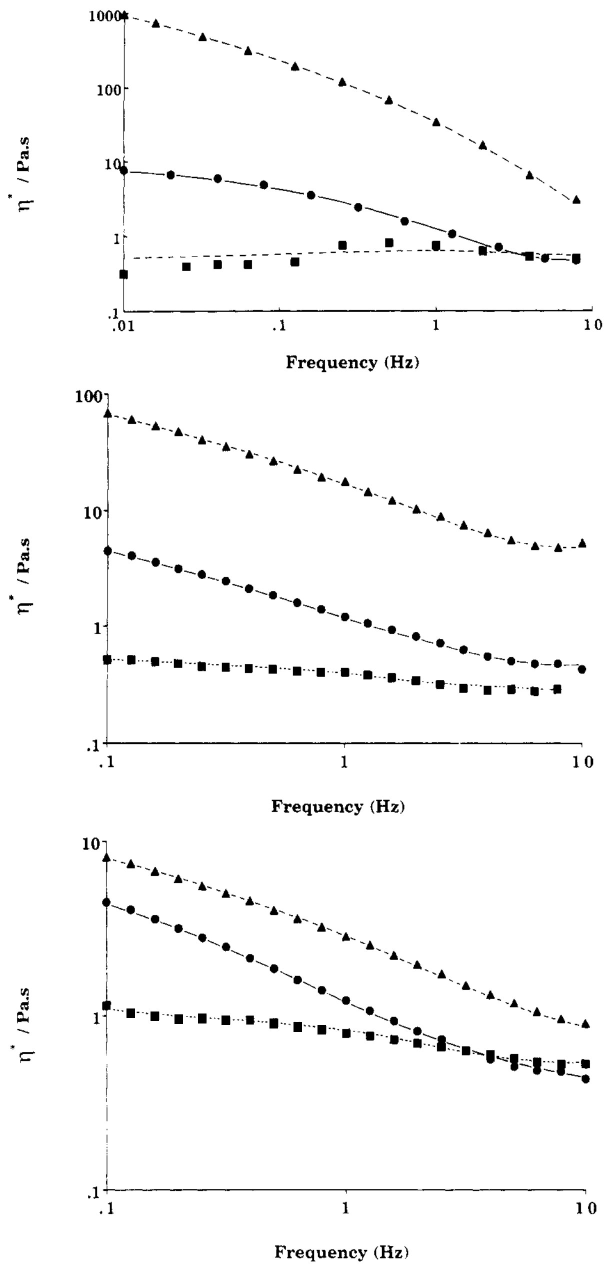

Figure 7. Double logarithmic scale plots of the effect of the frequency of oscillation on the dynamic viscosity, η^*, of 2% aqueous solutions of HMHEC in the presence of (i) (●) no added surfactant, (ii) (▲) $[S]_{max}$, and (iii) (■) excess surfactant for (a, top) sodium dodecyl sulfate, (b, middle) sodium decanoate, and (c, bottom) $C_{11}E_8$.

the SDS concentration from 4.8×10^{-3} to 7.2×10^{-3} mol dm^{-3}. In contrast, the average number of bound hydrophobes per mixed aggregate decreased from approximately 9 to 7 over the same increase in SDS concentration.

It can be seen from Figures 1–4 that, in general, the "constructive" interaction of surfactant with HMHEC, in terms of the structural enhancement of the polymer network, increased with increasing surfactant addition over a wide range of surfactant concentrations up to a level of $[S]_{max}$, at which G'_{max} and G''_{max} were observed. Gelman[8] found that for the HMHEC/sodium oleate system, the maximum enhancement in viscosity was observed at sodium oleate concentrations approximately equivalent to its expected cmc. However, if the values of $[S]_{max}$ and cmc for the various surfactants given in Table I are compared, it can be seen that, although there is essentially an equality between these two parameters for sodium dodecanoate and sodium dodecyl sulfate, the values of the other surfactants differ significantly. Furthermore, although the value of $[S]_{max}$ for the addition of SDS to HMHEC solutions in the presence of varying amounts of added electrolyte did decrease slightly with increasing electrolyte concentration, as illustrated in Figure 8, the extent of decrease in the value of $[S]_{max}$ was considerably less than the decrease in the values of the cmc of the free SDS molecules over that range of electrolyte concentrations (Table I). This indicates that Gelman's observation on the HMHEC (MS 2.5)/sodium oleate system are not applicable to the various HMHEC (MS 3.3)/surfactant systems investigated in this study and, therefore, that any apparent correlation between the maximum in storage and loss moduli or solution viscosity of mixed HMHEC/sur-

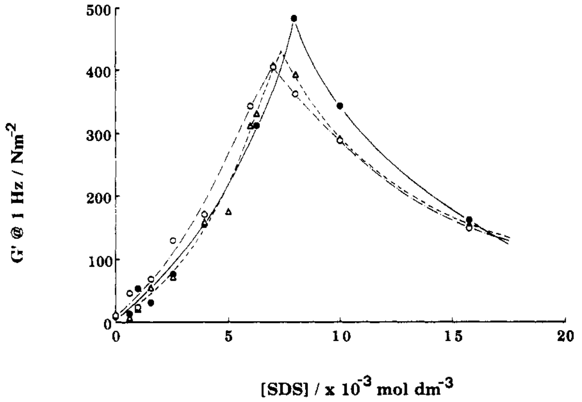

Figure 8. Effect of SDS on the storage moduli, G' (ω = 1 Hz), of 2% aqueous solutions of HMHEC in the presence of varying amounts of added sodium chloride: (●) no added electrolyte; (△) 0.01 mol dm^{-3} NaCl; (○) 0.1 mol dm^{-3} NaCl.

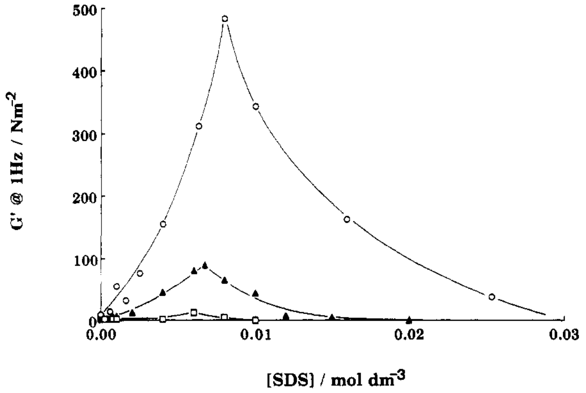

Figure 9. Effect of SDS on the storage moduli, G' (ω = 1 Hz), of aqueous solutions of HMHEC of varying concentrations: (□) 0.5% HMHEC, (▲) 1.0% HMHEC; (○) 2.0% HMHEC.

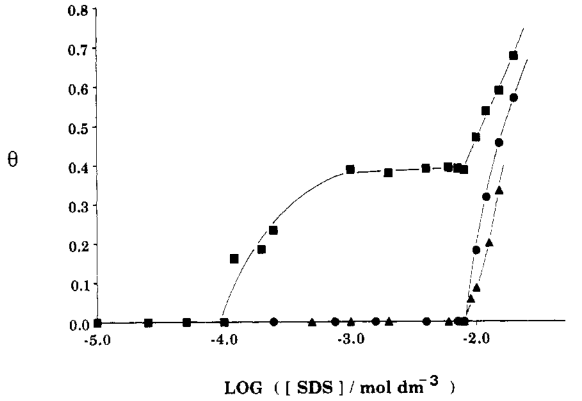

Figure 10. Fraction of condensed sodium ions, θ, as a function of added surfactant concentration for various polymer/surfactant systems: (●) SDS alone; (▲) SDS + 0.5% HEC; (■) SDS + 0.5% HMHEC.

factant solutions and the cmc of the added surfactant is perhaps coincidental.

Gelman[8] also noted that the amount of surfactant required to attain the maximum viscosity increased slightly with increasing polymer concentration. This is in agreement with the rheological data given in Figure 9 and indicates that the value of $[S]_{max}$ for any particular HMHEC/surfactant combination is dependent upon the number of regions of hydrophobic association present within the system, a finding which is concordant with results we have obtained for synthetic associative polymers containing varying proportions of hydrophobes.[6]

Comparison of the values of G'_{max} for the various series of surfactants given in Table I indicates that the ability to promote intermolecular hydrophobic association increased with increasing alkyl chain length of the surfactant. Increased polymer/surfactant interactions with increasing alkyl chain length of surfactant have also been reported for other systems.[24] This suggests that the hydrophobic interactions between the alkyl chain of the added surfactant and the bound hydrophobe of the polymer has an important bearing on the viscoelastic properties of the HMHEC/surfactant network. This point is further emphasized by the data given in Figure 5, which indicates that, for the various carboxylated and sulfated surfactants investigated in this study, the overall strength of the HMHEC/surfactant interaction was predominantly determined by the effective alkyl chain length of the added surfactant and was largely insensitive to the nature of the anionic head group.

In addition to the increased strength of each individual association of the longer alkyl chain surfactants with the bound hydrophobes, the profound influence of the alkyl chain length on the value of the storage and loss moduli may also, in part, be due to micellar size effects. At the concentrations used in our studies, all of the surfactants can be assumed to form purely spherical micelles.[25,26] The diameter of the anionic surfactant micelles would increase with increasing chain length,[25] and the larger micelles of the longer chain surfactants can, for geometric reasons, be considered to have a greater potential to act as "bridges" between two or more neighboring hydrophobes. The data given in Figure 5 suggest that an added anionic surfactant must have an effective alkyl chain length of >6 carbon atoms to be able to promote intermolecular association of the HMHEC molecules.

The addition of anionic surfactants could be expected to have a greater effect on the viscoelastic properties of HMHEC networks than nonionic surfactants due to interaction with the former class of surfactants producing a polyelectrolyte-type expansion of the HMHEC chains, thereby leading to a highly swollen polymer network. However, the limited effect of added electrolyte on the strength of the HMHEC/SDS interaction, as illustrated by the curves of G' as a function of added SDS concentration at different total ionic strengths given in Figure 8, indicates this contribution to be relatively small.

The considerably lower values of G'_{max} and G''_{max} obtained for the nonionic surfactants could be due to a result of steric factors. As the nonionic surfactants investigated in this study have an average of 8 ethylene oxide units in their structure, their hydrophilic head groups of some 24 carbon–carbon or carbon–oxygen bond units in length. The physical incorporation of the C_{12}–C_{18} polymer-bound hydrophobes within the hydrophobic interior of the nonionic surfactant aggregate and the resultant promotion of intermolecular association would, therefore, necessitate the cellulosic backbone of the HMHEC residing among the hydrated oligomeric ethylene oxide chains of the nonionic surfactant molecules, a situation which would be energetically unfavorable.

From the data described above, the complex rheological behavior of HMHEC in the presence of typical anionic surfactants, such as SDS, may be explained as follows:

In the absence of surfactant, HMHEC adopts an extensive three-dimensional structure in which the cellulosic polymer backbones are effectively and reversibly cross-linked by intermolecular hydrophobic associations between neighboring alkyl side chains. Goodwin et al.,[27] using pulse shearometry, found that in an aqueous solution of an HMHEC similar to that used in this study, the number of "cross-linking" sites per HMHEC molecule was in good agreement with a chemical estimation of the number of grafted alkyl chains per molecule. This observation implies that each grafted alkyl chain of HMHEC becomes incorporated into a region of intermolecular hydrophobic association.

At levels of surfactant addition considerably lower than its expected cmc, "micellar-type" aggregates of surfactant molecules form around the intermolecular hydrophobic "bridges". It is also possible that the presence of the surfactant molecules may enable grafted alkyl side chains which, for geometrical or thermodynamic reasons, were previously unassociated to become involved in the "bridging" network. The number of surfactant molecules associated with each hydrophobic bridge increases with increasing surfactant addition. The overall effect of this polymer–surfactant interaction would be to increase the degree and strength of the structure within the HMHEC network, thereby producing the increase in G' observed in the initial portion of the curves given in Figures 1–4. The "constructive" association of the free surfactant with the hydrophobic bridges and hence the increase in G' with increasing surfactant addition continues up until an added surfactant concentration of $[S]_{max}$ at which the optimum number and size of micellar bridges have been formed. The exact composition of such "optimum" micellar bridges is still a matter for speculation but, ideally, it may correspond to a situation where each surfactant aggregate incorporates a single grafted alkyl side chain from each of two neighboring polymer molecules, thereby maximizing the number of interpolymer associations. Previous investigations[28] using spin-labeled polymer molecules in conjunction with electron spin resonance spectroscopy have indicated that the molecular motion of the polymer chains is essentially the same in the absence of surfactant, as in the presence of surfactant concentrations corresponding to $[S]_{max}$. This indicates that very few of the polymer segments are involved in the bridging of the polymer molecules.

At concentrations of added surfactant above $[S]_{max}$, additional surfactant aggregates are available for the "solubilization" of the polymer-bound hydrophobes. Consequently, the average number of bound hydrophobes per surfactant aggregate would decrease, thereby reducing the number of effective micellar-type bridges and thus producing the decrease in G' with increasing surfactant addition observed in the latter portions of the curves given in Figures 1–4. At sufficiently high levels of surfactant addition, each bound hydrophobe would be encapsulated in its own individual surfactant micelle, thereby breaking all interpolymer bridges and causing the complete disruption of the network structure, as indicated by the very low values of G' observed at high surfactant additions.

It should be noted, though, that Dualeh and Steiner[12] have recently suggested that, as such relatively high concentrations of SDS would result in the solution becoming more hydrophobic, thereby improving the solubility of the bound hydrophobe within the aqueous media, then there may also be a significant number of free "unmicellized" bound hydrophobes within the system at high surfactant concentrations.

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