

Polymer-Surfactant Interactions and the Association Behavior of Hydrophobically Modified Hydroxyethylcellulose

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ABSTRACT

The association behavior of hydrophobically modified hydroxyethylcellulose (HMHEC) and its interactions with two different types of surfactants, sodium dodecyl sulphate (SDS) and dodecyloxyheptaethoxyethyl alcohol ($C_{12}EO_8$), in dilute solutions have been studied using fluorescence spectroscopy, surface tension and viscometric techniques. Unmodified hydroxyethylcellulose (HEC) of the same molecular weight and degree of substitution as the HMHEC has also been examined for the purpose of comparison. Fluorescence data show that the hydrophobic groups of the HMHEC associate to form clusters above a critical polymer concentration of 500 ppm. Also, the presence of hydrophobic groups on the polymer enhances the interactions between the polymer and nonionic surfactants. Surface tension results support this observation. The viscosity results suggest that the interactions between the surfactant and the polymer affect both inter-polymer-polymer association as well as chain expansion. Chain expansion due to changes in the polymer structure of the HMHEC is similar to that observed in a mixed solvent system. The increased polymer-polymer association in the case of HMHEC-SDS was found to cause phase separation. Such association was effectively prevented above the critical micellar concentration (c.m.c.) of SDS by the polymer bound micelles.

INTRODUCTION

The macromolecular chemistry and technology of water-soluble polymers have been actively pursued areas due to their ever increasing demand in many industries. Because of their usage in a variety of processes involving complex systems containing different chemical species including surfactants, their characterization and basic information regarding their interactions with other molecules in the system are important for optimizing their behavior. One of the major developments in the area of water-soluble polymers is the introduc-

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tion of polymeric surfactants with hydrophobic groups attached to the polymer backbone. Unusual rheological properties [1] which result from the association of hydrophobic groups are the main attractive feature of these polymers.

Hydrophobically modified celluloses have been studied in the past to a limited extent. Hydrodynamic properties of hydrophobically modified hydroxyethylcellulose (HMHEC) with various alkyl groups have been reported in the literature [2]. In this investigation our objective is to study the association behavior of HMHEC and its interactions with ionic and nonionic surfactants. We have used a fluorescence technique [3] with pyrene as a probe, in addition to conventional viscosity and surface tension methods, to investigate the association of hydrophobic groups on the polymer as well as their interactions with surfactant molecules.

EXPERIMENTAL

Materials

The hydroxyethylcellulose (HEC) and hydrophobically modified hydroxyethylcellulose (HMHEC) were commercial samples (Natrosol 250GR and Natrosol Plus) provided by Aqualon (U.S.A.) and were used as received. The hydrophobic group (C_{12} - C_{24} alkyl) content of the modified polymer was less than 1 wt%. The polymers were of comparable molecular weights (ca $3 \cdot 10^5$) and had the same degree of substitution ($MS = 2.5$). Sodium dodecyl sulphate (Fluka AG, purity 99%) and ethanol were of Reagent grade and used as received. Dodecyloxyheptaethoxyethyl alcohol ($C_{12}EO_8$) was purchased from Nikko Chemicals, Japan, and was specified to be 98% isomerically pure. All measurements were completed within 48 h of solution preparation to avoid any possible polymer degradation. Triply-distilled water was used for preparing all solutions.

Methods

Fluorescence measurement

The two pyrene monomer emission bands of interest in the fluorescence emission spectra obtained are at 373 (I_1) and 384 nm (I_3). Ratios of their intensities, I_3/I_1 , were calculated from the spectra. Micropolarity tests were done for pyrene (ca $2 \cdot 10^{-7}$ mol l^{-1}) containing polymer and polymer/surfactant solutions. These solutions were prepared by adding an aqueous saturated solution of pyrene to stock polymer solutions or surfactant containing polymer solutions.

Viscosity measurements

Viscosity measurements were made using an Ubbelohde suspension type capillary viscometer at $25 \pm 0.05^\circ\text{C}$. The intrinsic viscosities $[\eta]$, were determined from Huggins' equation by extrapolation to infinite dilution. The Huggins' equation for nonionic polymers is

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C$$

and the specific viscosity was calculated from

$$\eta_{sp} = (t - t_0)/t_0$$

where η_{sp}/C is the reduced viscosity, t is the flow time of the polymer solution, t_0 is the flow time of pure solvent, C is the polymer concentration in g dl^{-1} , k' is Huggins' constant and $[\eta]$ is the intrinsic viscosity. No shear-rate corrections were applied to these data.

Surface tension measurements

Surface tension was measured using the Wilhelmy plate method. This method is appropriate when surface ageing effects are significant.

RESULTS AND DISCUSSION

Micropolarity

Application of fluorescence spectroscopy as a method to study microheterogeneous systems has been well established [3-5]. The technique utilizes a fluorescence probe, the spectral characteristics of which are dependent on its microenvironment. Pyrene is a probe that prefers to be in hydrophobic environments. As the pyrene molecule experiences a change in its environment, the relative intensities of the third and first vibrational bands of the monomer emission are affected. The ratio, I_3/I_1 , is a measure of the effective polarity of the medium where the pyrene molecule is located.

Figure 1 shows the pyrene fluorescence parameter, I_3/I_1 , in the presence of varying concentrations of HEC and HMHEC. While the micropolarity of pyrene is insensitive to the polymer concentration in the case of HEC solutions, a sharp increase in I_3/I_1 (decrease in micropolarity) is observed when the HMHEC concentration exceeds a critical value (500 ppm) and reaches a plateau at 2000 ppm.

The results illustrate the association behavior of the hydrophobic groups attached to the polymer, which is significant above 500 ppm. At lower polymer concentrations, interactions between the hydrophobic groups are weak or, if they exist, the resulting hydrophobic microdomains are not large enough to attract the pyrene molecule and solubilize it.

It must be noted that the maximum value of I_3/I_1 obtained is lower than that

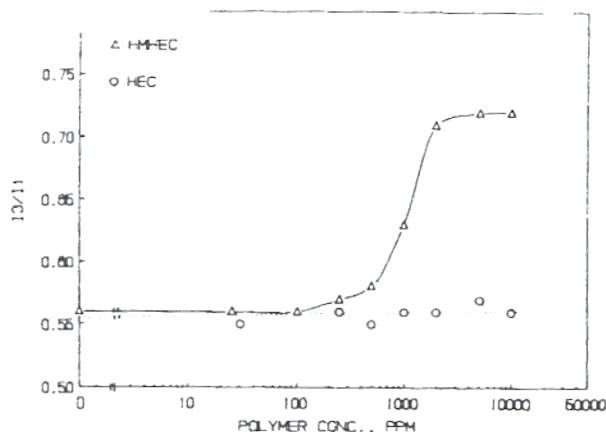


Fig. 1. The characteristic fluorescence parameter I_3/I_1 of pyrene in the presence of various concentrations of HEC and HMHEC.

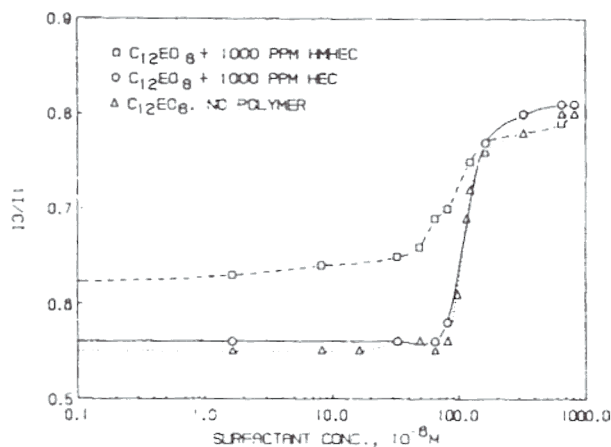


Fig. 2. The ratio I_3/I_1 of pyrene as a function of $C_{12}EO_8$ concentration in the absence and the presence of polymers (1000 ppm).

normally observed (0.8 to 0.9) for micelle solubilized pyrene. The reason may be a less ordered packing of hydrophobic groups in the case of the polymeric surfactant due to the large macromolecular chains attached to them and possible water penetration [6,7]. The hydrophobic clusters formed in this case cannot strictly be compared with regular surfactant micelles where a higher degree of packing is feasible. The possibility of water penetration into the hydrophobic micelle core, wherein the pyrene molecule is completely solubilized, is also expected to be less in the case of micelles.

Figures 2 and 3 show the variation of I_3/I_1 as a function of surfactant concentration for $C_{12}EO_8$ and SDS, respectively. The data presented are for sur-

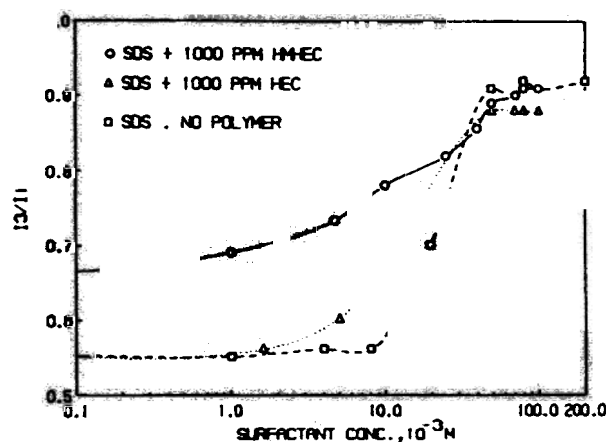


Fig. 3. The ratio I_3/I_1 of pyrene as a function of SDS concentration in the absence and the presence of polymers (1000 ppm).

factant solutions containing 1000 ppm polymer along with solutions without any polymer for comparison purposes. The I_3/I_1 value does not change appreciably below the c.m.c. ($7.8 \cdot 10^{-5}$ and $8 \cdot 10^{-3} M$) for surfactant solutions without polymer and increases sharply above the c.m.c. due to the formation of micelles and pyrene solubilization in them. Addition of the polymers influences the I_3/I_1 ratio to different extents depending on the type of surfactant and polymer. The presence of the unmodified HEC has no measurable effect on the micropolarity characteristics of the nonionic surfactant ($C_{12}EO_8$) and its micelles. The modified polymer, on the other hand, does produce measurable changes in I_3/I_1 at concentrations below the c.m.c. With SDS, both HEC and HMHEC exhibit interactions with marked increases in I_3/I_1 in the case of SDS-HMHEC, possibly through the hydrophobic groups of the polymer.

The binding of surfactant molecules to water soluble polymers can take place either by electrostatic interaction between charged groups or by other interactions leading to the formation of polymer-surfactant complexes. In the case of nonionic polymers containing hydrophobic groups, the predominating driving force for the interactions can be expected to be that between the hydrophobic groups of the polymer and the surfactant. The resultant bound parts will become substantially hydrophobic causing the increase in I_3/I_1 . The large I_3/I_1 values for polymer-surfactant solutions well below the c.m.c. suggest that the clusters of hydrophobe and surfactant molecules associate to form 'pseudo' micelles. The higher I_3/I_1 values for HMHEC-SDS solutions compared to those of HMHEC- $C_{12}EO_8$ also show that the complexes formed between SDS and HMHEC are more hydrophobic than those formed between $C_{12}EO_8$ and HMHEC.

Surface tension

Surface tension results obtained are plotted in Fig. 4 as a function of surfactant concentration for $C_{12}EO_8$ solutions, HEC- $C_{12}EO_8$ and HMHEC- $C_{12}EO_8$ solutions. The c.m.c. of $C_{12}EO_8$ is $8 \cdot 10^{-5} \text{ mol l}^{-1}$ and the polymer concentration used is 1000 ppm. The HMHEC solution itself is quite surface active and has a surface tension value of 58 dyn cm^{-1} . At very low surfactant concentrations (below $10^{-5} \text{ mol l}^{-1} C_{12}EO_8$), the surface tension of polymer/surfactant solutions remains invariant. Above $10^{-5} \text{ mol l}^{-1} C_{12}EO_8$, surface tension slowly decreases and reaches a constant value at about $3.2 \cdot 10^{-4} \text{ mol l}^{-1}$. In the case of HEC- $C_{12}EO_8$ solutions, except at low surfactant concentrations, the results obtained are similar to those for the pure surfactant solutions.

It is generally assumed that the surface tension of a solution of a weakly surface active nonionic polymer and a surfactant is a measure of the activity of the free surfactant molecules in solution and the surface activity of the polymer-surfactant complex is much less compared to that of the surfactant [8]. The results obtained here for the surface active polymer suggest that at low surfactant concentrations almost all the surfactant molecules are bound to the polymer. At concentrations above $10^{-5} \text{ mol l}^{-1}$ the surface tension decreases but is higher than that for the corresponding pure $C_{12}EO_8$ solutions. The higher surface tension values obtained imply the depletion of $C_{12}EO_8$ molecules as a result of complex formation. The concentration at which micelles begin to form has also been shifted in the case of HMHEC to a higher surfactant concentration, ca $3.2 \cdot 10^{-4} \text{ mol l}^{-1}$. At this concentration the binding sites on the polymer molecule are apparently saturated with surfactant molecules.

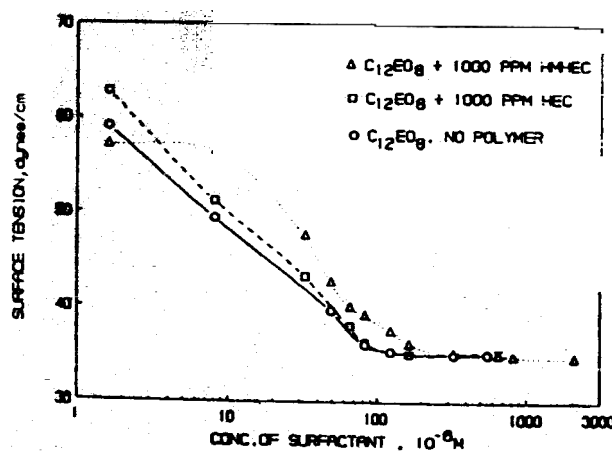


Fig. 4. Surface tension-concentration plot of $C_{12}EO_8$ solutions in the absence and the presence of polymers (1000 ppm).

Viscosity

Intrinsic viscosity in a mixed solvent

Intrinsic viscosity is a function of the hydrodynamic volume [9] of the individual macromolecule; the changes in macromolecular structure and conformation are reflected in the values obtained for this parameter.

The intrinsic viscosity, $[\eta]$, of HMHEC in water-ethanol mixtures is shown in Fig. 5. Since ethanol is a less polar solvent than water, the hydrophobic alkyl groups of the polymer are better solvated by the ethanol molecules than the water in the mixture. Thus ethanol decreases the interaction between alkyl groups and the resulting less compact polymer structure displays an increase in the intrinsic viscosity up to 50/50 (v/v) water-ethanol mixtures. It should also be noted that ethanol itself is not really a good solvent for the polymer and it would have produced a reduction in intrinsic viscosity but for the preferential solvation of the alkyl groups which causes dissociation of clusters of the alkyl groups. Low $[\eta]$ values obtained at higher ethanol to water ratios are due to these poor solvent characteristics of ethanol overall.

Polymer-nonionic surfactant interactions

Figure 6 shows the reduced viscosities for HEC and HMHEC solutions at a fixed concentration of 1000 ppm as a function of added $C_{12}EO_8$. The reduced viscosity of HMHEC gradually increases with surfactant concentration and then decreases in the vicinity of the critical micelle concentration. Minimum viscosity is observed at a surfactant concentration of $3.26 \cdot 10^{-4} \text{ mol l}^{-1}$. Above this concentration the viscosity again increases and approaches the value of pure aqueous solution at a surfactant concentration of $2.04 \cdot 10^{-3} \text{ mol l}^{-1}$. In

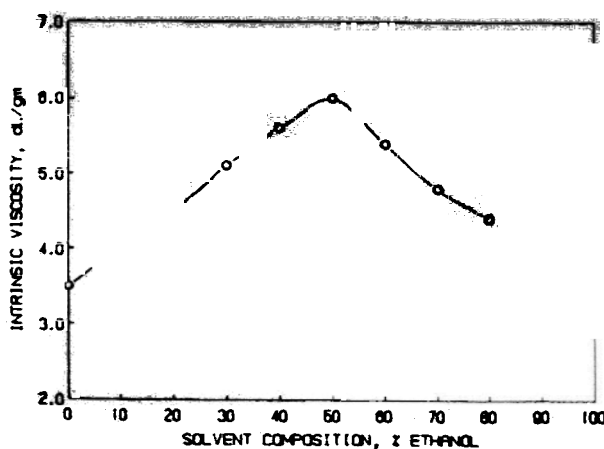


Fig. 5. Intrinsic viscosity of HMHEC as a function of solvent composition.

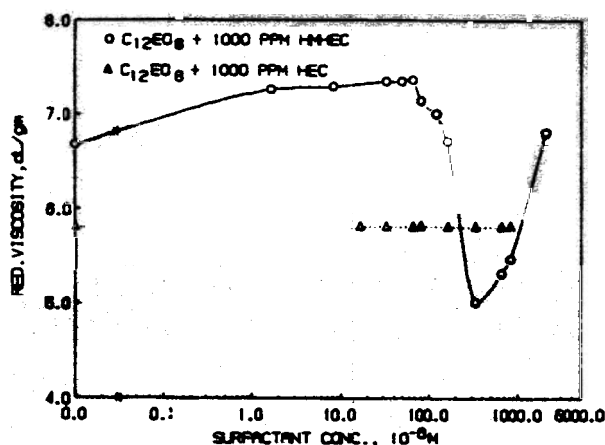


Fig. 6. The reduced viscosity of HEC and HMHEC solutions (1000 ppm) as a function of added $C_{12}EO_8$ concentration.

contrast to the above the viscosity of HEC solution is unaltered by the addition of the surfactant.

The reduced viscosity is a function of hydrodynamic volume, polymer-polymer interaction and polymer-solvent interaction [9]. Since the solvent power of the water is not greatly affected by the presence of the surfactant, the changes in reduced viscosity can be considered to be due to the changes in the hydrodynamic volume of the polymer molecule and the polymer-polymer interactions. In the dilute polymer concentration region the changes in the hydrodynamic volume are more significant than inter-polymer interactions and the variation in viscosity reflects the structural changes of the polymer. The low viscosity is the result of the compact polymer structure stabilized through the intra-molecular association of the hydrophobic groups on the polymer. Hence, the initial increase in viscosity can be attributed mainly to chain expansion due to the surfactant binding on polymer and the resultant less compact structure. This chain expansion is similar to that observed for HMHEC in ethanol-water mixed solvent systems. In the region of the c.m.c. of the surfactant, the bound surfactant molecules on the same chain associate to form a highly compact structure. The minimum obtained in Fig. 6 is the result of this intra-molecular (associated) polymer structure and the surfactant concentration ($3.26 \cdot 10^{-4} \text{ mol l}^{-1}$, $C_{12}EO_8$) here corresponds to the onset of free micelles in the system (see Fig. 4). Further increase in the viscosity in the micellar range may be due to the dissolution of the hydrophobic groups in micelles which reduce their association or the bridging of the polymer chain through micelles. The constant viscosity observed for the HEC- $C_{12}EO_8$ system implies a low degree of binding of the polymer with the individual surfactant molecules or its micelles.

Figure 7 shows the reduced viscosity of HMHEC as a function of its concen-

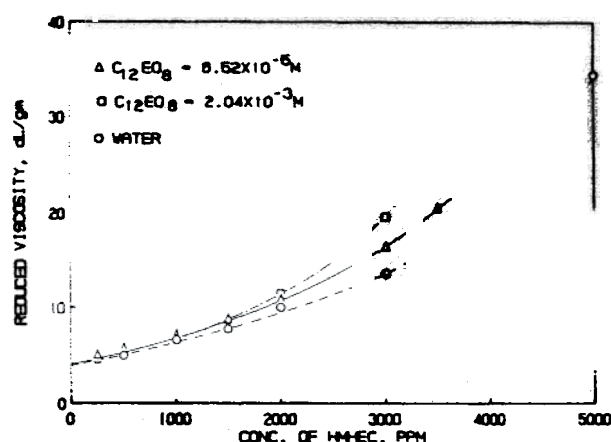


Fig. 7. The reduced viscosity of HMHEC as a function of its concentration in water and at two $C_{12}EO_8$ concentrations.

tration at two $C_{12}EO_8$ concentrations. The data show that at higher polymer concentrations the viscosities increase nonlinearly with polymer concentration. The values are considerably higher than those of pure polymer solutions in water at all added surfactant concentrations suggesting a polymer concentration dependent inter-polymer association.

Polymer-anionic surfactant interaction (HMHEC-SDS)

Interactions between HMHEC and SDS are rather marked. Addition of SDS to the polymer solution increased the viscosity initially as in the case of the nonionic surfactant; at concentrations above $5 \cdot 10^{-5} \text{ mol l}^{-1}$ SDS the polymer was observed to precipitate. However, the polymer redissolved at surfactant concentrations above $5 \cdot 10^{-3} \text{ mol l}^{-1}$ SDS. The reduced viscosities obtained after redissolution were very much lower than that observed for the polymer in water.

The observed behavior for HMHEC-SDS is very much different from that of many other uncharged polymer/ionic surfactant systems [8]. Binding of ionic surfactants on uncharged polymers usually leads to the formation of polyelectrolyte type complexes resulting in increased polymer dissolution and solution viscosity. This behavior has been confirmed by various investigators [10-12] for polyethyleneoxide-sodium dodecyl sulphate (PEO-SDS), polyvinylalcohol-sodium dodecyl sulphate (PVOH-SDS) and polyvinylacetate-dodecylbenzene sulphonate (PVAc-DDBS) systems. The hydrophobic groups of surfactant molecules in the above systems are normally considered to associate with polymers with the exposed ionic groups of the surfactant essentially increasing the charge density on the polymer. The large increase in solution viscosity is attributed to the expansion of the polymer coil owing to

possibly due to the fact that at high polymer concentrations, the polymer bound surfactant molecules are insufficient in number to form micelles individually. Under these conditions two hydrophobic microdomains from different polymer chains can rearrange to form micelles yielding a cross-linked polymer structure.

CONCLUSIONS

The alkyl groups of hydrophobically modified hydroxyethylcellulose (HMHEC) associate to form micelle-like hydrophobes in water. Fluorescence probing showed strong interactions between HMHEC and surfactants possibly at the hydrophobic sites of the polymer. Polymer-nonionic surfactant interactions lead to changes in polymer structure in dilute solutions while inter-polymer-polymer association is enhanced by the surfactant in concentrated polymer solutions. SDS, the ionic surfactant, at concentrations above its c.m.c., reduces the inter-polymer association through micelle formation around hydrophobic groups. The presence of a miscible organic solvent also reduces inter-polymer association by preferential solvation of the hydrophobic groups.

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