Interactions between Water-Soluble Cellulose Derivatives and Surfactants. 1. The HPMC/SDS/Water System

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ABSTRACT: The system hydroxypropyl methyl cellulose (HPMC)/sodium dodecyl sulfate (SDS)/water has been investigated over an extended composition interval from infinite dilution to a polymer concentration above the critical overlap concentration (c^*) and a surfactant concentration up to ~3 times the normal critical micelle concentration (cmc). The aim has been to characterize the redistribution (adsorption) of surfactant to the polymer and to investigate the system properties as a function of this adsorption. Several methods such as viscometry, equilibrium dialysis, cloud point determinations, dye solubilization, and fluorescence spectroscopy have been utilized. The onset of adsorption begins at ~4.3 mM, and then it increases as an increasingly cooperative phenomenon to a saturation maximum in a region below the normal cmc (~8 mM). This maximum approaches the normal cmc as the polymer concentration approaches zero. SDS adsorbs in a cooperative manner in the form of clusters, the average aggregation number (N) of which decreases with decreasing polymer concentration from ~50 for 0.2% HPMC to 20−25 at infinite dilution. The solubilization capacity of the HPMC/SDS/water system is somewhat less than previously reported for the ethyl hydroxyethyl cellulose/SDS/water system. Important rheological effects (high viscosity) are observed in a fairly limited composition range beginning at the onset of adsorption and ending long before adsorption saturation is reached. The maximum capacity of adsorption averaged over the entire polymer chain is found to be of the order of one adsorbed amphiphile molecule per polymer monomer unit.

Introduction

Cellulose derivatives and other water-soluble polymers play an important role in many technical applications and especially in pharmaceutical formulations. Here they may serve as part of a regulating system for the release rate, as stabilizers in emulsions, as a neutral substance to provide adequate flow properties, as an adsorbent for the drug, and so on. Many drugs are of an amphiphilic nature, and hence, the general physicochemical problem of amphiphile/polymer interaction is important. For the specific system ethyl hydroxyethyl cellulose (EHEC)/sodium dodecyl sulfate (SDS)/water, several investigations[1−5] have treated this problem and a fairly deep understanding has been achieved. However, the generality of the observations needs to be tested, and hence, a set of pharmaceutically important polymers has been selected. In this paper, the properties of a system containing hydroxypropyl methyl cellulose (HPMC) will be discussed. In a forthcoming publication, similar systems containing hydroxypropyl cellulose (HPC) and methyl cellulose (MC) will be treated. Important differences between the various cellulose derivatives have been identified, which necessitates fairly general studies before a meaningful comparison can be made.

The most important aspects of the interaction phenomenon are the degree of redistribution (adsorption) of amphiphile with respect to polymer, the hydrodynamic interaction obtained (for instance, enhanced viscosity), the type and size of adsorption clusters formed, the capacity of such clusters to solubilize other (lipophilic) compounds, and the influence of temperature on the system properties.

In the present paper, such aspects will be discussed and in particular results will be presented on rheological properties, thermodynamic interaction, phase behavior as a function of temperature, size of clusters, and capability to adsorb hydrophobic (dye) additives for the HPMC/SDS/water system at 20 °C as a function of surfactant concentration up to well above the critical micelle concentration (cmc) point and for polymer concentrations up to above the critical overlap concentration (c^*).

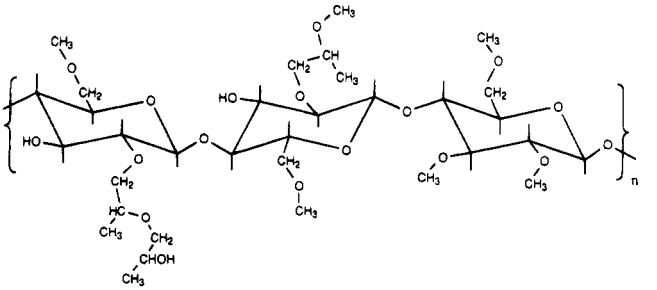

Figure 1. Possible structure segment in HPMC with $MS_{hydroxypropyl} = 1.0$, $DS_{methyl} = 2.0$, and degree of polymerization (DP) = $3n$.

Experimental Section

Materials. Hydroxypropyl methyl cellulose (trade name Methocel E4 EP; $DS_{methyl} \approx 2$, $MS_{propyleneoxide} \approx 0.4$) with a weight-average molecular weight (M_w) of ~3.0×10^5, a polydispersity index (M_w/M_n) of 2.2 as determined from size exclusion chromatography experiments (with LALLS and RI detection), and an intrinsic viscosity, [η], of 740 mL/g as determined from viscometry[6] was obtained from Colorcon Ltd., West Point, England. A typical HPMC structure is shown in Figure 1. The cloud point (CP) of this fraction of HPMC was determined to 55 °C for a 0.5% (w/w) aqueous solution by a method described previously.[2] After heating the samples above the clouding temperature, the value of CP recorded was the temperature when the last visible sign of clouding disappeared upon cooling.

The standardized procedure adopted to make a well-defined aqueous stock solution of a cellulose derivative like HPMC is described in a previous paper.[1] The stock solution of HPMC was dialyzed in tube membranes (Spectra/Por, Spectrum

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Medical Ind., LA) against Milli Q water (Millipore) for 1 week to remove salts and other low molecular weight material. Finally, the stock solution was filtered through 0.8 μm filters (Millex-AA, Millipore, SA, Molsheim, France) to remove undissolved substances, microgels, and dust particles before the concentration was determined by drying the samples to constant weight at 105 °C.

All HPMC/SDS solutions in this study were prepared by weighing the required amounts of the HPMC stock solution into appropriately diluted SDS stock solutions. This was done at least 24 h before experiments were performed or any further additive (benzophenone or Oil Orange SS) was added in order to reach equilibrium and to allow any time-dependent effect to settle.[2] HPMC concentrations are expressed in percent by weight (with good precision equal to grams per 100 mL). SDS concentrations are calculated as moles per 1000 g of solvent (molal), but since all solutions are dilute they will be given on the molar scale.

Analytical grade sodium dodecyl sulfate was obtained from Merck, Darmstadt, Germany, the radioactive SDS (^{35}S) was obtained from Amersham, England, benzophenone (+99%) from Aldrich-Chemie, Steinham, Germany, and Oil Orange SS (*o*-toluenazo-β-naphthol) from Tokyo Kasei Inc., Tokyo, Japan; they were all used as supplied. Pyrene (+98%) was obtained from Acros Chimica, Geel, Belgium, and twice purified by recrystallization from absolute ethanol. In this study, all solutions were prepared with Milli Q water as solvent.

Viscosity Measurements. The viscometric measurements on the HPMC/SDS/water solutions were carried out in ordinary Ostwald capillary viscometers (solvent flow time ~100 s) which were immersed in a water thermostat. Viscometric data were converted to reduced specific viscosity (η_{sp}/c) where c is the polymer concentration and η_{sp} is defined by

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 \quad (1)$$

Here η and η_0 are the viscosities of solution (HPMC/SDS/water) and solvent (SDS/water), respectively; i.e., the system was treated as a quasibinary one. Extrapolating η_{sp}/c to zero polymer concentration gives the intrinsic viscosity [η], using the expression

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c + \ldots \quad (2)$$

where higher terms have been omitted and k_H (Huggins constant) is a hydrodynamic measure of the intensity of the polymer/polymer interaction.

Densities were determined in a digital densitometer DMA 02C from Anton Paar K.G., A-8054 Graz, Austria, according to Kratky et al.[7]

Equilibrium Dialysis. The equilibrium dialysis experiments were carried out at 20 °C between HPMC and SDS solutions, the SDS solution containing a small amount of radioactively labeled SDS with an activity of ~25 000 dpm/mL. The experiments were performed in the type of cell used previously,[3,4] which is made of two compartments separated by a membrane (Spectra/por, M_w cutoff 12 000−14 000). The cells were rinsed throughly with deionized and Milli Q water before use. After the water had been removed, the HPMC and the SDS solutions were filled into their respective cell compartments. Each experiment was run in duplicate in two parallel cells. Preliminary results indicated that equilibrium was established after 48 hs, but as a precaution, the dialysis cells were allowed to stand for 7 days. The concentrations of DS^- ions in the HPMC/SDS and the SDS solutions, respectively, were determined by scintillation counting. Test experiments indicated that the presence of HPMC did not cause an extinction of the scintillation.

Dye Solubilization Measurements. Solubilization of the dye Oil Orange SS was studied by determination of the absorbance spectrophotometrically at 495 nm. The instrument used was a Beckman DU-68 spectrophotometer. Aqueous solutions of HPMC/SDS were prepared as described above. An excess of dye was then added, and the solutions were equilibrated for 3 days at 20 °C (room temperature) on a rotating table (Infors, AG CH-4103, Bottmingen, Germany). The excess of dye was then separated off by centrifugation and the absorbance of the supernatant determined, dilutions being performed for supernatants of absorbance greater than 1.3.

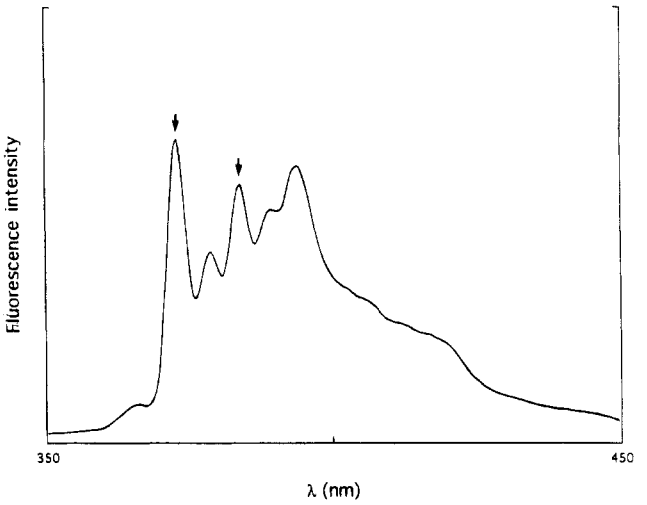

Figure 2. Emission spectra for pyrene in 20 mM SDS in water. Vibronic peaks 1 (λ = 373 nm) and 3 (λ = 384 nm) used in the determination of the hydrophobic index (I_1/I_3) and (I^o/I) ratios are marked with arrows.

Fluorescence Measurements. Steady-state fluorescence spectra were recorded on a Hitachi F-4000 fluorescence spectrophotometer in the uncorrected spectrum mode. Emission spectra (λ = 350−450 nm) for pyrene at 20 °C were obtained with the excitation wavelength set to 334 nm and the bandwidths set to 3.0 nm for excitation and 1.5 nm for emission. HPMC/SDS solutions for spectroscopic analysis contained a pyrene (probe) concentration less than 10^{-6} M (filtered saturated water solution), and the benzophenone (quencher) concentration was varied from 0 to 0.2 mM. The preparation procedures of HPMC/SDS solutions for the quenching experiments were similar to the ones adopted for the EHEC/SDS/water system as described in a previous paper.[3] A portion of the HPMC/SDS/water solution containing pyrene was saturated with benzophenone by sonication. Aliquots of the benzophenone-saturated solution were added to HPMC/SDS/water (including pyrene) solutions to cover the desired benzophenone concentration range. Benzophenone concentrations were determined spectrophotometrically at λ = 255 nm, dilutions being performed for solutions of absorbance greater than 1.3.

A fluorescence quenching technique was used in the determination of average aggregation numbers, N.[8,9] Ratios of fluorescence intensities in the absence (I^o) and presence (I) of quencher were calculated as an average between the intensity ratios at the first vibronic peak (λ = 373 nm) and at the third vibronic peak (λ = 384 nm) in the pyrene emission spectra (see Figure 2). Molar micelle concentrations, [micelles], were determined from plots of the logarithmic intensity ratio, ln(I^o/I) versus the quencher concentration, [Q], according to the method originally developed for anionic micelles (SDS) by Turro and Yekta[8] (but since then also extended to cationic and nonionic micelles[10]). This method has also been found suitable for the determination of N in uncharged polymer/SDS/water systems[3,9,11-14] and seems to give reliable results when the experimental conditions are chosen with care.[15] This means that a highly efficient probe/quencher pair is employed, the fraction of both probe and quencher in the aqueous phase should be very low, low probe concentration, and the micelles (clusters) should be relatively small (N < 100). N was finally calculated by dividing the amount of amphiphile redistributed—as determined in the equilibrium dialysis experiments—by the micelle concentration from the quenching measurements.[3]

The hydrophobic index, I_1/I_3, was taken as the ratio between the intensities at the first (λ = 373 nm) and at the third (λ = 384 nm) vibronic peaks in the pyrene emission spectrum.[16-18]

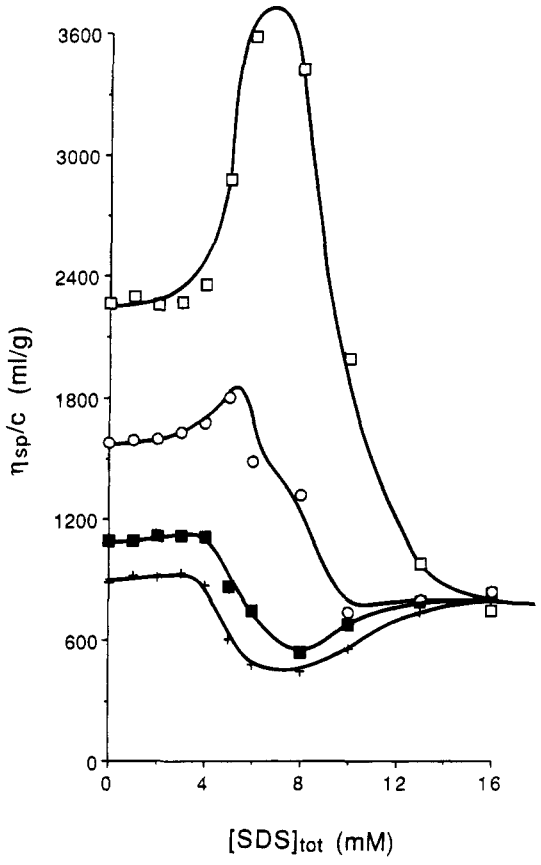

Figure 3. Reduced specific viscosity, η_{sp}/c, at 20 °C for the HPMC/SDS/water system as a function of the total SDS concentration and for different HPMC concentrations: (+) 0.05, (■) 0.10, (○) 0.20, and (□) 0.30% HPMC.

Results and Discussion

Several methods such as viscometry, equilibrium dialysis, dye solubilization, CP determinations, and fluorescence spectroscopy have been utilized to characterize the interaction between the nonionic cellulose derivative HPMC and the anionic surfactant SDS in this study. The experiments were performed for selected values of polymer concentrations in the range 0–0.3% and for surfactant contents from 0 to ~20 mM, and all results have been obtained at 20 °C.

In Figure 3 are shown the results from viscosity measurements on the HPMC/SDS/water system, here presented as reduced specific viscosity, η_{sp}/c, and where for each set of measurements the polymer concentration has been kept constant while the total SDS concentration varied. The viscosity profile can be classified into three regions: (region I) At low total SDS concentrations ($[SDS]_{tot}$), up to ~4 mM, the reduced specific viscosity is quite insensitive to the amount of SDS present and no interaction between SDS and HPMC is detected. (region II) In this middle range of $[SDS]_{tot}$ (4–12 mM), the reduced specific viscosity becomes very sensitive to the amount of SDS present. The curves for the higher polymer concentrations exhibit a pronounced maximum in η_{sp}/c while the lowest pass through a minimum. (region III) At $[SDS]_{tot}$ higher than 12 mM, the reduced specific viscosity becomes rather insensitive to changes in SDS concentration and all polymer concentrations approach the same value of η_{sp}/c.

Any change in cloud point of a polymer/water system due to the addition of a third component such as SDS can be referred to alterations of interaction and changes of the hydrophobic/hydrophilic balance in the system.

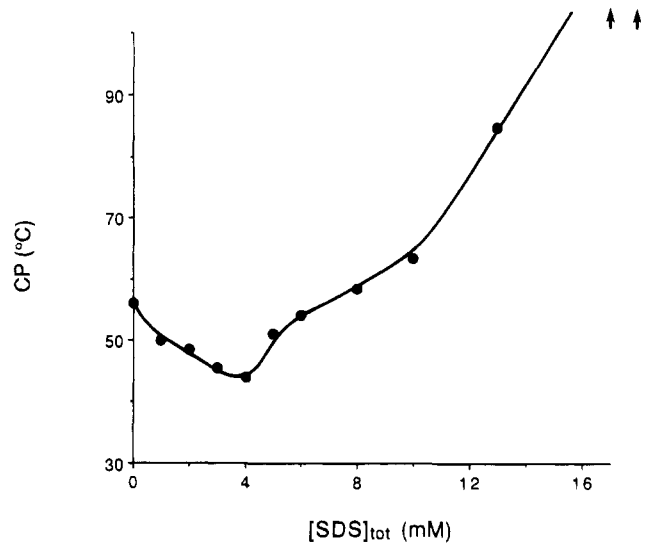

Figure 4. Cloud point versus the total SDS concentration for aqueous 0.30% HPMC/SDS solutions.

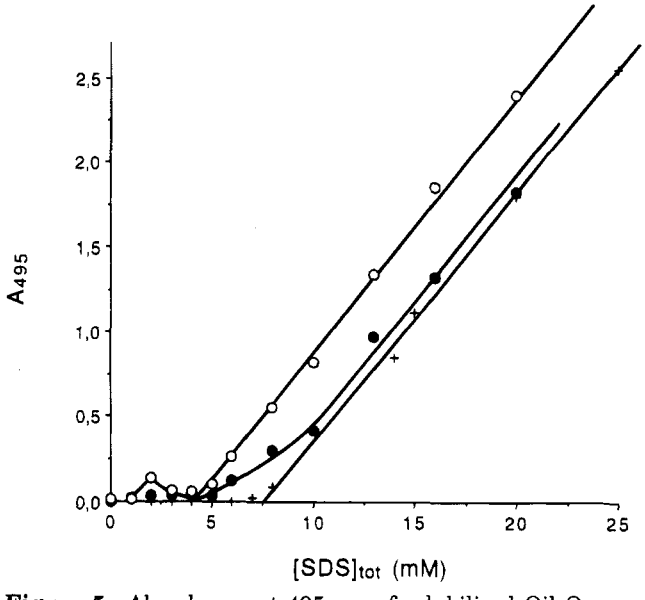

Figure 5. Absorbance at 495 nm of solubilized Oil Orange SS, A_{495}, as a function of the total SDS concentration in aqueous HPMC/SDS solutions at 20 °C: (○) 0.20, (●) 0.05, and (+) 0% HPMC.

CP determinations on aqueous salt free HPMC solutions are presented in Figure 4 as a function of SDS concentration. The addition of SDS induces, up to 4 mM, a lowering of CP, but when $[SDS]_{tot}$ is further increased, CP increases to above 100 °C. The minimum in CP (at $[SDS]_{tot}$ = 4 mM) correlates with the onset of change in viscosity (see above) and indicates the beginning of increased interaction between HPMC and SDS. Some related systems are reported to exhibit a similar minimum in CP (and solubility) with increased surfactant concentration[5,14,19] but others do not.[2,19] The explanation to this minimum has been discussed in terms of conformational changes of the polymer.[20] There has also been reported a synergistic surfactant/electrolyte effect[21] that gives an increased CP minimum with increased amount of electrolyte added.

Figure 5 presents the primary results of the solubilization of the dye Oil Orange SS given as a plot of the absorbance at 495 nm, A_{495}, versus the total SDS concentration for the binary SDS/water system and for the ternary HPMC/SDS/water system. The cmc for SDS

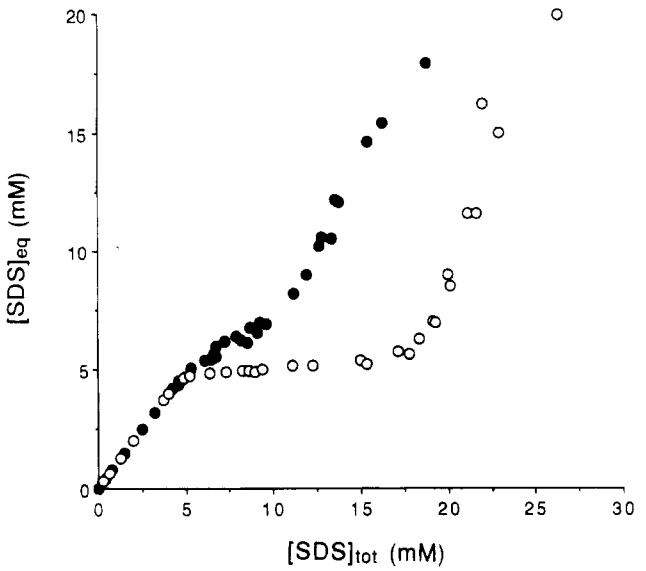

Figure 6. Equilibrium dialysis results at 20 °C in the HPMC/SDS/water system plotted as the equilibrium SDS concentration versus the total SDS concentration: (○) 0.20 and (●) 0.05% HPMC.

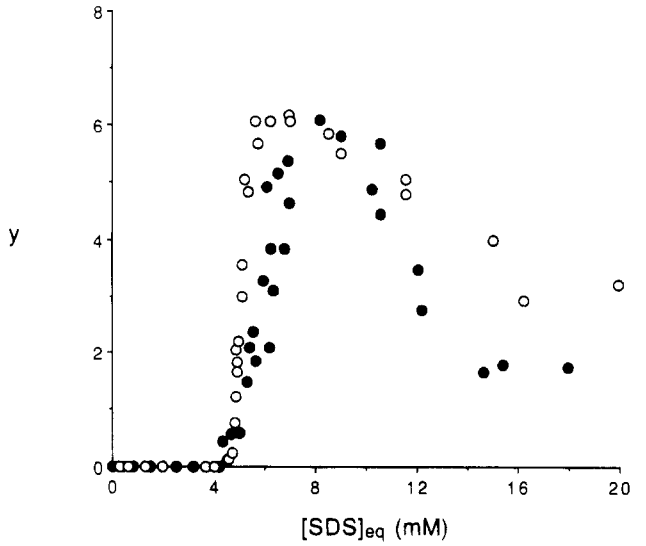

Figure 7. Equilibrium dialysis results at 20 °C presented as a plot of y (millimoles of SDS bound per gram of HPMC) as a function of the equilibrium SDS concentration for aqueous HPMC/SDS solutions: (○) 0.20 and (●) 0.05% HPMC.

in water is by regression calculation determined to be 7.5 mM, in fair agreement with the literature.[22] This number also agrees with the sharp decrease in hydrophobic index (I_1/I_3) of the SDS/water system (see below). The solubilization in aqueous 0.20% HPMC solutions begins at a sharp "footpoint" (CAC) of $[SDS]_{tot}$ equal to 4.3 mM while A_{495} for the lower HPMC concentration curves more smoothly from the same origin upward. The value of CAC is in good correlation with the onset of change of viscosity (cf. Figure 3). There exists a difference in solubilization capacity between the two polymer concentrations which qualitatively can be seen simply by comparing the absolute values of A_{495} of each curve. A relation defining the solubilization capacity, β, of a micellar system was presented in a previous paper[3]

$$\beta = A_{495}/(N[\text{micelles}]_{tot}) \quad (3)$$

where A_{495} is the absorbance at 495 nm, N is the average aggregation number of all micelles (clusters), and $[micelles]_{tot}$ is the total micelle (cluster) concentration present in the solution. The curve for 0.20% HPMC gave an average value of $\beta = 171\ M^{-1}$, which is ~20% higher than the average value of 0.05% HPMC but slightly lower than the reported β for 0.20% EHEC (fraction CST-103, $\beta = 183\ M^{-1}$).[3]

The polymer properties change with the amount of redistributed (bound) surfactant. The equilibrium dialysis experiments provide qualitative information about this redistribution of SDS to HPMC as a function of composition. Figure 6 shows the SDS concentration in equilibrium with the polymer, $[SDS]_{eq}$, as a function of the total SDS concentration, $[SDS]_{tot}$. Figure 7 presents a plot of the amount of SDS redistributed to HPMC, y, as a function of $[SDS]_{eq}$ for two HPMC concentrations (0.20 and 0.05%). $[SDS]_{eq}$, $[SDS]_{tot}$, and the redistribution parameter y (millimoles of SDS adsorbed per gram of HPMC) have been calculated according to the model described in a previous paper.[1] The calculations include a *correction for the Donnan effect*. $[SDS]_{eq}$ is thus the true value of the molar concentration of surfactant in equilibrium with polymer. The mass balance equation then becomes

$$[SDS]_{tot} = [SDS]_{eq} + c_p y \quad (4)$$

where c_p is the polymer concentration expressed as grams per liter. (For simplicity, the numerical value of y will, in this discussion and in the figures, be expressed as millimoles of SDS adsorbed per gram of HPMC.)

The equilibrium dialysis results presented in Figures 6 and 7 can be divided into three parts: (I) $[SDS]_{tot}$ = 0–4.4 mM SDS; at low SDS concentrations there is no redistribution of surfactant to the polymer. (II) At medium SDS concentrations, the redistribution starts abruptly at a specific concentration (4.4 mM), the footpoint (often referred to as CAC), and then it increases almost linearly with $[SDS]_{tot}$ to a maximum. The footpoint is independent of polymer concentration, and it reveals itself as the onset of increase in y in Figure 7 or as a change to smaller slope when $[SDS]_{eq}$ is plotted versus $[SDS]_{tot}$ in Figure 6. (III) The calculated redistribution, y, passes through a maximum and then decreases (see Figure 7). This concentration corresponds to an increase in the slope of the curves in Figure 6. It has been suggested that the maximum in adsorption is connected to saturation of the polymer and/or onset of formation of normal micelles.[3] Similar maxima in the adsorption isotherms have been reported for the EHEC/SDS/water system,[1,3] the PVP/SDS/water system,[23] the PVA/SDS/water system,[23] and the MC/SDS/water system.[24,25]

It should be observed that there is a difference concerning the SDS redistribution between the high and the low polymer concentrations, 0.20 and 0.05% HPMC, respectively. The intensity of interaction (degree of cooperativity) is higher for the higher polymer concentration, which is seen, for example, as an almost constant level of $[SDS]_{eq}$ with $[SDS]_{tot}$ above CAC in Figure 6. It is sometimes assumed that all surfactant in excess of CAC, independent of polymer concentration, is adsorbed until saturation of the polymer.[26] Our dialysis results in the HPMC/SDS/water system contradict this assumption and show that for the system in question it is correct only for sufficiently high polymer concentrations (see Figure 6).

By combining the results from viscometry presented in Figure 3 and equilibrium dialysis in Figures 6 and

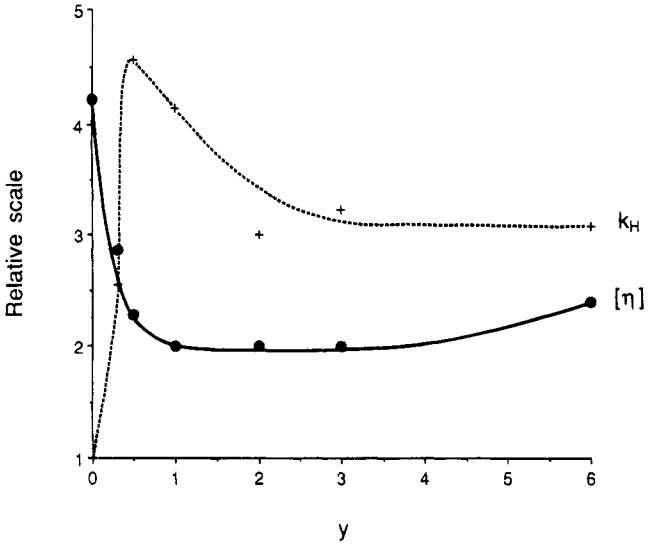

Figure 8. Intrinsic viscosity, $[\eta]$, and Huggins constant, k_H, in the HPMC/SDS/water system as a function of increasing values of y (millimoles of SDS bound per gram of HPMC). These results have been calculated through a combination of the viscosity results in Figure 3 with the equilibrium dialysis results in Figures 6 and 7, and they are valid at 20 °C. The ordinate scale is given in relative units and the following conversion factors apply: Multiplication by 175 gives $[\eta]$ (in mL/g) and by 0.54 gives k_H in "real" dimensionless units.

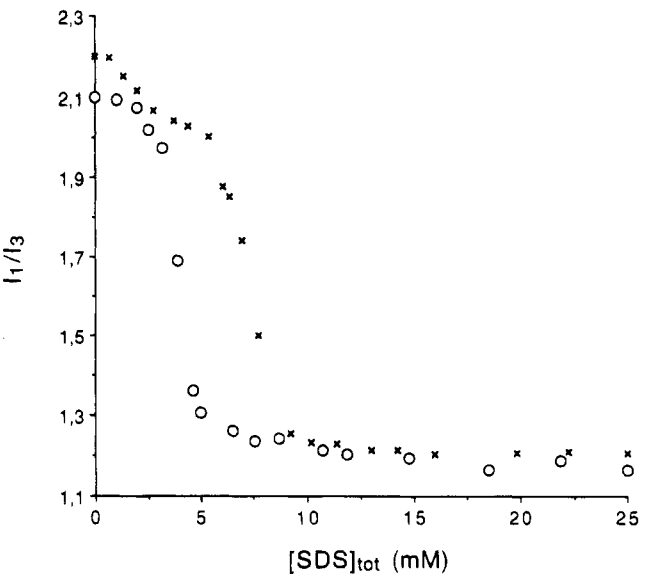

Figure 9. Hydrophobic index (I_1/I_3) for pyrene (<10^{-6} M) luminescence in aqueous HPMC/SDS solutions as a function of the total SDS concentration at 20 °C: (○) 0.20 and (×) 0% HPMC.

7, it is possible to transform the viscosity data to sets of values of the reduced specific viscosity for constant values of y as a function of polymer concentration by a procedure used in a previous paper.[1] From such a plot, the intrinsic viscosity, $[\eta]$, and Huggins constant, k_H, of HPMC can be extracted for a constant SDS adsorption, i.e., constant y. Figure 8 presents $[\eta]$ and k_H as functions of y. The intrinsic viscosity shows a rapid decrease to half its initial value when y is increased from 0 to 1.5 mmol of SDS bound per gram of HPMC and then it passes a shallow minimum after which a slight increase of $[\eta]$ sets in. Huggins constant, which is a measure of polymer/polymer interaction, passes through a maximum at $y \approx 0.5$ and then declines to an almost constant level at higher values of y. The qualitative picture of a shrinking polymer coil in dilute solution as the surfactant is adsorbed with a high degree of polymer/polymer attractive interaction is similar to the model described for the EHEC/SDS/water system.[1] Results have also been reported for the MC/SDS/water system showing a reduction and minimum in $[\eta]$ as the SDS concentration is increased.[24]

The ratio I_1/I_3 of the first (λ = 373 nm) and third (λ = 384 nm) vibronic peaks in the pyrene emission spectrum (see Figure 2) is known to be a monitor of the pyrene microenvironment polarity.[16-18] A decrease in I_1/I_3 reflects the transfer of pyrene from a hydrophilic to a more hydrophobic microenvironment. It is well documented that this type of change is connected to micelle (cluster) formation both in the absence[16,17] and presence of polymer.[14,27,28]

From Figure 9, where the hydrophobic index (I_1/I_3) is given for water solutions containing either only surfactant (SDS) or both surfactant and polymer (HPMC), it is possible to determine a value of cmc for the binary SDS/water system and a value of CAC for the ternary HPMC/SDS/water system. The values of cmc and CAC were 7.0 and 3.9 mM, respectively, and were taken as the inflection points of the sharply decreasing parts of the plots of I_1/I_3 versus $[SDS]_{tot}$ in Figure 9. The onset of interaction (at CAC) between HPMC and SDS is sampled at slightly lower surfactant concentration (although in good correlation) by the hydrophobic index as compared to the other methods used in this study. This fact has been observed and reported earlier for related systems.[3,16,29] The same observation holds for the cmc determination by I_1/I_3 since the normal cmc of aqueous SDS at 20 °C as determined by many classical techniques is often found in an interval 8.0–8.3 mM.[2,22]

One should observe the slightly lower I_1/I_3 value (indicating a less polar environment of pyrene) for the aqueous HPMC solution compared to pure water and also the identical value of I_1/I_3 at high $[SDS]_{tot}$ for both systems, indicating that the interiors of the polymer-bound SDS clusters and normal SDS micelles have almost equal polarity.[3] It was also stated, in a recent NMR study on the HPMC/SDS/water system, that the structure of the polymer-bound clusters is very similar to ordinary micelles.[30]

The average aggregation number, N, of SDS micelles (clusters) formed on HPMC in aqueous solutions was determined by a combination of the steady-state fluorescence quenching method proposed by Turro and Yekta[8] and equilibrium dialysis experiments and using the same methodology as had previously been applied to the EHEC/SDS/water system.[3] The total micelle molarity, $[micelles]_{tot}$, in the HPMC/SDS/water system was determined from plots of the logarithmic intensity ratio, $\ln(I^o/I)$, versus the quencher concentration, [Q], according to the expression

$$\ln(I^o/I) = [Q]/[micelles]_{tot} \quad (5)$$

where I^o and I are the fluorescence intensities in the absence and presence of quencher (Q), respectively, and the inverse slope was equal to $[micelles]_{tot}$. For SDS concentrations close to and above cmc, there will also be normal (not polymer bound) SDS micelles present and the total micelle molarity then consists of two parts. If $[micelles]_p$ denotes the molarity of polymer-bound micelles (clusters) and $[micelles]_n$ denotes normal micelles, we have

$$[\text{micelles}]_{tot} = [\text{micelles}]_p + [\text{micelles}]_n \quad (6)$$

From the equilibrium dialysis results presented in Figures 6 and 7, data are available of the redistribution "situation", i.e., the total SDS concentration, $[SDS]_{tot}$, and the equilibrium SDS concentration, $[SDS]_{eq}$, for a certain HPMC concentration as defined above. Average aggregation numbers of normal micelles, N_n, were determined in separate fluorescence quenching experiments and agreed with literature data.[31,32] When $[SDS]_{eq}$ > cmc is the molarity of normal micelles, $[\text{micelles}]_n$, given by

$$[\text{micelles}]_n = ([SDS]_{eq} - \text{cmc})/N_n \quad (7)$$

The average aggregation number of polymer-bound SDS clusters, N_p, was finally calculated from the following expression

$$N_p = ([SDS]_{tot} - [SDS]_{eq})/[\text{micelles}]_p \quad (8)$$

Combining the values of $[\text{micelles}]_{tot}$, $[SDS]_{tot}$, $[SDS]_{eq}$, and N_n, the average aggregation number of polymer-bound SDS clusters, N_p, has been calculated according to eq 8. The results are found in Table 1. To illustrate the effects observed, the values of N_p have been plotted as a function of $[SDS]_{eq}$ and $[SDS]_{tot}$ (see Figures 10 and 11, respectively), and the values of $[\text{micelles}]_{tot}$ and $[\text{micelles}]_p$ have been plotted versus $[SDS]_{eq}$ (see Figure 12). It is seen in Figures 10 and 11 that the values of N_p show the same footpoint (CAC) as the equilibrium dialysis (see above) after which there is a rapid increase in N_p to a weakly developed maximum after which N_p levels off or slightly decreases. The higher HPMC concentration (0.20%) gives larger clusters than the low concentration (0.05%), as has also been reported for the EHEC/SDS/water system.[3] For all compositions it is found that $N_p < N_n$ within the composition range investigated and the experimental values of N_p should be compared with $N_n \approx 60-70$ as has been reported for normal SDS micelles.[8,13,31,32] In Figure 12 the values of $[\text{micelles}]_{tot}$ and $[\text{micelles}]_p$ are presented as functions of $[SDS]_{eq}$ for two concentrations of HPMC (0.20 and 0.05%). The cluster concentration increases rapidly from CAC up to the point where normal micelles form ($[SDS]_{eq}$ = cmc) for the 0.20% HPMC solution while the more diluted polymer solution shows an almost constant cluster concentration in the same interval. This means that the number of cluster binding "sites" on the polymer increases with increasing SDS redistribution (up to cmc) for the high HPMC concentration but is almost constant for the dilute polymer solution. The concentration of micelles bound to the polymer, $[\text{micelles}]_p$, decreases slightly for both HPMC concentrations when $[SDS]_{eq}$ > cmc and the formation of normal micelles (not polymer bound) begins. The polymer can for such concentrations solubilize its hydrophobic "sites" also in normal micelles (see discussion below). When $[SDS]_{eq}$ > cmc, the total micelle concentration, $[\text{micelles}]_{tot}$, approaches gradually for all polymer concentrations, an increase characteristic of the binary SDS/water system.

In Table 1 are given the numbers m (number of polymer-bound SDS monomers per glucose unit) and n (number of glucose units per polymer-bound SDS cluster), which have both been calculated from the experimental data of $[\text{micelles}]_p$, N_p, and an estimated average molecular weight for a glucose unit of HPMC (including substituents). The number m is an indicator of the amount of SDS that is bound to HPMC and can be compared with equilibrium dialysis data. It is seen that m increases from the footpoint up to approximately one SDS monomer per glucose unit. The number n defines the average distance between the clusters along the

Table 1. Summary of Experimental Data and Calculated Values

HPMC (%)	$[SDS]_{tot}$ (mM)	$[SDS]_{eq}$ (mM)	N_p	$[\text{micelles}]_p$ (mM)	$[\text{micelles}]_{tot}$ (mM)	m	n
0.20	6.00	4.80	10.2	0.117	0.117	0.1	74
	8.00	4.80	17.3	0.185	0.185	0.4	46
	10.00	5.00	28.8	0.174	0.174	0.6	49
	13.00	5.20	42.7	0.182	0.182	0.9	47
	16.00	5.50	51.0	0.206	0.206	1.2	42
	20.00	8.70	48.3	0.234	0.261	1.3	37
0.05	6.00	5.60	3.4	0.118	0.118	0.2	19
	8.00	6.30	16.3	0.104	0.104	0.8	21
	10.00	7.10	26.7	0.109	0.110	1.4	20
	13.00	10.70	22.1	0.104	0.162	1.1	21
	16.00	14.00	22.6	0.089	0.195	0.9	24
	20.00	18.00	30.3	0.066	0.228	0.9	33

[a] n, number of glucose units per polymer–bound SDS cluster; m, number of polymer–bound SDS monomers per glucose unit.

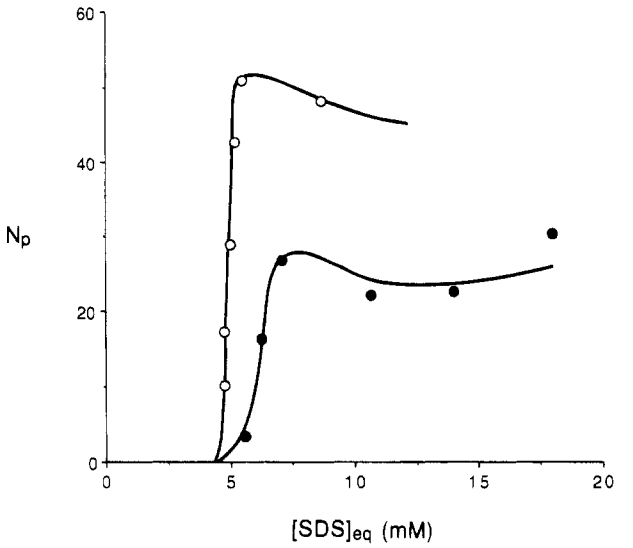

Figure 10. Average aggregation number of polymer-bound SDS clusters, N_p, as a function of the equilibrium SDS concentration at 20 °C: (○) 0.20 and (●) 0.05% HPMC.

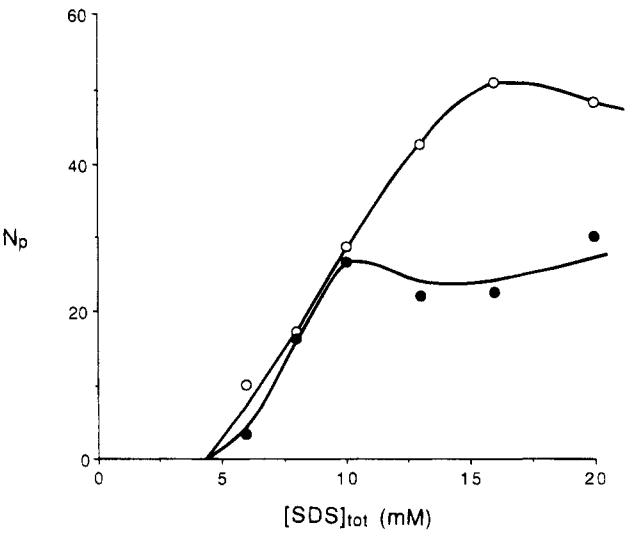

Figure 11. Average aggregation number of polymer-bound SDS clusters, N_p, as a function of the total SDS concentration at 20 °C: (○) 0.20 and (●) 0.05% HPMC.

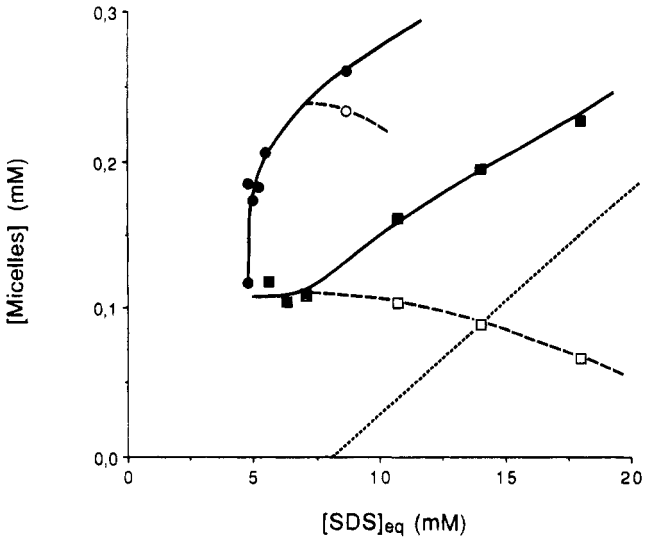

Figure 12. Total and polymer-bound cluster concentrations ($[micelles]_{tot}$ and $[micelles]_p$, respectively) as a function of the equilibrium SDS concentration for aqueous HPMC/SDS solutions at 20 °C. $[micelles]_{tot}$: (●) 0.20 and (■) 0.05% HPMC. $[micelles]_p$: (○) 0.20 and (□) 0.05% HPMC. The dotted line refers to an "ideal" reference situation in the binary SDS/water system assuming a fixed aggregation number of 65 and cmc = 8.2 mM.

HPMC backbone. There exists a clear difference in n between the two polymer concentrations. The clusters are closer to each other (and smaller) at the low HPMC concentration. This might be explained by the same model proposed for the EHEC/SDS/water system;[3] i.e., at the higher polymer concentrations the tendency by different polymer molecules to share a cluster should increase and both n and N_p should be large.

The main features of the HPMC/SDS/water system can be summarized in the following way (see Figure 13). When SDS is added to an aqueous solution of HPMC, no interaction is detected up to a specific concentration denoted critical adsorption concentration (CAC or footpoint). At this concentration, SDS starts to adsorb to the HPMC chain in a cooperative manner in the form of small micelles (clusters). By the different methods used in this study, the value of CAC is found to fall in the range 3.9–4.4 mM SDS, in accordance with previous reports on the same system,[14,30] and seems to be insensitive to polymer concentration. The adsorbed clusters increase in size with both polymer and surfactant concentration up to a certain limiting plateau value. There exists a pronounced difference between a solution very dilute ($c_p < c^*$) with respect to the polymer and a solution of higher concentration ($c_p \geq c^*$). The number of cluster binding "sites" on the polymer increases strongly as the adsorption begins and continues in the high polymer concentration regime in contrast to the dilute polymer regime where there is almost a constant number of "sites" (see Figure 12). At a high polymer concentration there is also a larger degree of cooperativity in the surfactant/polymer interaction as compared to a low polymer concentration, e.g., revealed by the difference in slopes of the adsorption isotherms seen in Figure 7. For the higher polymer concentrations, the clustering adsorption tends to become intermolecular in nature; i.e., one cluster is shared by two or more polymer molecules creating a three-dimensional network. This explains the high viscosity observed in Figure 3. In dilute polymer solutions, on the other hand, the clustering process is probably an intramolecular phenomenon which leads to shrinkage of the

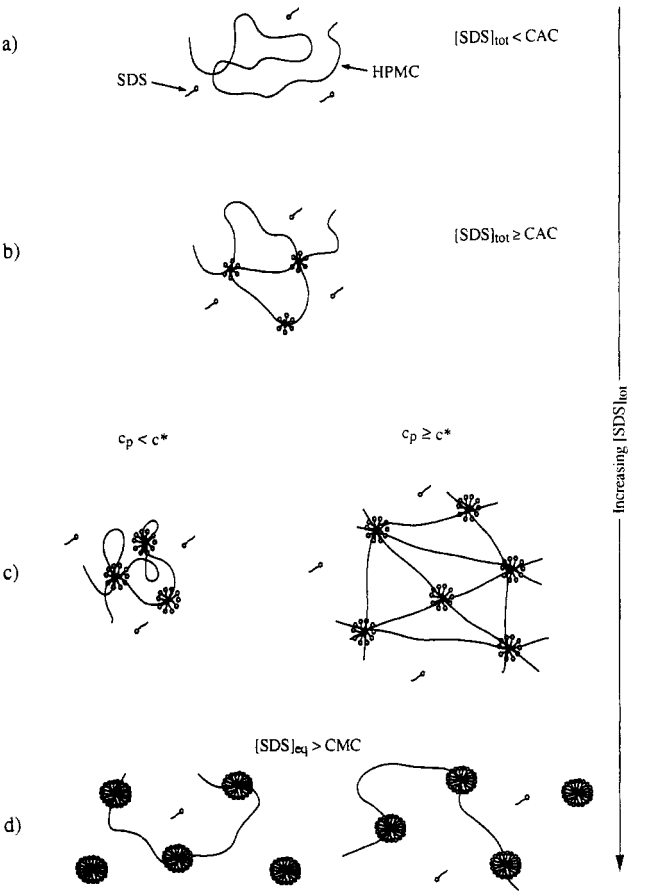

Figure 13. Schematic representation of the model proposed for the interaction between HPMC and SDS: (a) At low SDS concentrations, $[SDS]_{tot} < CAC$, there is no adsorption of SDS to the HPMC chain. (b) SDS starts to adsorb as clusters to the HPMC chain at $[SDS]_{tot} \geq CAC$. These polymer-bound SDS clusters grow in size as the SDS concentration is increased. (c) At low polymer concentration ($c_p < c^*$), there is an intramolecular clustering process operating which leads to shrinkage of the polymer coil while at higher polymer concentrations ($c_p > c^*$) the clustering process tends to become intermolecular in nature creating a three-dimensional network. (d) At high SDS concentrations, $[SDS]_{eq} >$ cmc; also normal micelles form into which HPMC may distribute.

polymer coil (reduction in intrinsic viscosity, see Figure 8) and a low solution viscosity (see Figure 3).

The redistribution of SDS to HPMC continues until "saturation" of the polymer. When more SDS is added, normal micelles begin to form. A particular polymer molecule may then solubilize its hydrophobic "sites" also in normal "free" micelles. This competition will favor the normal micelles as their relative number increases with increasing total SDS concentration and the networking tendency of the polymer solution will eventually be lost. This effect shows itself in Figure 3 as a low value of η_{sp}/c almost identical for all polymer concentrations at high total SDS concentrations.

Obviously the important rheological changes, giving rise to strongly enhanced viscosities, take place in a fairly limited composition range beginning at the onset of adsorption and ending long before adsorption saturation is reached. The maximum capacity of adsorption seems to be of the order of one adsorbed amphiphile molecule per polymer glucose unit.

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