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Carbohydrate Polymers 40 (1999) 293–298

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Microstructures formed in aqueous solutions of a hydrophobically modified nonionic cellulose derivative and sodium dodecyl sulfate: a fluorescence probe investigation

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Received 18 February 1998; received in revised form 30 March 1999; accepted 28 April 1999

Abstract

The association behavior of hydrophobically modified ethyl hydroxyethyl cellulose (HM-EHEC) and its interaction with the anionic surfactant sodium dodecyl sulfate (SDS) has been studied in the dilute concentration regime. Steady-state fluorescence probe techniques have been utilized to obtain microstructural information of the system properties and combined with macroscopic bulk information from equilibrium dialysis experiments in order to determine binding isotherms of SDS to HM-EHEC. HM-EHEC was found to self-associate and form polymeric micelles in semi-dilute aqueous solutions. c^* for the self-association process was determined to be approximately 0.4%. The microviscosity of the polymeric micelles is much higher, and the micropolarity slightly higher, than that of ordinary SDS micelles. The onset of interaction between HM-EHEC and SDS was evidenced by a simultaneous strong increase in microviscosity and decrease in micropolarity upon successive addition of SDS. There is a minor, noncooperative SDS binding to the HM-EHEC starting from low concentrations of SDS (< 5 mM) followed by a highly cooperative binding region at SDS concentrations ≥ 5 mM. The polymer–surfactant aggregates are rigid and hydrophobic with a maximum in microviscosity in the noncooperative binding region at a very low degree of SDS-adsorption.

Keywords: Ethyl hydroxyethyl cellulose; Sodium dodecyl sulfate; Fluorescence probe technique; Microviscosity; Micropolarity; Hydrophobically modified polymer

1. Introduction

The association between polymers and surfactants in aqueous solutions has attracted much interest during the last two decades and the topic has recently been reviewed (Brackman & Engberts, 1993; Goddard & Ananthapadmanabhan, 1993). The study of these systems is important both from an applied standpoint due to the numerous uses of these substances in a wide range of industrial fields, and from a fundamental point of view for obtaining a detailed knowledge about the structures formed and the mechanisms operating in the polymer–surfactant association. Nonionic cellulose derivatives and surfactants are today frequently used and combined as standard ingredients in a number of pharmaceutical formulations, cosmetics and food products and these types of systems have been specifically studied in this laboratory (Evertsson & Nilsson, 1997; Evertsson & Nilsson, 1998; Evertsson, Nilsson, Holmberg, & Sundelöf, 1996; Nilsson, 1995; Nilsson, Holmberg, & Sundelöf, 1995). A number of experimental methods have, over the years, been utilized for the detection of polymer–surfactant complexation and fluorescence probe techniques have proved to be a valuable tool for obtaining microstructural information (Winnik & Regismond, 1996). The generally accepted model for describing polymer–surfactant complexation involves a cooperative adsorption of surfactant molecules to the polymer, forming mixed micelles or clusters along the polymer backbone. Fluorescent probes have been used in this laboratory for the determination of the critical surfactant concentration where adsorption to the polymer starts (here referred to as c_1), the average aggregation number of the polymer–surfactant complexes (N_p) and the micropolarity and microviscosity within these complexes.

A relatively new class of polymers containing small numbers of hydrophobic substituents has been intensively studied in recent years. These so-called hydrophobically modified polymers (HMP) have a strong tendency for intra- or intermolecular hydrophobic self-association and

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0144-8617/99/$ - see front matter
PII: S0144-8617(99)00065-X

for interaction with surfactants (Dubin, Bock, Davies, Schulz, & Thies, 1994; Hansson & Lindman, 1996). The major part of the investigations made on HMP-systems deals with rheological aspects while the ones treating molecular aspects are more rare (Dualeh & Steiner, 1991; Magny, Iliopoulos, Zana, & Audebert, 1994; Nishikawa, Yekta, Pham, Winnik, & Sau, 1998; Nivaggioli, Tsao, Alexandrridis, & Hatton, 1995; Tanaka, Meadows, Philips, & Williams, 1990; Winnik, Ringsdorf, & Venzmer, 1991a; Winnik, Winnik, Ringsdorf, & Venzmer, 1991b; Yekta, Duhamel, Brochard, Adiwidjaja, & Winnik, 1993). Thuresson, Söderman, Hansson, and Wang (1996) studied semidilute solutions of a hydrophobically modified ethyl(hydroxyethyl)cellulose (HM-EHEC) and SDS and reported two regimes of surfactant adsorption: At first they reported a noncooperative surfactant adsorption with low aggregation numbers at low surfactant concentrations and secondly, a cooperative binding regime with higher aggregation numbers at elevated surfactant concentrations. This study presents the results of the association behavior between HM-EHEC and SDS in dilute aqueous solutions with a particular focus on microstructural information such as microviscosity, micropolarity and aggregation numbers obtained from steady-state fluorescence probe techniques which is combined, for comparative reasons, with macroscopic bulk information of surfactant binding isotherms obtained from equilibrium dialysis measurements.

2. Materials

Hydrophobically modified ethyl(hydroxyethyl)cellulose, HM-EHEC, fraction Bermocoll EHM-100, $M_w = 496\,800$ and $M_n = 116\,200$ as determined from SEC/LALLS/RI, molar substitution of ethylene oxide (MS_{EO}) = 2.0, degree of substitution of ethyl groups (DS_{Et}) = 0.8, degree of substitution of nonylphenol groups (DS_{NF}) = 0.007 (= 0.7% (mol/mol) nonylphenol groups per glucose unit), intrinsic viscosity ($[\eta]$) of 393 ml/g as determined with capillary viscometry, and surface tension as determined by the pendant drop method equals 50 mN/m, was supplied by Akzo Nobel, Stenungsund, Sweden. The dry HM-EHEC powder was washed with acetone to rinse it from low-weight hydrophobic impurities. The HM-EHEC stock solution was prepared as described elsewhere (Holmberg, Nilsson, Singh, & Sundelöf, 1992) and was freed from remaining salt by dialysis in tube membranes (MW cut-off approximately 10 000) from Union Carbide, Chicago IL, and then centrifuged. The following chemicals were used as supplied: sodium dodecyl sulfate (SDS), 99.9% pure, Merck, Darmstadt, Germany. Radioactive SDS, ^{35}S, Amersham, Buckinghamshire, England. 1,3-di(1-pyrenyl)propane (P3P) from Molecular Probes, Eugene, OR, USA. Tris(2,2′-bipyridyl)ruthenium(II)chloride ($Ru(bipy)_3^{2+}$) and 9-methylanthracene (9-MA) (98%) from Aldrich-Chemie, Steinham, Germany. Pyrene (98+%), from Acros Chimica, Belgium, was twice recrystallized from absolute ethanol. All solutions were made with MilliQ water (Millipore) as solvent.

3. Methods

3.1. Fluorescence

It is well-established (Kalyanasundaram & Thomas, 1977) that the ratio of the first and third vibrational peaks in the emission spectrum of pyrene, I_1/I_3, is a measure of the micropolarity it senses in a certain environment. Pyrene dissolved in pure water gives an I_1/I_3-value of approximately 1.9 and I_1/I_3 decreases when the polarity of the medium decreases. A sudden drop in I_1/I_3 occurs when micelles are formed at cmc for binary surfactant/water systems (Kalyanasundaram & Thomas, 1977) and at c_1, the critical surfactant concentration where adsorption to the polymer starts, in the presence of the polymer (Evertsson et al., 1996; Nilsson, 1995; Nilsson et al., 1995; Turro, Baretz, & Kuo, 1984; Zana, Lianos, & Lang, 1985). It has been argued that the pyrene-probe in itself (and at low concentrations) does not have any significant effect on surfactant aggregation behavior mostly based on the fact that cmc- and c_1-values obtained with I_1/I_3-measurements are in fair agreement with other physical methods (Ananthapadmanabhan, Goddard, Turro, & Kuo, 1985; Sivadasan & Somasundaran, 1990; Tanaka et al., 1990). However, fluorescence probe analysis is largely empirical in nature and the interpretation must be carefully done since fluorescence probe techniques only monitors the ensemble of probes at the site of solubilization, and hence, only aggregates "perturbed" by the presence of the probe.

The values of average aggregation numbers of polymer-bound clusters, N_p, have been obtained using the steady-state fluorescence quenching (SSFQ) method developed by Turro and Yekta (1978). The model assumes that micelles (or more generally hydrophobic zones) containing both probe and quencher do not contribute to the fluorescence intensity i.e. the quencher is 100% effective. Further, small monodisperse micelles are presumed among which both probe and quencher are randomly distributed in a poissonian way. With an average of n quencher per micelle, e^{-n} micelles are empty and we have the relationship

$$\ln(I^0/I) = n \tag{1}$$

where I and I^0 (are the fluorescence intensity with, and without the added quencher, respectively. We also have that

$$n = [Q]/[\text{micelle}]_{tot} \tag{2}$$

where $[Q]$ is the quencher concentration and $[\text{micelle}]_{tot}$ is the total micellar concentration. Thus, if $\ln(I^0/I)$ is plotted against $[Q]$ for a series of micelle solutions differing only in the quencher concentration the inverse slope of the straight line obtained equals $[\text{micelle}]_{tot}$. In recent publications from

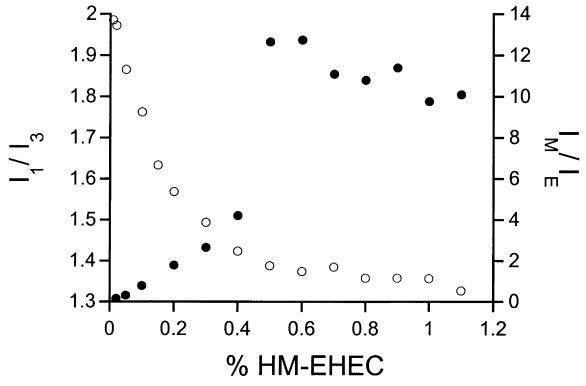

Fig. 1. The monomer to excimer intensity ratio of P3P, I_M/I_E (●), and the hydrophobic index of pyrene, I_1/I_3 (○), as functions of the HM-EHEC concentration for the binary system HM-EHEC/water at 20°C.

this laboratory, SSFQ has been utilized (Evertsson et al., 1996; Nilsson, 1995; Nilsson et al., 1995) and validated (Evertsson et al., 1996) on nonionic cellulose ether/SDS/water systems. N_p was obtained by combining fluorescence quenching data with results from equilibrium dialysis as described earlier (Nilsson et al., 1995).

The microviscosity of the HM-EHEC/SDS/water- system has been explored utilizing the probe 1,3-di(1-pyrenyl)propane, P3P, which first was used by Zachariasse (1978). In a recent work from this laboratory (Evertsson & Nilsson, 1997), P3P was found to be suitable for microviscosity-studies on the system EHEC/SDS/water and the results correlate well qualitatively with steady-state depolarization-results using perylene as well as with results from intramolecular relaxation about bonds of *p*-(*N*-dimethylaminobenzylidene), BMN. The extent of intramolecular excimer formation and emission of P3P is dependent on the local friction of the probe imposed by its microenvironment. Hence, the monomer to excimer intensity ratio, I_M/I_E, provides a qualitative index of the microviscosity as sensed by the probe.

All fluorescence measurements were recorded on a SPEX Fluorolog 2 steady-state spectrofluorometer using the same settings as described earlier (Evertsson & Nilsson, 1997). Pyrene was excited at ($\lambda = 334$ nm and emission spectra were recorded. The I_1/I_3-ratio was taken as the first ($\lambda \approx 374$ nm) and third ($\lambda \approx 388$ nm) intensity peak-height-ratio in the fine vibrational emission spectrum of pyrene. Steady-state fluorescence quenching experiments were performed with $Ru(bipy)_3^{2+}$ as the probe and 9-MA as the quencher. $Ru(bipy)_3^{2+}$ was excited at $\lambda = 450$ nm and the emission was recorded at $\lambda = 625$ nm. The 9-MA concentration was determined spectrophotometrically at $\lambda = 388$ nm. P3P was excited at $\lambda = 348$ nm and emission spectra were recorded between 350 and 500 nm. The I_M/I_E-ratio was taken as the monomer ($\lambda \approx 377$ nm) to excimer ($\lambda \approx 485$ nm) peak-height-ratio. All fluorescence measurements were run in duplicates and the error was 5% or less.

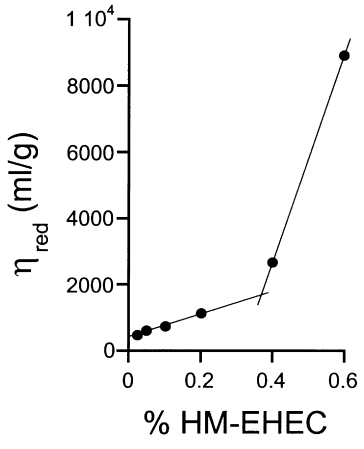

Fig. 2. The reduced specific viscosity, η_{red}, as a function of the polymer concentration for the binary system HM-EHEC/water at 20°C.

3.2. Equilibrium dialysis

SDS is bound to a nonionic cellulose derivative in the form of aggregates or mixed micelles (Nilsson et al., 1995). $[SDS]_{tot}$ is the sum of the free and aggregate-bound SDS and $[SDS]_{eq}$ is the surfactant concentration in equilibrium with the SDS–polymer aggregates. The dialysis equilibrium can be expressed as

$$[SDS]_{tot} = [SDS]_{eq} + c_p y \quad (3)$$

where c_p is the polymer concentration represented in grams per litre, and y is expressed as millimoles of SDS adsorbed per gram of polymer. The equilibrium dialysis experiments were carried out in specially designed cells, with retentate and dialysate compartments separated by a Spectra/Por membrane (MW cut-off 12–14 000). The cell design was similar to the one used by Fischman and Eirich (1971). The effect of the Donnan equilibrium has been corrected for as described earlier (Holmberg et al., 1992; Holmberg, Nilsson, & Sundelöf, 1997).

4. Results and discussion

The introduction of a minor amount of very hydrophobic groups onto a polymer changes, in some important aspects, its association behavior with surfactants (Hansson & Lindman, 1996; Varelas, Dualeh, & Steineret, 1994). Also, the tendency for hydrophobic self-association is affected and increases quantitatively with the polymer concentration (Varadaraj, Branham, McCormick, & Bock, 1994). Fig. 1 shows the variation in the intensity ratio I_1/I_3 of pyrene (micropolarity) and monomer to excimer intensity ratio I_M/I_E of P3P (microviscosity) with concentration of HM-EHEC for binary HM-EHEC/water solutions. I_1/I_3 is seen to decrease exponentially from a value of 2 for 0% HM-EHEC to about 1.35 for 1% HM-EHEC. The exponential decrease ends at about 0.4% HM-EHEC after which there is a linear slightly declining region in micropolarity. I_M/I_E, however, is found to follow a moderate linear increase up

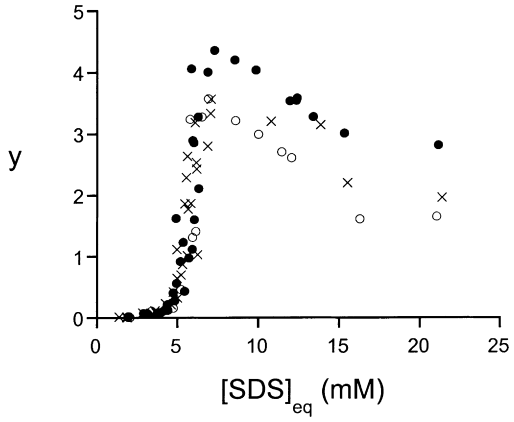

Fig. 3. Equilibrium dialysis results for the HM-EHEC/SDS/water system at 20°C. Millimoles of SDS bound per gram of HM-EHEC, *y*, as a function of the equilibrium SDS concentration, $[SDS]_{eq}$: ○, 0.10% HM-EHEC; ●, 0.20% HM-EHEC; ×, 0.40% HM-EHEC.

to 0.4% above which the rigidity of the system abruptly raises and stays at an almost constant level. These results give evidence for the formation of polymeric micelles of HM-EHEC in an aqueous solution. The critical overlap concentration, c^*, for this associative process is estimated to be 0.4% from these fluorescence probe techniques and at this point the association turns from being mostly intramolecular in nature for a HM-EHEC solution less than c^* to being dominantly intermolecular above c^*. Also rheological measurements performed with capillary viscometry presented as reduced specific viscosity versus polymer concentration in Fig. 2 shows that c^* is close to 0.4% (0.38% from the break-point of the two straight lines) for this specific HM-EHEC. For polymer concentrations higher than c^* the degree of interpolymeric cross-linking increases in the solution. This correlation between rheological and spectroscopic fluorescence probing measurements verifies the existence of microscopic interactions, which affect macroscopic solution properties. The polymeric micelles of HM-EHEC formed above c^* have a very rigid structure ($I_M/I_E \approx 12-13$) and the rigidity is comparable to the maximum in microviscosity seen for the aggregates formed between SDS and HM-EHEC ($I_M/I_E \approx 13.5$, see Fig. 5) and much larger than the microviscosity of ordinary SDS-micelles ($I_M/I_E \approx 1$, see Fig. 5). The micropolarity sensed by pyrene is constant in the region above c^* ($I_1/I_3 \approx 1.35$) and just slightly more polar than the interior of ordinary SDS micelles ($I_1/I_3 \approx 1.15$, see Fig. 4), indicating a rather compact structure with a low water-penetration. At polymer concentrations less than c^* there is most likely a continuous growth in the size of the polymeric micelles sampled as a slow increase in rigidity and a rather major decrease in micropolarity. The rather hydrophobic, but not hydrophobically modified, EHEC-fraction CST-103 has recently been shown (Evertsson et al., 1996) to give a drop in I_1/I_3 from approximately 1.9 to 1.7 upon raising the polymer concentration from 0 to 1% and complementary unpublished measurements of I_M/I_E have also shown that the rigidity inside these self-associations of CST-103 is much less than found for HM-EHEC. Evidently, the nonylphenol groups onto HM-EHEC is a crucial factor needed for the formation of interpolymeric associations (i.e. polymeric micelles) with a physical nature which resembles ordinary micelles. Other well-described aqueous systems of HM-polymers such as HM-Polyacrylamide (Ringsdorf, Venzmer, & Winnik, 1991), HM-PEO copolymer (Wang & Winnik, 1990), and HM-HEC (Nishikawa et al., 1998) in which they have measured the micropolarity of the pyrene probe and demonstrated the presence of polymeric micelles, have also reported a decrease in I_1/I_3 with a polymer concentration that is in quantitative magnitude comparable to our data for HM-EHEC.

Knowledge of a macroscopic bulk property such as the binding isotherm is a fundamental and important factor in investigations of polymer/surfactant complexes. The equilibrium dialysis method can provide quantitative information about this macroscopic binding and has been utilized in this laboratory in several recent investigations dealing with nonionic cellulose derivatives and surfactants (Evertsson

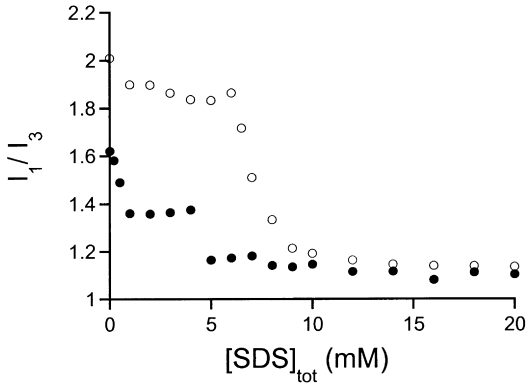

Fig. 4. The hydrophobic index of pyrene, I_1/I_3, as a function of the total SDS concentration, $[SDS]_{tot}$, at 20°C: ○ the binary system SDS/water; ●, 0.20% HM-EHEC.

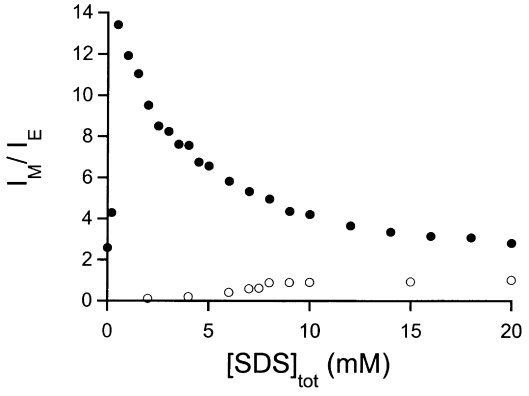

Fig. 5. The monomer to excimer intensity ratio of P3P, I_M/I_E, as a function of the total SDS concentration, $[SDS]_{tot}$, at 20°C: ○, the binary system SDS/water; ●, 0.20% HM-EHEC.

et al., 1996; Holmberg et al., 1992; Holmberg et al., 1997; Nilsson et al., 1995). Fig. 3 shows the amount of SDS adsorbed per gram of HM-EHEC, *y*, as a function of the SDS concentration in equilibrium with the polymer, $[SDS]_{eq}$. The binding isotherm of SDS to HM-EHEC can be divided into three regions: At low SDS concentrations (0–5 mM) there is a region of noncooperative and a very low degree adsorption. This binding seems to start at about 2 mM of $[SDS]_{tot}$ (c_1) but might possibly proceed already from the very first addition of the surfactant. At intermediate SDS concentrations, there is a highly cooperative region of adsorption starting at 5 mM and followed by an almost linear increase up to a maximum. In this region, mixed micelles are formed between HM-EHEC and SDS in a cooperative manner. At high SDS concentrations the calculated degree of binding (*y*) decreases most likely due to saturation of the polymer and formation of ordinary SDS micelles into which SDS and HM-EHEC can distribute. Similar maxima have been reported for related systems (Evertsson et al., 1996; Holmberg et al., 1992; Nilsson et al., 1995; Sakamoto, 1987). The total degree of SDS binding is lower for HM-EHEC compared to other nonionic cellulose ethers such as EHEC (fraction CST-103) or HPMC, about 2/3 if to compare their maxima in *y*. This effect originates most likely in a rather low quantitative amount of hydrophobic substituents (i.e. nonylphenol and ethyl groups) onto HM-EHEC. These findings are in agreement with the picture given by Thuresson et al. (1996) who studied a related HM-EHEC-fraction and its interaction with SDS by means of NMR self-diffusion and a surfactant-specific electrode technique.

Fig. 4 shows the variation in the hydrophobic index, I_1/I_3, for HM-EHEC/SDS/water and SDS/water solutions as a function of the total SDS concentration. I_1/I_3 decreases abruptly in the region between 6 and 8 mM for the binary SDS/water system (cmc can be judged to 7.0 mM from the arbitrarily chosen inflection point of the curve). The value of I_1/I_3 drops immediately for the HM-EHEC/SDS/water system upon successive addition of SDS indicating that the interaction might possibly start almost from the very first addition of SDS-monomers to the polymer solution, i.e. the first significant sign that c_1 is close to 0 mM. Evidently, the c_1-value is sampled at a lower concentration by the microscopic pyrene-method compared to the macroscopic bulk method equilibrium dialysis. However, the fluorescence technique is in general more sensitive to qualitative microstructural changes than to the quantitative magnitude of this change compared to a bulk method such as equilibrium dialysis.

Fig. 5 shows the monomer to excimer intensity ratio of P3P, I_M/I_E, for aqueous HM-EHEC/SDS and pure SDS solutions as a function of the total SDS concentration. The microviscosity (I_M/I_E) for the HM-EHEC/SDS/water system is seen to increase almost immediately as SDS is added to the solution and to develop a maximum at approximately 0.5 mM of $[SDS]_{tot}$, followed by exponentially decreasing values at the higher SDS concentrations investigated. Evidently, P3P also detects the start of the interaction between HM-EHEC and SDS already in the noncooperative binding region, in correlation with the micropolarity-results shown in Fig. 4. It is most likely that the already existing polymeric aggregates are strengthened and stabilized by the rather few SDS monomers which are distributed to the polymer chains giving rise to this increased level of microscopic rigidity in the solution. The maximum in microviscosity corresponds to a complex, which contains a high polymer content and as the binding of SDS continues, the relative fraction of the polymer decreases and consequently the microviscosity as well (Evertsson & Nilsson, 1997; Evertsson & Nilsson, 1998). All compositions of HM-EHEC/SDS aggregates have much higher microviscosities than ordinary SDS micelles. These findings are supported by the deuterium NMR relaxation measurements made by Thuresson et al. (1996) showing slower molecular tumbling for the aggregates formed in the HM-EHEC/SDS/water system compared to free SDS micelles. Generally it is found that an increase in hydrophobicity of a cellulose ether (i.e. increase in surface activity or decrease in CP) gives an increased rigidity of the corresponding polymer–surfactant aggregates. An approximately exponential relationship has recently been reported (Evertsson & Nilsson, 1998) between the surface activities of a set of ordinary nonionic cellulose ethers and I_M/I_E-max for the corresponding complexes formed with SDS. HM-EHEC/SDS complexes have a much higher maximum in I_M/I_E (13.5) than expected from its rather moderate surface activity. The surface tension against air is equal to 50 mN/m for a 0.2% aqueous solution which, according to this exponential relationship discussed, should correspond to a maximum in I_M/I_E of about 3.

The average aggregation number or the number of SDS monomers in each aggregate of SDS and HM-EHEC, N_p, was determined by a combination of steady-state fluorescence quenching and equilibrium dialysis. In the cooperative binding range (5 mM $\leq [SDS]_{tot}$) the mixed micelles between HM-EHEC and SDS was found to grow (i.e. N_p increased) from 25 gradually with an increase in the SDS concentration up to a maximum at about 45–50 following qualitatively the same pattern as been shown for the EHEC/SDS/water and some other related polymer–surfactant systems (Evertsson et al., 1996; Nilsson, 1995; Thuresson et al., 1996; van Stam, Almgren, & Lindblad, 1991). Almost constant micellar concentrations (about 0.02 mM for 0.1% HM-EHEC) was found in the noncooperative binding region followed by a rapid increase in $[micelle]_{tot}$ from the onset of cooperative interaction up to the composition at which normal free micelles begin to form ($[SDS]_{eq}$ = cmc $\approx$ 7 mM) in the solution (observations in harmony with the findings by Thuresson et al. (1996)). These observations support the conclusion that SDS-monomers, in the noncooperative interaction region, strengthens already existing polymeric self-associations while new mixed

micelles are created between HM-EHEC and SDS in the cooperative binding region. If one assumes that all nonylphenol groups onto HM-EHEC are distributed into mixed micelles in the solution, a ratio between the average number of nonylphenol groups per micelle can be calculated. This ratio is found to decrease from about 2 in the noncooperative binding region to 0.3–0.4 for the compositions equal to the maximum in SDS-binding.

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