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Microviscosity in dilute aqueous solutions of SDS and non-ionic cellulose derivatives of different hydrophobicity: fluorescence probe investigations

Hans Evertsson and Stefan Nilsson*

Physical Pharmaceutical Chemistry, Uppsala University, Uppsala Biomedical Centre, Box 574, S-751 22 Uppsala, Sweden

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The microviscosity in mixed micelles formed in dilute aqueous solutions of sodium dodecyl sulphate (SDS) and a set of non-ionic cellulose ethers of different hydrophobicity has been determined by means of steady-state fluorescence probe techniques. Two hydrophobic probes have been applied in this investigation: 1,3-di(1-pyrenyl)propane (P3P) and perylene. Reference measurements of microviscosity have also been performed on SDS solutions including the uncharged polymers poly(ethyleneoxide) (PEO) or poly(vinylpyrrolidone) (PVP). All compositions investigated showed qualitatively the same general behaviour with an abrupt increase in microviscosity at the critical surfactant concentration where the polymer–surfactant interaction starts (c_1) followed by a maximum and an asymptotically declining region as the surfactant concentration was increased further. Comparison with a recent investigation of a specific ethyl(hydroxyethyl)cellulose (EHEC fraction CST-103)/SDS/water system (Evertsson & Nilsson (1997) *Macromolecules*, *30*, 2377) revealed that the maximum in microviscosity generally corresponds to a low degree of SDS adsorption ($\approx$ 0.5 mmol of SDS per gram of polymer) and consequently to a high polymer content of the mixed micelles formed in the type of systems studied herein. The hydrophobicity of the cellulose derivatives was found to correlate to the amplitude of the overall microviscosity pattern for the mixed micelles, i.e. an increased polymer hydrophobicity gave an increased rigidity of the polymer–surfactant aggregates. An approximately exponential relation was demonstrated between the maxima in microviscosity of the different mixed micelles and the surface activities of the corresponding cellulose derivatives. All polymer/surfactant combinations investigated gave aggregates with a higher rigidity than ordinary SDS micelles. The microviscosity of the mixed micelles of the cellulose derivatives and SDS formed close to c_1 increased as the temperature rose from 20 to 50°C. This effect was attributed to an increased hydrophobicity of the cellulose ethers upon temperature elevation, hence giving rise to further close-packing of the aggregate structures. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Amphiphilic polymers are constituted of hydrophobic and hydrophilic segments. Their physical properties depend to a large extent on the chemical composition and the balance between hydrophobic and hydrophilic moieties. Cellulose derivatives represent one typical class of amphiphilic and surface active polymers (Greminger and Krumel, 1980; Persson et al., 1996) which is of great interest from a pharmaceutical point of view due to its frequent use in many different types of formulations (Florence and Attwood, 1993).

In the last two decades there has been an increasing interest in water-soluble polymer–surfactant systems, both for academic and industrial reasons, due to the intricate nature of the interaction and the wide area of applications such as

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*To whom correspondence should be addressed.

in foods, cosmetics, pharmaceutical preparations and other industrial sectors. Several reviews on this topic exist (Brackman and Engberts, 1993; Goddard, 1993; Lindman and Thalberg, 1993). In this laboratory, a number of papers have been published on the interaction between non-ionic cellulose derivatives and surfactants in dilute aqueous solutions (Holmberg et al., 1992; Nilsson et al., 1994; Nilsson et al., 1995a; Nilsson, 1995; Evertsson et al., 1996; Holmberg, 1996; Holmberg and Sundelöf, 1996; Evertsson and Nilsson, 1997) with a particular focus on the combination of ethyl hydroxyethyl cellulose (EHEC) and sodium dodecyl sulphate (SDS). A delicate and complex behaviour, critically dependent on the polymer investigated and both polymer and surfactant concentration, has been observed which has been attributed to a cooperative clustering adsorption of surfactant onto the polymer as a key part in the proposed interaction mechanism (Nilsson, 1995; Nilsson et al., 1995a). The interaction between non-ionic cellulose derivatives and SDS can also be described as a mixed micellisation between a surfactant and a polymer both of amphiphilic character. The main goal of these investigations is to provide further details, both specific and general ones, to deepen the general knowledge and understanding of this and related types of systems, and especially on properties with importance for pharmaceutical applications.

Fluorescence probe techniques have proven to be powerful tools for investigation of colloidal systems (Grätzel and Thomas, 1976; Kalyanasundaram, 1987; Zana, 1987; Grieser and Drummond, 1988; Winnik and Regismond, 1996), and have been utilised in this laboratory on non-ionic cellulose ether/SDS/water systems (Nilsson, 1995; Nilsson et al., 1995a; Evertsson et al., 1996; Evertsson and Nilsson, 1997) to yield information on micropolarity, microviscosity and average aggregation numbers of polymer-bound surfactant clusters. In a recent work (Evertsson and Nilsson, 1997) the microviscosity of the system EHEC (fraction CST-103)/SDS/water was investigated using three fluorescence probe techniques. The results obtained with these techniques were compared, and to some degree validated, but they all gave, with minor differences, the same qualitative picture of the microviscosity in the system with dramatic changes in the microrigidity as the SDS concentration was altered in the range 0–20 mM. The microviscosity was considered in relation to other important system features, such as the bulk viscosity, the adsorption isotherm of SDS onto EHEC, the average aggregation numbers, N_p, and the micropolarity (as sensed by pyrene) of the EHEC/SDS clusters formed. A well-developed maximum in microviscosity was observed almost immediately after the onset of polymer–surfactant interaction, where the total SDS concentration in the solution, the quantitative magnitude of SDS adsorption and N_p, have low values. This maximum in microviscosity was also found to coincide, according to the surfactant concentration, with a maximum in bulk viscosity when polymer concentrations equal to or higher than the critical overlap concentration, c^*, were applied. It was suggested that these two maxima derive from different mechanisms: the maximum in bulk viscosity from a three-dimensional network of polymer and cluster tie-points and the maximum in microviscosity originating in the high content of hydrophobic polymer segments, covalently linked together, in the clusters. As more SDS was added to the solution N_p increased while the microviscosity decreased. This molecular description is consistent with the general conclusion by Piculell et al. (1995) that a break-down of the polymer/surfactant networks starts as the surfactant dominates in the clusters. However, all compositions of EHEC/SDS/water investigated were found to have higher microviscosities than ordinary SDS micelles.

Several papers exist where fluorescence probe techniques have been used to examine the microviscosity in binary surfactant/water (Kalyanasundaram, 1987; Zana, 1987; Grieser and Drummond, 1988 Malliaris, 1988; Miyagishi et al., 1996) and amphiphilic self-aggregating polymer/water systems (Chu and Thomas, 1991; Winnik et al., 1991b; Yekta et al., 1993; Varadaraj et al., 1994; Nivaggioli et al., 1995; Benjelloun et al., 1996), while there are only a few investigations in the case of ternary polymer/surfactant/water systems (McGlade et al., 1987; Winnik et al., 1987; Winnik et al., 1991a; Anthony and Zana, 1996a; Anthony and Zana, 1996b; Evertsson and Nilsson, 1997). This paper reports on the microviscosity of SDS interacting with a set of previously well-characterised (Nilsson et al., 1995b; Persson et al., 1996) non-ionic cellulose derivatives primarily in order to investigate the role of polymer hydrophobicity on the microviscosity of the mixed micelles or clusters formed and furthermore, to test the generality of some observations previously made (Evertsson and Nilsson, 1997). As reference measurements poly(ethyleneoxide) (PEO) and poly(vinylpyrrolidone) (PVP) are also included in the study because of the extensive information available on both the PEO/SDS/water and the PVP/SDS/water systems (Robb, 1981; Brackman and Engberts, 1993; Goddard, 1993; Lindman and Thalberg, 1993).

MATERIALS

All ethyl(hydroxyethyl)cellulose (EHEC) fractions were supplied by Akzo Nobel AB (Stenungsund, Sweden). Hydroxyethyl cellulose (HEC) and methyl cellulose (MC) were obtained from Aldrich Chemie (Steinham, Germany). Hydroxypropyl methyl cellulose (HPMC) was obtained from Colorcon Ltd. (West Point, England), and hydroxypropyl cellulose (HPC) from Hercules Inc. (Wilmington, USA). Some important data on the cellulose ethers under study are summarised in Table 1. The substitution of the cellulose ethers is normally characterised by the numbers DS_{alkyl} (degree of substitution) and $MS_{ethylene\ oxide}$ (molar substitution). DS_{alkyl} is the average number of hydroxyl groups per anhydroglucose unit which has been substituted by alkyl groups ($0 < DS_{alkyl} < 3$). $MS_{ethylene\ oxide}$ is the average of the total number of alkylene oxide groups (hydroxyethyl or hydroxypropyl) per anhydroglucose unit. Due to formation

Table 1. Some critical parameters of the cellulose derivatives used in this study

Substance	M_w ($\times 10^5$)	CP (°C)	$[\eta]$ (ml g^{-1})	c^* (%)	DS^a_{alkyl}	$\mathrm{MS}^a_{\text{alkylene oxide}}$
EHEC Fractions						
CST-103	1.89	28	455	0.22	1.5	0.7
DVT-87014	1.33	28	290	0.34	1.4	0.9
E230G	5.35	65	410	0.24	0.9	0.9
E411G	7.85	58	1000	0.10	1.2	1.7
Other cellulose ethers						
MC	1.62	65	400	0.25	≈ 2	—
HPC	1.06	42	134	0.74	—	≈ 0.4
HPMC	3.01	55	740	0.13	≈ 2	≈ 0.4
HEC	1.89	> 100	273	0.37	—	≈ 3

M_w, molecular weight as determined from SEC/LALLS/RI; CP, cloud point; $[\eta]$, intrinsic viscosity; c^*, critical overlap concentration; $\mathrm{DS}_{\text{alkyl}}$, number of alkyl substituents per anhydroglucose unit; $\mathrm{MS}_{\text{alkylene oxide}}$, number of alkylene oxide substituents per anhydroglucose unit
[a]Values for the EHEC fractions are determined by the producer and values for HPMC, HPC, MC and HEC are estimated

of oligo(alkylene oxide) chains the quantity $\mathrm{MS}_{\text{ethylene oxide}}$ could in principle be any positive number, but in practice the highest value is only a few units. The cloud point (CP) of aqueous cellulose ether solutions was determined by visual observation in glass tubes and taken as the temperature when the last visible sign of clouding in the solution disappeared upon cooling (Nilsson et al., 1994). The M_w of the samples was determined by size-exclusion chromatography (with LALLS and RI detection) (Nilsson et al., 1995b) and intrinsic viscosity ($[\eta]$) and the critical overlap concentration (c^*) were determined by capillary viscometry (Nilsson et al., 1995b). The polydispersity of these cellulose ethers is rather large, with values of M_w/M_n of about 2 (Nilsson et al., 1995b). Poly(ethyleneoxide) (PEO), M_w (300 000 and CP > 90°C, was bought from Acros Chimica (Geel, Belgium) and poly(vinylpyrrolidone) (PVP), $M_w \approx 350\,000$, from Polysciences Inc. (Warrington, USA). Analytical-grade sodium dodecyl sulphate (SDS) was obtained from Merck (Darmstadt, Germany), the radioactive SDS (^{35}S) from Amersham (Buckinghamshire, England), 1,3-bis(1-pyrenyl)propane (P3P) from Molecular Probes (Eugene, OR, USA), perylene (99.5 + %), from Aldrich-Chemie, and they were all used as supplied. Pyrene (98%) was bought from Acros Chimica, and was twice recrystallised from absolute ethanol. Spectra/Por® tube dialysis membrane, with a molecular weight cut-off at 12 000–14 000, was obtained from Spectrum Medical Ind. (Los Angeles, CA, USA). All solutions were prepared using Milli-Q water (Millipore).

METHODS

Preparation of solutions

The standard procedure of preparing cellulose ether stock solutions is described in a previous paper (Holmberg et al., 1992). After preparation, the cellulose ether stock solutions were rinsed from low-molecular weight material and salts using a dialysis tube membrane. Dialysis was performed against Milli-Q water during 1 week, and then the stock solutions were filtered through 0.8 μm filters (Millex-AA, Millipore, SA, Molsheim, France) for removal of undissolved polymer, microgels and dust particles. The conductivity of the dialysed stock solutions was as low as 4–6 μS, which corresponds to a concentration of sodium chloride of approximately 0.03 mM. Finally, the concentrations were determined by drying samples to constant weight at 105°C. All polymer–SDS solutions in this work were prepared by weighing the desired amounts of polymer stock solution into appropriately diluted SDS solutions at least 24 h before the samples were used for experiments, in order to let the previously reported time-dependent effects settle (Nilsson et al., 1994). Polymer concentrations are given in percent by weight and are 0.20% (w/w) throughout the study. SDS concentrations are calculated as moles per kilograms of solvent but, since all the solutions used in this study are dilute, SDS concentrations are given in the molar scale. For experiments with P3P and perylene, these probes were dissolved in acetone, pro analysi (Merck). Aliquots of the probe–acetone solutions were added to the polymer/SDS/water solutions to achieve final approximate probe concentrations of 1×10^{-6} M for P3P and perylene. In order to avoid formation of P3P microcrystals, a problem also described with the closely related probe dipyme (Winnik et al., 1991b), the P3P aliquots were added to a 100 mM SDS stock solution and then further diluted. The final polymer/SDS/water/P3P solutions were kept on a rotating table in the dark for 3 days until equilibrated.

Fluorescence measurements

All fluorescence measurements were recorded on a SPEX Fluorolog 2 model FL1T2 steady-state spectrofluorometer in the 's'-mode with 0.5 mm excitation and emission slits. The cell holder was thermostated to the desired temperature using a circulating water bath. For P3P the excitation wavelength was set 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 ($\lambda = 377$ nm) to excimer ($\lambda = 485$ nm) intensity peak–height ratio. Fluorescence depolarisation experiments were performed with perylene as the probe, excited at $\lambda = 412$ nm and emission recorded at λ = 443 nm, using manually operated prism polarisers. All experiments were run in duplicate and the reproducibility was 5% or better.

For hydrophobic index (I_1/I_3) measurements, the excitation of pyrene was performed at λ = 334 nm and emission spectra were recorded. The I_1/I_3 ratio was taken as the intensity peak-height ratio between the first (λ = 377 nm) and the third (λ = 388 nm) peaks in the fine vibrational spectrum of pyrene, since this ratio is a sensitive indicator of the pyrene microenvironment polarity (Kalyanasundaram and Thomas, 1977).

Bulk viscosity measurements

Bulk viscosity of the polymer/SDS/water solutions was measured using ordinary Ostwald capillary viscometers, with approximate flow times of 100 s for pure water at 20°C, which were immersed in a water thermostat. The reduced specific viscosity, $\eta_{sp}/c(\eta_{sp} = (\eta - \eta_0)/\eta_0)$, was calculated, treating the system as a quasibinary one, from viscometric data where c is the polymer concentration and η and η_0 are the viscosities of solution (polymer/SDS/water) and solvent (SDS/water), respectively.

Equilibrium dialysis

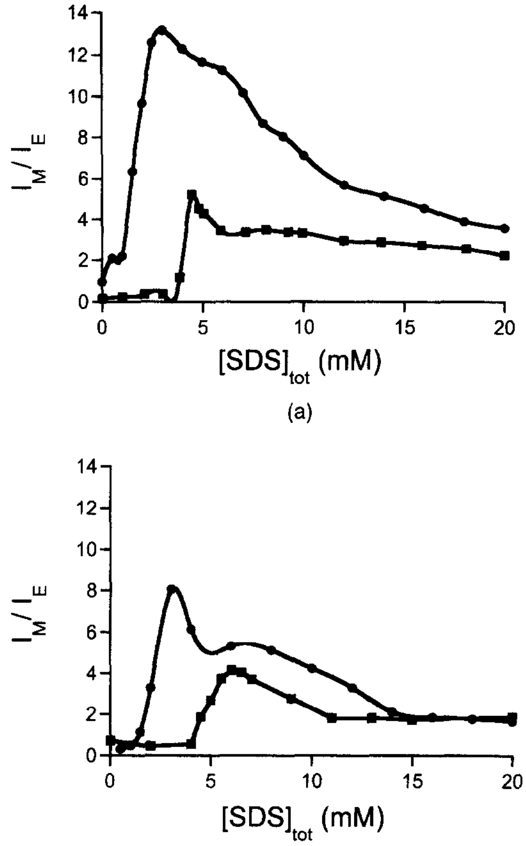
The equilibrium dialysis experiments were performed at 20°C using the same methodology and type of dialysis cells as used previously in several investigations (Holmberg et al., 1992; Holmberg et al., 1997; Nilsson, 1995; Nilsson et al., 1995a; Evertsson et al., 1996). The SDS solutions contained a small amount of ^{35}SDS, enough to achieve an activity of approximately 25 000 cpm ml^{-1}, and was used to determine the SDS content by scintillation counting. The equilibrium dialysis method gives both quantitative and qualitative information about the binding of SDS to the polymer from which the SDS concentration in equilibrium with the polymer, $[\mathrm{SDS}]_{eq}$, the amount of SDS bound to the polymer, y, and the total SDS concentration, $[\mathrm{SDS}]_{tot}$, can be calculated. Since the systems studied are salt free, a correction for the Donnan effect has been made, as described elsewhere (Holmberg et al., 1992; Holmberg et al., 1997).

RESULTS AND DISCUSSION

Microviscosity is an important parameter describing a heterogeneous system in which micelle or cluster formation is present. This paper is an investigation of the microviscosity in dilute aqueous solutions of eight different non-ionic cellulose ether samples and the anionic surfactant SDS. The set of cellulose ethers has been characterised by a rather wide selection of physico-chemical techniques (Nilsson et al., 1995b; Persson et al., 1996), and it has been shown that these samples cover a broad range in hydrophobicity (hydrophobic/hydrophilic balance) and surface activity. Measurements of microviscosity in two well-described reference systems—the PVP/SDS/water and the PEO/SDS/water systems—will also be presented. In a recent paper from this laboratory on the microviscosity of a specific EHEC (fraction CST-103)/SDS/water system (Evertsson and Nilsson, 1997), three fluorescence probe techniques were applied and compared. One of these probe techniques, namely the intramolecular excimer formation of 1,3-bis(1-pyrenyl)propane, P3P, was selected as the main method for this work since it was shown to be very sensitive to the microrigidity in this EHEC/SDS/water system, and is comparably easy and straightforward to use. In this paper, as complementary information, some depolarisation measurements with perylene as the probe are also given. The intramolecular excimer formation in P3P is dependent on the local friction induced by the microenvironment and was first used by Zachariasse (1978) on SDS micelles. The formation of intramolecular excimers is hindered by a high microrigidity, and thus the monomer to excimer ratio, I_M/I_E, is a qualitative index of the microviscosity. Intramolecular excimer formation in P3P and in the closely related substance 1,1-dipyrenyl methyl ether (dipyme) (Georgescauld et al., 1980) can be detected at very low probe concentrations, which avoids problems like large micelle perturbations and uncertain probe distribution among the micelles—problems associated with intermolecular excimer formation of, e.g. pyrene (Zana, 1987).

The microviscosity of normal SDS micelles, as measured in this laboratory utilising P3P and a glycerol–ethanol calibration curve, is 20 cP (LaPorte et al., 1995). This value is in good agreement with the ones found by others (Zachariasse, 1978; Lianos et al., 1982) (19–21 cP) using P3P as probe. It is however, very difficult to make accurate calculations of absolute values of the microviscosity, since no continuous phase can truly represent the fluidity in organised aggregates, such as ordinary micelles or mixed micelles of polymer and surfactant (Hare and Lussan, 1977; Zachariasse et al., 1982; Zana, 1987; Grieser and Drummond, 1988). For this reason this paper focuses on the qualitative variation in the microviscosity index with the surfactant concentration and does not attempt to present absolute values of the microviscosity in the systems investigated. For comparative reasons, a polymer concentration of 0.20% was selected for all polymer/surfactant solutions examined, although it has been shown, both by preliminary experiments and in a recent paper (Evertsson and Nilsson, 1997), that the microviscosity does not vary much with the polymer content for cellulose ethers in the dilute/semidilute regime; i.e. slightly below and above the critical overlap concentration, c^* (defined as $1/[\eta]$ (Weisberg et al., 1951)), of the polymer.

Fig. 1*a*, Fig. 1*b* and Fig. 2 present the monomer to excimer intensity ratio, I_M/I_E, of P3P in aqueous 0.20% cellulose ether solutions for some of the samples investigated as a function of the SDS concentration. Also included are reference measurements of I_M/I_E for 0.20% PEO/SDS and binary SDS/water solutions. Qualitatively, all polymer/SDS systems investigated show the same general behaviour in



(a)

(b)

Fig. 1. The monomer to excimer intensity ratio, I_M/I_E, of P3P as a function of the total SDS concentration, $[SDS]_{tot}$, at 20°C in 0.20% aqueous polymer solutions. (*a*) EHEC fraction CST-103 (●); HPMC (■). (*b*) EHEC fraction DVT 87014 (●); PEO (■).

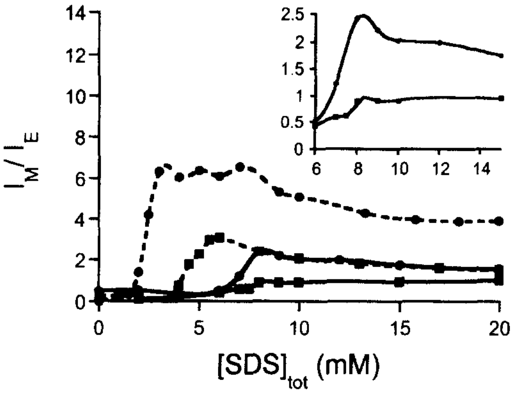


Fig. 2. The monomer to excimer intensity ratio, I_M/I_E, of P3P as a function of the total SDS concentration, $[SDS]_{tot}$, at 20°C in 0.20% aqueous polymer solutions. ● and dotted line, HPC; ■ and dotted line, MC; ● and full line, HEC; ■ and full line, the binary SDS/water system. Inserted: upper curve, HEC; lower curve, the binary SDS/water system.

microviscosity as the SDS concentration is altered in the range from 0 to 20 mM. At the critical surfactant concentration where the clustering process starts, here termed c_1, the I_M/I_E-index and microviscosity in the system increases abruptly to a maximum after which it decreases to an asymptotic level at the highest SDS concentrations studied. However, some important differences in the microviscosity pattern exists between the different systems, which can be related to the chemical composition and hydrophobic/hydrophilic balance of the cellulose ethers investigated. It is found that the most hydrophobic cellulose derivative, EHEC fraction CST-103, (CP ≈ 28°C, see Table 1) gives the most rigid mixed micelles with SDS of all cellulose ethers under study. The strong increase in microviscosity for CST-103 develops in a range of low SDS concentrations (c_1 = 1.5 mM of SDS as determined from the inflection point) and gives a maximum in I_M/I_E of ≈ 13. The pronounced maximum in microviscosity thus corresponds to a low degree of SDS adsorption and to a relatively high polymer content in the mixed micelles or clusters (Evertsson and Nilsson, 1997).

As the hydrophobicity among the cellulose ethers decreases, i.e. the CP of the samples increases (see Table 1), the amplitude of the overall microviscosity pattern for the mixed polymer/surfactant micelles formed also decreases. This effect becomes obvious by comparing the maxima in I_M/I_E among the different samples, as shown in Table 2.

Fig. 2 shows measurements of I_M/I_E for the binary SDS/water system. The microviscosity increases at CMC ($[SDS]_{tot}$ ≈ 8 mM ((AphA), 1986)) indicating the onset of formation of normal micelles. All cellulose ether/surfactant solutions investigated give microviscosities significantly larger than that of ordinary free micelles. A similar behaviour has been reported by others for related systems (McGlade et al., 1987; Winnik et al., 1991a; Anthony and Zana, 1996a; Anthony and Zana, 1996b).

Even the least hydrophobic cellulose ether HEC (CP > 100°C, see Table 1) interacts with SDS and forms mixed aggregates with an increased rigidity compared to normal SDS micelles (see insert in Fig. 2), and it is seen that the increase in microviscosity is located, according to the surfactant concentration, close to the normal CMC of the binary SDS/water system. In the literature it is usually stated that HEC does not (or very weakly (Goddard and Hannan, 1977)) interact with SDS. This absence of obvious interaction has been explained as due to a combination of the low hydrophobicity and a low chain flexibility (Nagarajan and Kalpakci, 1982) of HEC. However, our results provide straightforward evidence for the existence of an interaction and formation of mixed micelles, although the intensity of the interaction is the lowest of all polymers herein investigated and by no means high. The microviscosity of the HEC/SDS aggregates is, immediately after c_1, about two to three times higher than that of ordinary SDS micelles.

The PEO/SDS/water (Fig. 1*b*) and PVP/SDS/water (results not shown) reference systems schematically give the same microviscosity behaviour, with a steep increase at c_1 followed by a maximum. While the microviscosity pattern of the rather hydrophilic PEO (c_1 ≈ 4.8 mM) is

Table 2. I_M/I_E**-max, the maximum value in** I_M/I_E **measured for each polymer/SDS/water system**

Substance	I_M/I_E-max	I_M/I_E^a	c_1^a (mM)	c_1^b (mM)	γ^* (mN/m)	$\gamma_{H_2O} - \gamma^*$ (mN/m)
EHEC fractions						
CST-103	13.2	3.7	1.5	1.5	37	35
DVT-87014	8.1	1.8	1.5	1.9	40	32
E230 G	3.2	2.0	3.9	3.8	48	24
E411 C	3.2	2.2	3.7	3.9	52	20
Other cellulose ethers						
MC	3.1	1.5	4.1	4.3	47	25
HPC	6.6	3.9	2.0	2.0	42	30
HPMC	5.2	2.2	3.9	3.9	47	25
HEC	2.4	1.5	7.0	7.0	63	9
Reference polymers						
PVP	28	4.4	2.1	2.2	—	—
PEO	4.2	1.5	4.7	4.8	—	—

[a] I_M/I_E the asymptotic I_M/I_E-value at $[\mathrm{SDS}]_{\mathrm{tot}} = 20$ mM; c_1^a, the onset of polymer–surfactant interaction as sensed by the hydrophobic index (I_1/I_3) of pyrene; c_1^b, the onset of polymer–surfactant interaction as sensed by P3P. c_1^a and c_1^b were taken as the inflection points of the curves; γ^*, apparent steady-state surface tension of an aqueous solution of cellulose ether; $\gamma_{H_2O} - \gamma^*$, the apparent surface activity taken as the difference between the surface tension of water and γ^*.

quite moderate in amplitude (I_M/I_E-max ≈ 4.2), PVP ($c_1 \approx$ 2.2 mM) gives mixed micelles with a comparatively huge rigidity and a maximum in I_M/I_E of about 28.

In order to further validate the effects in microviscosity as sensed by P3P, anisotropy measurements with perylene were performed as a complement on four of the polymers, namely EHEC fractions CST-103 and DVT 87014, as well as on HPMC and PEO. The microviscosity of the four polymers as sensed by P3P is shown in Fig. 1*a* and Fig. 1*b* and the corresponding anisotropy results are shown in Fig. 3*a* and Fig. 3*b* where the anisotropy, *r*, is plotted as a function of the total SDS concentration, $[\mathrm{SDS}]_{\mathrm{tot}}$. Qualitatively the anisotropy measurements monitors the same behaviour of the rigidity in the systems as P3P with a sharp increase in microviscosity from a specific surfactant concentration (c_1) up to a maximum followed by decreasing values at higher SDS contents. Both methods also give the same order in amplitude maxima of the microviscosity between the polymers: CST-103 gives the highest amplitude both in I_M/I_E and *r* on the SDS scale, followed in decreasing order by DVT-870114 > HPMC > PEO. However, while I_M/I_E obtained by P3P is an index of the micoviscosity or rigidity in the microenvironment of the probe, the anisotropy, here obtained with perylene as the probe, is necessarily not since the microviscosity depends not only on the anisotropy but also on the lifetime of the probe according to the Perrin equation (Perrin, 1926)

$$r_0/r = 1 + kT\tau/\eta V_0 \tag{1}$$

where r_0 is the limiting value of emission anisotropy obtained in the absence of rotational freedom, τ is the average lifetime of the fluorophore excited state, T is the absolute temperature, k is the Boltzmann constant, V_0 is the effective molecular volume of the probe, and η is the microviscosity of the probe. As pointed out by Shinitzky and Inbar (1976), the lifetime of the probe increases with increasing microviscosity at constant temperature, resulting in a non-linear relationship between *r* and the microviscosity. In the type of systems herein investigated, this effect should be most pronounced close to the onset of interaction (c_1), where the microviscosity

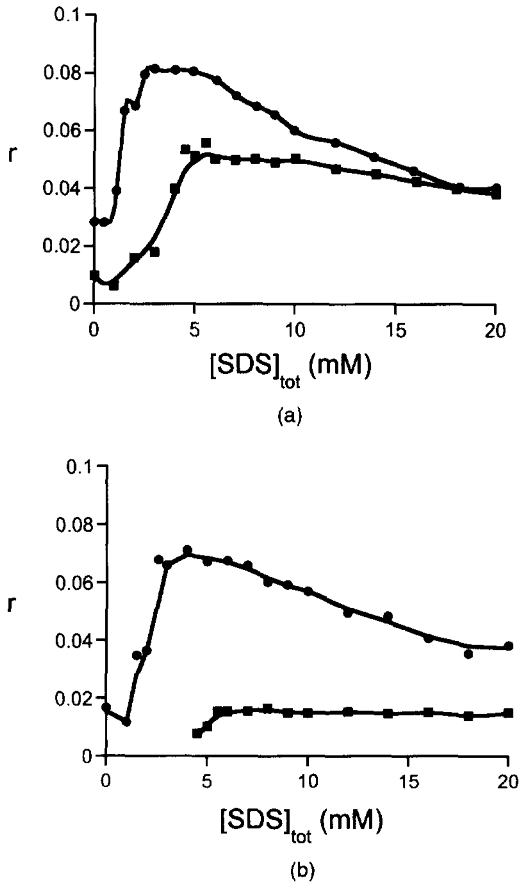


Fig. 3. The emission anisotropy, *r*, of perylene as a function of the total SDS concentration, $[\mathrm{SDS}]_{\mathrm{tot}}$, in 0.20% aqueous polymer solutions at 20°C. (*a*) EHEC fraction CST-103 (●); HPMC (■). (*b*) EHEC fraction DVT 87014 (●); PEO (■).

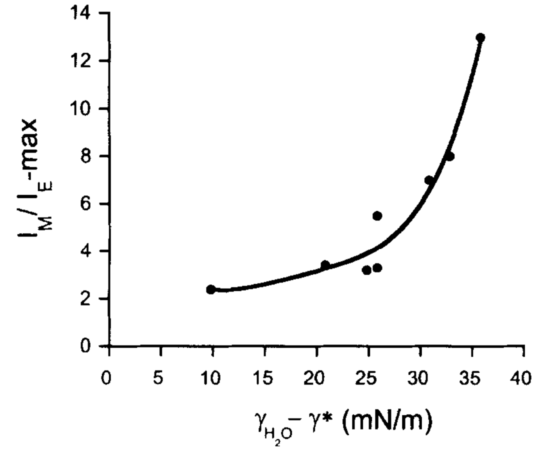


Fig. 4. The maximum in monomer to excimer intensity ratio I_M/I_E-max, of P3P for each polymer as a function of their apparent surface activity, $\gamma_{H_2O} - \gamma^*$, at 20°C.

and, most likely, also the lifetime of the probe reach their maxima.

Table 2 summarises the microviscosity parameters I_M/I_E-max, the asymptotic value of I_M/I_E and c_1 for all polymer/SDS systems investigated. Also included are c_1 values as determined with microenvironment polarity measurements using pyrene (Kalyanasundaram and Thomas, 1977) (I_1/I_3) and surface activity data for the cellulose ethers (Persson et al., 1996). A high agreement is found between the values of c_1 for the different systems obtained with the two fluorescence probe techniques utilising P3P and pyrene, respectively (Evertsson and Nilsson, 1997). The general trend is that I_M/I_E-max increases with decreasing values of CP and c_1. In other words, a hydrophobic cellulose derivative with a low CP and a strong tendency for surfactant interaction (i.e. a low value of c_1) generally forms more rigid mixed micelles compared to a more hydrophilic derivative. However, no high correlation is seen when I_M/I_E-max is plotted *versus* c_1 or CP. A much better correlation appears between I_M/I_E-max and the surface activities of the cellulose ethers, a relation illustrated in Fig. 4. It is seen that I_M/I_E-max increases exponentially when the surface activity of the samples, here expressed as the difference between the surface tension of pure water ($\gamma_{H_2O} \approx 72$ mN/m) and an aqueous solution of cellulose ether (γ^*) (Persson et al., 1996), increases. Thus, the polymer hydrophobicity, as judged by ability to lower the surface tension of water, seems to be the dominating factor in governing the rigidity of the mixed micelles formed.

As expected, in these systems there is no obvious dependence of microviscosity on the molecular weight (M_w) or on the intrinsic viscosity ([η]) of the polymer (compare Tables 1 and 2). For instance, HPC has rather low values of both M_w and [η], but gives mixed micelles with SDS which have a quite high rigidity. On the other hand, a crucial factor for the features of a cellulose derivative is naturally its substitution. The balance between hydrophobic and hydrophilic substituents is reflected in, for instance, varying degrees of surface activity, water solubility, CP, tendency for self-aggregation, and intensity in interaction with surfactants.

The two EHEC fractions, CST-103 and DVT 87014, have very similar degree and total amount of substitution (DS_{alkyl} and $MS_{alkylene\ oxide}$, see Table 1), as is seen also from their equality in CP or hydrophobicity. But one aspect of the substitution in which they differ is the distribution pattern along the backbone. It is known (information from the supplier Akzo Nobel AB) that DVT 87014 has a rather homogeneous distribution of substituents in contrast to CST-103, which has a kind of block tendency of its substituents. CST-103 thus has more well-recognised and separated segments of hydrophobic and hydrophilic character. Such a polymer will more easily find and form low-energetic conformations suitable for both hydrophobic and hydrophilic moieties. This qualitative difference between the two EHEC fractions is reflected in the higher surface activity of CST-103 compared to DVT 87014 (see Table 2). Furthermore, the tendency to form mixed micelles with SDS as estimated by c_1 is almost identical for these two substances, while the rigidity of the clusters formed is significantly larger for CST-103. In short, this high microviscosity of the CST-103/SDS clusters can be attributed to the block-like distribution and high surface activity of CST-103 constituting preferred binding sites for SDS and rather compact, closely packed mixed micelles.

The reference substances PVP and PEO differ in some important aspects from the cellulose derivatives. PVP and PEO are homogeneous structures composed of a number of identical unsubstituted monomer repeat units, and they both have a rather high chain flexibility. In contrast, the cellulose ethers are substitution polymers with a cellulose backbone and different types of substituents attached, and they are known as stiff and rigid types of polymers (Wirick and Waldman, 1970). The mixed micelles of PVP and SDS have a very high microviscosity. This most likely derives from the well-documented (Breuer and Robb, 1972) high reactivity of PVP and anionic surfactants (as also can be deduced from the low value of $c_1 \approx 2.2$ mM SDS) and from the high chain flexibility which give polymer-dense and closely packed cluster structures. An additional effect might also be a slight positive residual charge onto PVP, promoting interaction with SDS (Goddard, 1993). PEO interacts less intensely with SDS compared to PVP, as evidenced by a higher value of c_1 (≈ 4.8 mM), and gives mixed micelles with much lower microviscosity comparable to that of rather hydrophilic cellulose derivatives.

The bulk viscosity of many non-ionic cellulose derivatives goes through a maximum upon addition of surfactant (Lewis and Robinson, 1970; Sakamoto, 1987; Tanaka et al., 1990; Holmberg et al., 1992; Goddard, 1993; Lindman and Thalberg, 1993; Nilsson, 1995; Nyström et al., 1995; Piculell et al., 1995; Wang and Olofsson, 1995). It has been shown that the amplitude and position of the maximum varies with the polymer content (Holmberg et al., 1992; Nilsson, 1995; Piculell et al., 1995) and that even a minimum in bulk viscosity is found at low polymer concentrations (Holmberg et al., 1992; Nilsson, 1995). An explanation for this behaviour has been suggested (Holmberg et al., 1992; Nilsson, 1995; Nilsson et al., 1995a) based on the relation between polymer concentration (c_p) and the critical overlap concentration (c^*). In very dilute polymer solutions ($c_p < c^*$) the clustering process or mixed micellisation is preferably an intramolecular phenomenon according to the polymer, with multiple mixing of several hydrophobic segments of the polymer in the same cluster leading to shrinkage of the polymer coil and reduction in intrinsic viscosity (Holmberg et al., 1992; Nilsson, 1995). At higher polymer concentrations ($c_p > c^*$) the mixed micellisation tends to become intermolecular in nature. The mixed micelles constitute connective tie-points between polymer chains creating a three-dimensional network. Fig. 5 shows the bulk viscosity behaviour, here expressed as η_{sp}/c, as a function of the SDS concentration for three cellulose derivatives at a concentration of 0.20%, which is slightly higher than c^* for all three polymers (see Table 1). Maxima in η_{sp}/c are developed in all three cases. The amplitude of each maximum varies among the samples and depends evidently on both the chemical features of the cellulose derivative and the relative relation between c_p and c^*. The onset of interaction also varies among the samples, but is known (Goddard, 1993; Lindman and Thalberg, 1993) to be independent of polymer concentration. In the case of c_1, there is a rough correlation between hydrophobicity of the polymer, as judged by CP or surface activity, and c_1; i.e. the higher the hydrophobicity of the cellulose derivative, the lower is c_1. Persson et al. (1996) have previously shown an approximately linear relation between the surface activity for these non-ionic cellulose derivatives and their corresponding c_1 values for the interaction with SDS.

In a recent paper Evertsson and Nilsson (1997) found that the maximum in microviscosity almost coincides, according to the surfactant concentration, with the maximum in bulk viscosity for the EHEC(CST-103)/SDS/water system. An explanation was suggested, stating that the maxima originate from two different mechanisms: the maximum in bulk viscosity from the formation of a three-dimensional network of polymer and cluster tie points, and the maximum in microviscosity deriving from the high content of hydrophobic polymer segments in the clusters. In this study the microviscosity of the dilute aqueous solutions of non-ionic cellulose derivatives and SDS is examined on a broad base, and it can be concluded that there is a general coincidence between the maxima in bulk and microviscosity on the surfactant concentration scale, although the agreement might be somewhat changed upon variation of polymer concentration.

When structures in polymer/surfactant systems are explored, the most fundamental information to consider is the features of the surfactant–polymer binding isotherm. Fig. 6 gives a typical example of adsorption isotherms for two cellulose derivatives as the parameter y (mmoles of SDS bound per gram of polymer) as a function of the SDS concentration in equilibrium with the polymer, $[\mathrm{SDS}]_{\mathrm{eq}}$. The adsorption parameter y has been calculated with a correction for the Donnan effect, as been described in recent papers (Holmberg et al., 1992; Holmberg et al., 1997). The SDS adsorption starts at a well-defined surfactant concentration, c_1, and increases with a certain cooperativity up to a maximum. Both c_1 and the degree of cooperativity for the adsorption isotherm are characteristic features of a given non-ionic cellulose ether with a specific hydrophobicity. In general, an increased hydrophobicity gives both a decrease in c_1 and in the cooperativity of the binding. Evidently, as the hydrophobicity of the polymer increases, the intensity in the interaction with SDS increases as well. In the EHEC/SDS/water system it has recently been shown that the cooperativity decreases when the polymer concentration decreases (Nilsson et al., 1995a; Holmberg et al., 1997) or if the temperature is raised (Kamenka et al., 1994; Evertsson et al., 1996). The maximum in microviscosity is found to correspond to a low degree of adsorption ($y \approx 0.5$) and to very low values of average aggregation numbers of polymer-bound clusters, N_p (about 10) for all systems herein investigated. These observations are consistent with previous findings (Anthony and Zana,

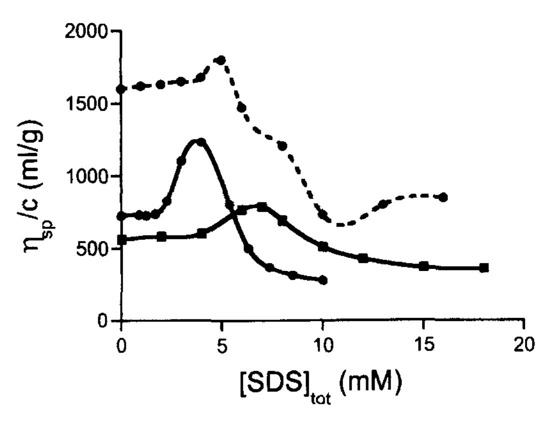


Fig. 5. The reduced specific viscosity, η_{sp}/c, of 0.20% aqueous polymer solutions as a function of the total SDS concentration, $[\mathrm{SDS}]_{\mathrm{tot}}$, at 20°C. ● and full line, EHEC fraction CST-103; ■ and full line, EHEC fraction E 230G; ● and dotted line, HPMC.

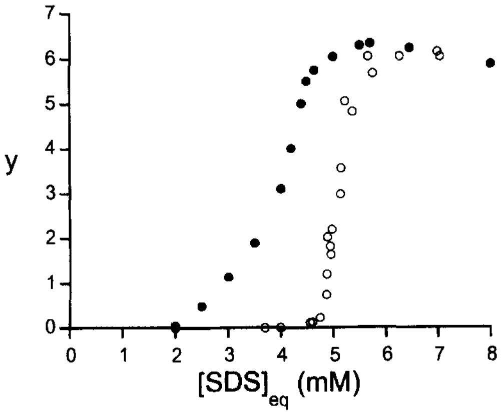


Fig. 6. Equilibrium dialysis results at 20°C of 0.20% aqueous polymer solutions presented as a plot of y (millimoles of SDS bound per gram of polymer) as a function of the equilibrium SDS concentration. (●) EHEC fraction CST-103; (○) HPMC.

1996a; Evertsson and Nilsson, 1997) and provide further evidence for a recently proposed mechanism (Evertsson and Nilsson, 1997) stating that the maximum in microviscosity originates in a high content of covalently linked hydrophobic polymer segments in the mixed micelles of polymer and surfactant.

The temperature has been shown to have a definite effect on the detailed appearance of aqueous solutions of non-ionic cellulose derivatives and surfactants. As the temperature increases the solubility in this type of solutions decreases due to an increased hydrophobicity of the cellulose ethers deriving from conformational rearrangements (Carlsson et al., 1989; Karlström et al., 1990) and dehydration (Carlsson et al., 1986) of the polymer chains. Furthermore, upon temperature elevation a decrease in c_1 and cooperativity of the surfactant adsorption and, in general, a decrease in size (N_p) but increase in total number of mixed micelles (clusters) formed has been reported (Kamenka et al., 1994; Evertsson et al., 1996) for the EHEC/SDS/water system. These findings point to the conclusion that the polymer/surfactant interaction gets more intensive in its nature at elevated temperatures. The microviscosity has been measured as a function of temperature (from 20 to 50°C) for several of the systems included in this study. Two regimes, according to the composition, have been distinguished upon temperature elevation: (i) an increased microviscosity for the solutions including SDS contents up to the surfactant concentration corresponding to the maximum in microviscosity; and (ii) a decrease in microviscosity for the compositions with larger SDS contents. These effects can be understood and explained in the following way: In regime (i) the values of N_p are low and the polymer content of the clusters high. As the temperature is raised, the hydrophobicity of the polymer increases which gives a further close packing and, consequently, an increase in rigidity of the mixed micelles. In addition, also the decrease in c_1 promotes this effect due to an increased surfactant binding with temperature at low surfactant concentrations. In regime (ii) the values of N_p are high and the polymer content in each cluster is rather low, i.e. the character of the clusters there is more like ordinary SDS micelles. Both preliminary experiments made in this laboratory and a previous investigation (Miyagishi et al., 1987) on binary micellar SDS/water solutions have also shown decreasing values of the microviscosity upon temperature elevation in the range from 20 to 50°C. A qualitatively similar behaviour is also found for the bulk viscosity of homogeneous solvents (such as water) although the relative magnitude of this effect is not as pronounced as the decrease in microviscosity of SDS micelles (Miyagishi et al., 1987). Thus, it is not surprising that the rigidity of the mixed polymer–surfactant micelles formed in regime (ii) is effected by temperature in the same way as the ordinary SDS micelles are.

CONCLUSIONS

The microviscosity has been measured in dilute aqueous solutions containing mixed micelles of the anionic surfactant SDS and non-ionic cellulose ethers of different hydrophobicity. For the sake of comparison, the uncharged polymers PVP and PEO have also been included in this investigation. Qualitatively, all polymer/SDS systems investigated show the same general behaviour in microviscosity as the SDS concentration is altered and give, for all compositions, higher rigidities than ordinary SDS micelles. At the critical surfactant concentration where the clustering process starts (c_1) the microviscosity in the system increases abruptly to a maximum, after which it decreases to an asymptotic level at the highest SDS concentrations. The maximum in microviscosity has been found, in all cases, to correspond to a low degree of SDS adsorption and consequently to a high polymer content in the mixed micelles, in harmony with recent findings (Evertsson and Nilsson, 1997). A good correlation is shown between polymer hydrophobicity and the rigidity of the polymer/surfactant complex formed. Generally, as the hydrophobicity of the polymer increases, c_1 decreases, and the amplitude of the overall microviscosity pattern of the mixed micelles is raised. An approximately exponential relation is demonstrated between the maxima in microviscosity and the surface activities of the corresponding cellulose derivatives. These facts point to the important conclusion that the polymer hydrophobicity, as judged by ability to decrease the surface tension of water, is a major factor in governing the rigidity of mixed micelles formed by non-ionic cellulose ethers and surfactants. The microviscosity for the cellulose ether/SDS aggregates formed close to c_1 has been found to increase with temperature. This effect has been rationalised in terms of an increased hydrophobicity of these type of polymers upon temperature elevation which gives a further close packing of the aggregates formed.

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