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# On the characterization principles of some technically important water-soluble nonionic cellulose derivatives. Part II: Surface tension and interaction with a surfactant

**Bengt Persson, Stefan Nilsson* & Lars-Olof Sundelöf**

*Physical Pharmaceutical Chemistry, Uppsala University, Uppsala Biomedical Center, P.O. Box 574, S-751 23 Uppsala, Sweden*

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Some surface tension properties of aqueous solutions of eight well characterized nonionic cellulose derivatives are presented. The measurements of surface tension have been performed by the pendant drop method. Due to the initial strong time dependence of the surface tension, the measurements were performed as a function of time up to slightly less than 12 h after forming the drop. After this time there was only a very slow change in surface tension and the value after 11.7 h was taken as the apparent steady-state value of the surface tension ($\gamma^*$). The set of cellulose derivatives investigated covers a broad range in surface activity and gives values of $\gamma^*$ from 37 to 63 mN/m. The interaction of these cellulose ethers with an anionic surfactant SDS has been studied both by a fluorescence probe and a dye solubilization technique. The intensity of interaction has been expressed as the surfactant concentration where the polymer–surfactant interaction starts (CAC); the lower the value of CAC the higher is the interaction intensity. A good correlation between surface activity and hydrophobicity of the polymers as well as with the interaction intensity is shown. An approximately linear relation between surface activity of the cellulose derivatives and the CAC values is obtained. Copyright © 1996 Elsevier Science Ltd

## INTRODUCTION

Cellulose derivatives and other water-soluble polymers play an important role in different kinds of technical applications as well as in pharmaceutical systems (Florence & Attwood, 1988). They may serve as part of a regulating system to control the release rate of active substances from formulations, as stabilizers of suspensions and emulsions, to provide suitable flow properties (Greminger & Krumel, 1980; Daul & Mitchell, 1971), and so on.

Because of the high surface tension of water and the mixed hydrophobic/hydrophilic structure of the nonionic cellulose derivatives (see Fig. 1), most water-soluble cellulose ethers will be preferentially adsorbed at the air–aqueous polymer solution interface. In several practical applications, the interfacial properties of the cellulose derivatives are of specific interest and importance.

The surface/interfacial tension of aqueous solutions of surfactants (Elworthy & MacFarlane, 1962; Neumann & Tanner, 1967; Hua & Rosen, 1988, 1991; Fang *et al.*, 1995) and proteins (Miller & Bach, 1973; Tornberg, 1978; Ward & Regan, 1980; Magdassi & Garti, 1991) has been extensively studied by various methods under a variety of experimental conditions as reported in the literature. Studies of dynamic surface/interfacial tension on solutions of nonionic water-soluble polymers are more rare, but include PVA (poly(vinyl alcohol)) (Frisch & Al-Madfai, 1958; Lankveld & Lyklema, 1972), PEO (poly(ethylene oxide)) (Glass, 1968), HPC (hydroxypropyl cellulose) (Chang & Gray, 1978). Recently, dynamic results have also been published for the cellulose derivative EHEC (ethyl(hydroxyethyl)cellulose) (Nahringbauer, 1991, 1995).

The interaction between ionic surfactants and nonionic polymers in aqueous solutions has gained considerable interest, both academically and industrially, during the last 20–30 years and the system PEO/sodium dodecyl sulphate (SDS)/water is probably the most thoroughly investigated and best known (Goddard, 1986; Breuer & Robb, 1972). Recent studies on the specific systems EHEC/SDS/water (Holmberg *et al.*, 1992;

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*Author to whom correspondence should be addressed.

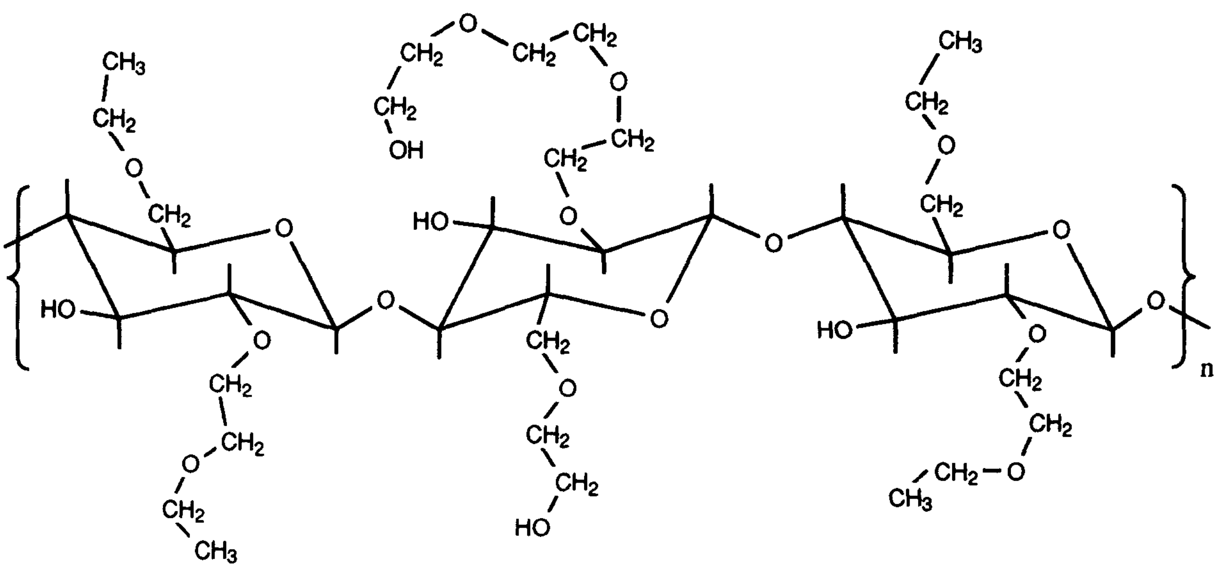

**Fig. 1.** Possible structure segment in EHEC with $MS_{\mathrm{alkylene\ oxide}} = 2$, $DS_{\mathrm{alkyl}} = 1.3$ and DP (degree of polymerization) =

Nilsson *et al.*, 1994, 1995; Carlsson, 1989) and HPMC (hydroxypropyl(methyl)cellulose)/SDS/water (Nilsson, 1995; Löfroth *et al.*, 1991) have revealed similarities, but also some basic differences in the interaction behaviour compared to the PEO/SDS/water system. Various topologies of polymer–surfactant complexes have been visualized (Nagarajan & Kalpakci, 1985; Cabane & Duplessix, 1985; Winnik & Winnik, 1990; Nilsson, 1995) which are all based on a micellar aggregation process of surfactant adsorbed along the polymer chain. In this investigation, we have studied the relations between surface activity and hydrophobicity of the nonionic cellulose ethers as well as the degree of 'reactivity' for the interaction with an ionic surfactant. In this case, the surfactant concentration where interaction starts (CAC) is used as an indicator for reactivity.

Surface tension measurement is a classical approach for the study of aqueous polymer–surfactant systems (Jones, 1967; Schwuger, 1973; Tadros, 1974; Bahadur *et al.*, 1988; Sivadasan & Somasundaran, 1990). However, it has been found that the applicability of the method and the interpretation of the experimental results are restricted if both the surfactant and the polymer are surface active as in the case of nonionic cellulose ethers (Carlsson, 1989).

In a previous study from our laboratory (Nilsson *et al.*, 1995), results are reported concerning the physico-chemical characterization of a set of eight water-soluble nonionic cellulose ethers samples. A wide selection of techniques were applied including viscometry, static light scattering (LS), dynamic light scattering (DLS) and size exclusion chromatography with both refractive index (RI) and low angle laser light scattering (LALLS) detection. The present paper is intended to be a complementary study in which surface tension data for the same set of cellulose ethers are reported and discussed in relation to other characterization parameters. Also the intensity of interaction between these polymers and a low molecular weight anionic surfactant (SDS) in aqueous solution is treated.

## EXPERIMENTAL

### Materials

In Table 1, data on the non-ionic cellulose derivatives used in this study are presented.

All of the ethyl(hydroxyethyl)cellulose (EHEC) fractions were kindly supplied by Akzo Nobel AB, Stenungsund, Sweden. Hydroxyethylcellulose (HEC) and methylcellulose (MC) were obtained from Aldrich-Chemie, Steinham, Germany. Hydroxypropyl(methyl) cellulose (HPMC) was obtained from Colorcon Ltd, West Point, England, and hydroxypropylcellulose (HPC) from Hercules Inc., Wilmington, USA. A typical cellulose ether structure is shown in Fig. 1.

The substitution of the cellulose ethers is normally characterized by the numbers $DS_{\mathrm{alkyl}}$ (degree of substitution) and $MS_{\mathrm{alkylene\ oxide}}$ (molar substitution). $DS_{\mathrm{alkyl}}$ is the average number of hydroxyl groups on the anhydroglucose unit which has been substituted by alkyl groups ($0 < DS_{\mathrm{alkyl}} < 3$). $MS_{\mathrm{alkylene\ oxide}}$ is the average of the total number of alkylene oxide groups (hydroxyethyl or hydroxypropyl) per anhydroglucose unit. Due to formation of oligo(alkylene oxide) chains the quantity $MS_{\mathrm{alkylene\ oxide}}$ could in principle be almost any positive number. In practice the highest value encountered 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).

**Table 1. Data for the set of non-ionic cellulose ethers investigated**

| Polymer | Trade name | CP (°C) | $DS_{alkyl}$ | $MS_{alkylene\ oxide}$ |
|---|---|---|---|---|
| EHEC | Bermocoll CST-103 | 28 | 1.5 | 0.7 |
| EHEC | Bermocoll DVT-87014 | 28 | 1.4 | 0.9 |
| EHEC | Bermocoll E230G | 65 | 0.9 | 0.9 |
| EHEC | Bermocoll E411G | 58 | 1.2 | 1.7 |
| HPMC | Methocel E4 EP | 55 | ~2 | ~0.4 |
| HPC | Klucel LF | 42 | - | ~0.4 |
| MC | - | 65 | ~2 | - |
| HEC | - | > 100 | - | ~3 |

CP - Refers to 0.5%(w/w) aqueous solutions

$DS_{alkyl}$, $MS_{alkylene\ oxide}$ - Values for the EHEC fractions are determined by the producer and the values for HEC, MC, HPC and HPMC are estimated.

The standardized procedure adopted to make an aqueous stock solution of a cellulose ether is described elsewhere (Holmberg *et al.*, 1992). The stock solutions were dialyzed in tube membranes (cut-off 12–14000, Spectra/Por®, Spectrum Medical Ind., USA) against Milli Q water (Millipore) for one week to remove salts and other low molecular weight material. In the end the stock solutions were filtered through 0.8 μm filters (Millex-AA, Millipore SA, France) to remove undissolved substance, microgels and dust particles before the concentrations were determined by drying the samples to constant weight at 105 °C.

All solutions were prepared by weight at least 24 h before an experiment was performed in order to reach equilibrium and to allow any time-dependent effect to settle (Nilsson *et al.*, 1994). The cellulose ether samples made for surface tension measurements were prepared in very carefully cleaned glassware and kept at +5°C (refrigerator) during these 24 h. Concentrations of the cellulose ether samples are expressed in per cent by weight %(w/w) or parts per million (ppm, w/w) and the concentration range of SDS used was 0–25 mM. Analytical grade sodium dodecyl sulphate (SDS) was obtained from Merck, Germany and Oil Orange SS (*o*-toluenazo-*b*-naphthol) from Tokyo Kasei Inc., Japan and they were both used without further purification. Pyrene (+98%) was obtained from Acros Chimica, Belgium and twice purified by recrystallization from absolute ethanol. Filtered (0.8 μm, Millex-AA, Millipore SA, France) Milli Q water was used in the preparation of all solutions in this study.

## Surface tension measurements

The surface tension was measured with a pendant drop technique apparatus (Andreas *et al.*, 1938; Adamson, 1990) designed and constructed at this department. This method was used since it enables surface tension measurements to be made over a long time scale without disturbing the liquid–air interface and is therefore suitable for investigations of both kinetic effects and equilibrium properties of polymer solutions (Padday, 1969). For polymeric systems the pendant drop technique indicates a complex time dependence in the approach to equilibrium which necessitates experiments of long duration. The measurements were performed at 19.5°C in a room where the temperature is stable to within ±0.5°C. The equipment is fixed on an optical rail and mounted on a heavy vibration insulated table. The pendant drop is illuminated with parallel light from a helium–neon laser. The drops were formed at the end of a glass syringe in a spectrophotometer cuvette partly filled with water giving a high local humidity as an aid to avoid evaporation from the drop surface. To avoid disturbing condensation on the inside of the cuvette this was rinsed with alcohol and filled with deionized filtered (0.45 μm, Millex-HA, Millipore, France) water. Solutions were thermostated for at least 1/2 h in the syringe before a drop was formed and measurements were made.

The drop contour was automatically recorded through a black and white CCD video camera (Ikegami, 44 L, 512 x 582 pixels) with macro optics, a video monitor (Ikegami, PM-127 resolution 650 lines or better), and a personal computer (Victor 286C, 80286 processor) with a frame grabber card (microeye RT card). Forty-one drop profiles were sampled during 11.7 h. Ten or 11 of these profiles were selected and processed to give dynamic surface tension data. The magnification of the drop is determined by the measurement of a ball bearing ball which is pasted to the drop-forming capillary. The drop profile typically consists of 750–800 data points, but only half of them were used in the calculations. The surface tension was calculated by a least-square fit of the theoretical shape to the measured drop contour. This was performed by a computer program, designed by Rotenberg and co-workers (Rotenberg *et al.*, 1983) and was run on a personal computer.

## Fluorescence measurements

Steady-state fluorescence spectra were recorded on a SPEX Fluorolog-2 fluorescence spectrophotometer in the uncorrected spectrum mode. Emission spectra ($\lambda = 350$–$450$ nm) for pyrene at 20°C were obtained with the excitation wavelength set to 334 nm and the bandwidths set to 1.88 nm for excitation and 0.85 nm for emission. Aqueous solutions of nonionic cellulose ethers and surfactant (SDS) for spectroscopic analysis contained a pyrene concentration less than $10^{-6}$ M (filtered saturated water solution). The hydrophobic index, $I_1/I_3$, was taken as the ratio between the intensities at the first ($\lambda$ =373 nm) and at the third ($\lambda$ =384 nm) vibronic peaks in the pyrene emission spectrum (Kalyanasundaram & Thomas, 1977; Thomas, 1980).

### Dye solubilization measurements

Solubilization of the dye Oil Orange SS by aqueous solutions of nonionic cellulose ether and surfactant (SDS) was studied spectrophotometrically by determining the absorbance at 495 nm. All experimental procedures were similar to the ones adopted and described in previous papers from our laboratory (Nilsson *et al.*, 1995; Nilsson, 1995). The instrument used was a Milton Roy Spectronic® Genesys™ 5 spectrophotometer. The preparation of aqueous solutions of cellulose ether/SDS was performed 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). The excess of dye was separated off by centrifugation (Beckman Avanti™ Centrifuge) and the absorbance of the supernatant determined, dilutions being performed for supernatants of absorbance greater than 1.3.

## RESULTS AND DISCUSSION

It is well known that water-soluble cellulose derivatives are surface active and reduce the surface tension of aqueous systems (Greminger & Krumel, 1980; Doelker, 1990; Jullander, 1952). The surface activity of a macromolecule like a protein or a cellulose derivative depends possibly on a number of general factors (Brash & Horbett, 1987), such as the chemical structure of the backbone, type and number of substituents, molecular size, hydrophobicity (hydrophilic/hydrophobic balance), flexibility and charge of the polymer chain. In this paper, data will be presented for the surface tension of a set of eight well-characterized (Nilsson *et al.*, 1995) nonionic cellulose derivatives in water solution.

In Table 1 some basic data are shown for the set of nonionic cellulose ethers investigated. Both the substitution ($DS_{alkyl}$, $MS_{alkylene\ oxide}$) and CP ('index' of hydrophilic/hydrophobic balance) cover a rather broad range which definitely will give differences in the physico-chemical properties. CP is a parameter that is found to be closely related to surface activity (see below) and depends on a number of factors (Sarkar, 1979; Dönges, 1990) such as type and degree of substitution, molecular weight and concentration. In most cellulose derivatives one could in many cases also expect a marked heterogeneity in the distribution of substituents along the cellulose backbone.

For the comparative discussion, a summary of the parameters obtained in the characterization of the set of nonionic cellulose derivatives from a recent paper (Nilsson *et al.*, 1995) is presented in Table 2. The four methods of viscometry, static light scattering (LS), size exclusion chromatography — with both refractive index and low angle laser light scattering detection (SEC/RI/LALLS) — and dynamic light scattering (DLS) were combined and experiments were performed in two solvents of different hydrophobicity in order to give a detailed and dependable description of the samples

**Table 2. Summary of parameters, for the set of nonionic cellulose ethers investigated (published in a previous paper Nilsson *et al.*, 1995), obtained from viscometry, static light scattering (LS), size exclusion chromatography with low angle laser light and refractive index detection (SEC/LALLS/RI) and dynamic light scattering (DLS) at 20°C in water and in 50% methanol/50% 10 mM NaCl in water**

| Substance | water | | | | 50% methanol/50% 10mM NaCl in water | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | viscometry | | DLS | | viscometry | | LS | | | SEC/LALLS/RI | | DLS | |
| | [$\eta$] (ml/g) | $k_H$ | $d^1$ (nm) | $D\times10^8$ (cm$^2$/s) | [$\eta$] (ml/g) | $k_H$ | $M_w\times10^{-5}$ | $R_g$ (nm) | $A_2\times10^4$ (ml·mol/g$^2$) | $M_w\times10^{-5}$ | $M_w/M_n$ | $d^1$ (nm) | $D\times10^8$ (cm$^2$/s) |
| A. EHEC | | | | | | | | | | | | | |
| CST-103 | 455 | 0.68 | 63 | 6.59 | 320 | 1.31 | 5.11 | 66 | −0.04 | 1.89 | 2.1 | 64 | 3.59 |
| DVT-87014 | 290 | 1.03 | 55 | 7.55 | 244 | 1.25 | 2.35 | 47 | 2.0 | 1.33 | 1.8 | 49 | 4.68 |
| E230G | 410 | 0.48 | 56 | 7.65 | 270 | 1.19 | ~50 | — | −0.3 | 5.35 | 1.8 | 42 | 5.62 |
| E411 | 1000 | 0.62 | 66 | 6.30 | 980 | 0.44 | 11.0 | 78 | 5.1 | 7.85 | 1.6 | 72 | 3.18 |
| B. Others | | | | | | | | | | | | | |
| HPMC | 740 | 0.54 | 64 | 6.48 | 620 | 0.80 | 3.85 | 64 | 3.3 | 3.01 | 2.2 | 59 | 3.89 |
| HPC | 134 | 0.83 | 34 | 12.22 | 110 | 1.80 | 2.62 | 33 | 9.8 | 1.06 | 2.0 | 25 | 9.18 |
| MC | 400 | 1.20 | 51 | 8.37 | 395 | 0.36 | 2.98 | 57 | 4.4 | 1.62 | 1.8 | 55 | 4.17 |
| HEC | 273 | 1.22 | 55 | 7.55 | 285 | 0.88 | 2.28 | 47 | 3.5 | 1.89 | 4.8 | 55 | 4.17 |

[$\eta$] = intrinsic viscosity, $k_H$ = Huggins constant, $d^1$ = the average particle (molecule) diameter, D = the diffusion coefficient, $M_w$ = the weight average molecular weight, $R_g$ = the radius of gyration, $A_2$ = the second virial coefficient, $M_w/M_n$ = the polydispersity index.

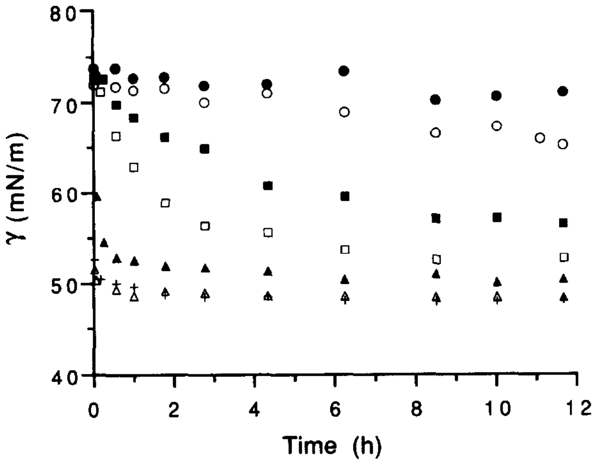

**Fig. 2.** Time dependence of surface tension for aqueous EHEC/E230G solutions at 20°C; 1 ppm (●), 1.4 ppm (○), 2 ppm (■), 3 ppm (□), 10 ppm (▲), 100 ppm (△), 500 (+).

under study. These results show that the set of cellulose ethers investigated is a heterogeneous group of substances, which differ in many aspects such as size and interaction and cover a broad range in molecular weight and molecular weight distribution. Thus they are ideally suited for a comparative analysis with other techniques that rely more directly on specific molecular properties.

Figure 2 gives a typical example of primary data for the time dependence of surface tension, $\gamma$, for one fraction of EHEC (E230G) at different polymer concentrations. The surface tension decreases exponentially with time towards an asymptotic steady-state value. Sometimes a well-defined steady-state is not reached, but rather a slowly decreasing $\gamma$-value. The true reason for this is not known, but there are indications that the slow decrease might be caused by slow conformational rearrangements (Nahringbauer, 1995). The surface tension profile can be classified into two regions. Region I: At low polymer concentrations (0–10 ppm for EHEC/E230G), the magnitude of the decrease of $\gamma$ and the time-dependence function of $\gamma$ are highly sensitive to the polymer concentration, $c_p$. For the lowest concentrations (1, 1.4 ppm), a steady-state value of $\gamma$ is not reached even within 11.7 h. We designate by $\gamma^*$ the surface tension at this (arbitrarily chosen) time after formation of the drop and note that the difference between $\gamma^*$ and the true steady-state value should be very small as can be seen from the slopes of $\gamma$ versus time curves and almost within the experimental error of the pendant drop method as indicated in experiments run for 24 h for some of the compositions. Hence, for practical reasons, all measurements have been continued up to the arbitrarily chosen value 11.7 h and $\gamma^*$ is taken to represent an apparent steady-state value. Region II: At high polymer concentrations (10–500 ppm for EHEC/E230G), the time dependence is almost insensitive to polymer concentration and all curves show the same feature with a steep drop of $\gamma$ at short times followed by a flattening out to the steady-state value of $\gamma$ which for this fraction of EHEC (E230G) is 48 mN/m.

Previous workers (Ward & Regan, 1980; Tornberg, 1978; Magdassi & Garti, 1991; Nahringbauer, 1995) have described the adsorption process of a macromolecule at an interface by three main processes:

(1) diffusion of the macromolecule from the bulk to the interface region where it is 'adsorbed';
(2) spreading or unfolding of the adsorbed macromolecules;
(3) molecular rearrangements of the adsorbed macromolecules.

The process of adsorption can be followed by a reduction in the surface/interfacial tension or as an increase in the surface pressure. It has been proposed that the time dependence of $\gamma$ is related to the number of adsorbed surface active segments at the surface per unit area with time (Lankveld & Lyklema, 1972). A classical analysis of the kinetics of adsorption was performed by Ward and Tordai (Ward & Tordai, 1946, 1952), who considered the effects of diffusion from the bulk to the surface and the energy barrier which the molecules must overcome in order to be adsorbed. Initially, at low surface coverage, the kinetics is determined by process (a), but at higher coverages when there is an energy barrier to adsorption, the processes (b) and (c) become more important (Lankveld & Lyklema, 1972; Graham & Phillips, 1979).

Figure 3 gives a typical example of the change in $\gamma$ with time (log scale) for the sample HPC at the concentration 3 ppm. It is seen that the approach of $\gamma$ towards the steady-state follows a sigmoidal curve. At first, there is a lag time (for this specific sample approximately equal to 1/2 h) where $\gamma$ remains close to that of pure water before dropping steeply and approaching the steady-state value asymptotically. This general behaviour of $\gamma$ as a function of time is similar to what has

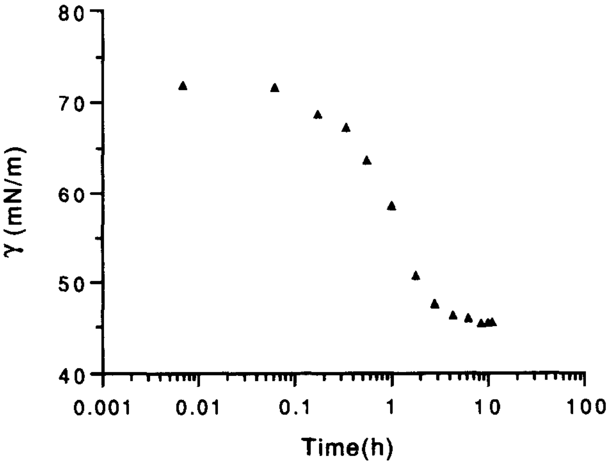

**Fig. 3.** A typical curve of change in surface tension versus log time for the sample HPC at the concentration 3 ppm.

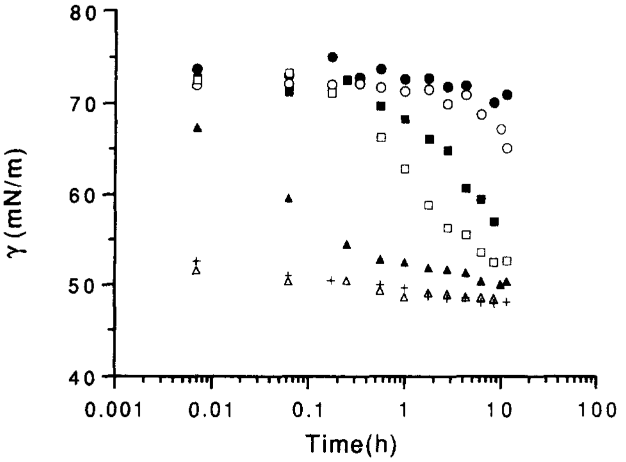

**Fig. 4.** Surface tension versus log time for aqueous EHEC/E230G solutions at 20°C; 1 ppm (●), 1.4 ppm (○), 2 ppm (■), 3 ppm (□), 10 ppm (▲), 100 ppm (△), 500 (+).

been reported for related systems by others (Chang & Gray, 1978; Nahringbauer, 1995).

In Fig. 4 $\gamma$ is plotted against the logarithmic time for the same primary results as presented in Fig. 2. It is seen that the lag time increases with decreasing polymer concentration, $c_p$, in the low concentration region (Region I, 0–10 ppm). For the highest polymer concentrations (Region II, 10–500 ppm), there is no observable lag time (the pendant drop method cannot sample this fast process) and only the asymptotic approach to the steady-state value of $\gamma$ is seen.

From Figs 2 and 4 it is evident that the rate of approach to the steady-state is strongly dependent on the bulk concentration of the polymer and that the time scale runs over many hours for all samples. Two possible explanations for this are a slow diffusion transport of polymer to the interface and a slow process of molecular rearrangements of already adsorbed polymer or a mixture of both.

Figure 5 shows $\gamma^*$ as a function of log $c_p$ for three cellulose ethers EHEC/E411, HPMC and HPC. The curves consist of two linear parts intersecting at a breakpoint. In the low polymer concentration regime (0–3 ppm) there is a strong concentration dependence of $\gamma^*$ and a total reduction in $\gamma^*$ of approximately 30 mN/m when increasing $c_p$ from 0 to 3 ppm. The high polymer concentration regime (3–100 ppm) gives an almost constant or slightly decreasing value of $\gamma^*$ when raising $c_p$ from 3 to 100 ppm. The breakpoint between these curves, denoted the critical polymer concentration, *cpc*, should be characteristic for a given polymer and it is related to the critical micelle concentration (*cmc*) of low molecular weight surfactants (see for example Elworthy & MacFarlane, 1962). The values of *cpc* and also the corresponding value of $\gamma$ at *cpc* ($\gamma_{cpc}$, see Fig. 5) are summarized for all nonionic cellulose ethers together with $\gamma^*$ in Table 3. It is seen that all the investigated cellulose derivatives except HEC are rather surface active

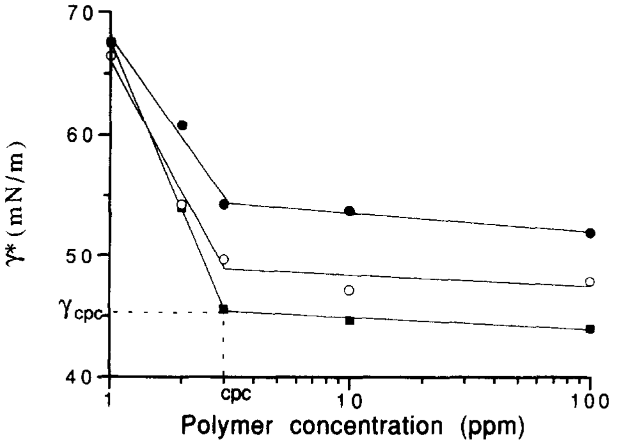

**Fig. 5.** Surface tension ($\gamma^*$) as a function of log concentration for the cellulose ethers E411 (●), HPMC (○) and HPC (■). For the specific sample HPC is marked $\gamma_{cpc}$ = 45.5 mN/m and *cpc* = 3 ppm.

**Table 3. Surface tension (against air) results at 20°C for aqueous solutions of the set of nonionic cellulose ethers investigated**

| Substance | $\gamma^*$ (mN/m) | $\gamma_{rel}$ | *cpc* (ppm) | $\gamma_{cpc}$ (mN/m) |
|---|---|---|---|---|
| A. EHEC | | | | |
| CST-103 | 37 | 0.51 | 3.2 | 40.7 |
| DVT-87014 | 40 | 0.55 | 2.8 | 43.2 |
| E230G | 48 | 0.66 | 3.1 | 50.9 |
| E411 | 52 | 0.71 | 3.2 | 54.4 |
| B. Others | | | | |
| HPMC | 47 | 0.65 | 3.0 | 48.9 |
| HPC | 42 | 0.58 | 3.0 | 45.5 |
| MC | 47 | 0.65 | 2.8 | 51.9 |
| HEC | ˜63 | 0.87 | - | - |

$\gamma^*$ - Surface tension after 11.7 h (not steady-state).
$\gamma_{rel}$ - $\gamma^*/\gamma_{H_2O}$ (20 °C). $\gamma_{H_2O}$ (20 °C) = 72.8 mN/m.
*cpc* - Critical polymer concentration, see Fig. 5.
$\gamma_{cpc}$ - The values of the surface tension at the critical polymer concentration, see Fig. 5.

with values of $\gamma^*$ ranging from 37 to 52 mN/m, i.e. the most surface active substance (CST-103) reduces the surface tension of water to approximately one half of its original value (72.8 mN/m at 20 °C (*Handbook of Chemistry and Physics*, 1985)). We have found that all of the cellulose ether samples investigated give almost the same value of *cpc*, ranging from 2.8 to 3.2 ppm. This fact shows that in this type of systems the molecular weight and the type and degree of substitution have a low influence on *cpc*. The origin to this is not clear, but an explanation could be a combination of effects deriving from the stiff and rigid cellulose backbone (Wirick & Waldman, 1970), the rather high polydispersity ($M_w/M_n \approx 2$, see Table 2) and the relatively similar range of molecular weights of the samples investigated in this study. By comparison with reported results for other related systems like HPC (Chang & Gray, 1978), EHEC

(Nahringbauer, 1995) and a nonionic surfactant hexadecyl polyoxyethylene ether (Elworthy & MacFarlane, 1962) it is found that our values of *cpc* are in approximately the same concentration range as the estimated values of *cpc* (≈4–8 ppm) in all these systems. The values of $\gamma_{cpc}$ show a larger variation since they are related to the surface activity of a given polymer.

Nonionic polymers such as PEO, PVP (polyvinylpyrrolidone) and the nonionic cellulose ethers form complexes with surfactants in aqueous solution (Breuer & Robb, 1972; Goddard, 1986, 1994). The field has been extensively studied for some time and many interaction models have been proposed which are all based on a micellar aggregation process of the surfactant adsorbed along the polymer chain. It has been proposed that the hydrophobicity of the polymer is a major factor which determines the strength of interaction (reactivity) with surfactants. A reactivity series of the nonionic polymers toward ionic surfactants has been set up on the basis of hydrophobicity of the polymers (Breuer & Robb, 1972). Recent works by Winnik and coworkers (Winnik *et al.*, 1987) using HPC, Bahadur and coworkers (Bahadur *et al.*, 1988) using styrene-ethylene oxide block copolymer and Witte and Engberts (Witte & Engberts, 1989) using PEO and PPO (poly(propylene-oxide)) also suggest that the hydrophobicity of the polymer is a major factor in governing the reactivity in the polymer–surfactant complexation.

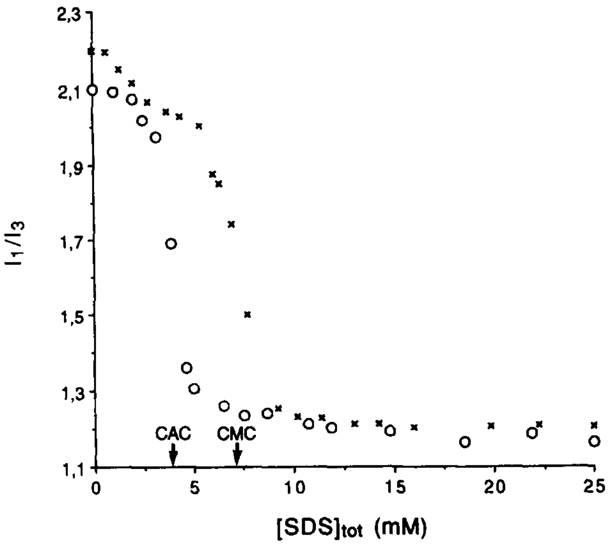

**Fig. 6.** Hydrophobic index ($I_1/I_3$) for pyrene (conc. < $10^{-6}$ M) luminescence in aqueous HPMC/SDS solutions as a function of the total SDS concentration at 20°C. The CAC value was taken as the inflection point of the sharply decreasing part of the curve (for this specific system is CAC = 3.9 mM and CMC for the binary SDS/water system is 7.0 mM). 0.20% HPMC (○), 0% HPMC (×).

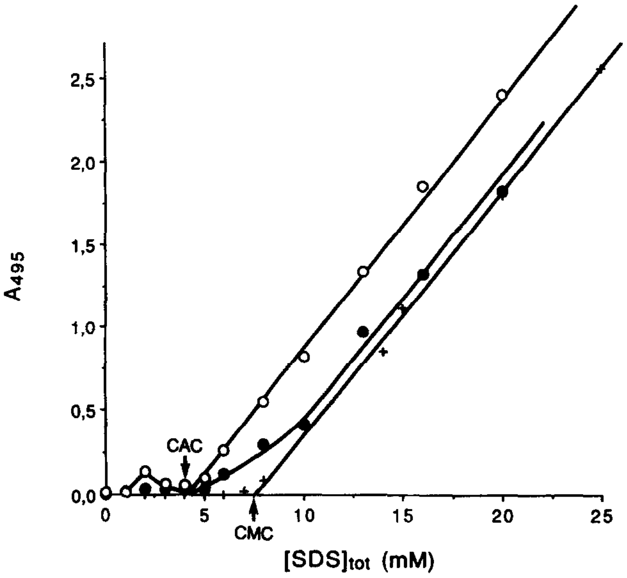

**Fig. 7.** Absorbance at 495 nm of solubilized Oil Orange SS, $A_{495}$, as a function of the total SDS concentration in aqueous HPMC/SDS solutions at 20°C. The CAC value was taken at the sharp "footpoint" of increasing $A_{495}$ (for this specific system is CAC = 4.3 mM and CMC for the binary SDS/water system is 7.5 mM). 0.20% HPMC (○), 0.05% HPMC (●), 0% HPMC (+).

The interaction between a surfactant and a polymer is usually a cooperative process and it starts at a well-defined surfactant concentration termed the critical aggregation (adsorption) concentration, denoted CAC. CAC is lower than the ordinary critical micelle concentration, denoted CMC, for the binary surfactant–water system and represents the onset of surfactant binding to the polymer. In this paper we use CAC as an indicator of reactivity in the polymer–surfactant interaction, meaning that the lower the value of CAC, the higher is the reactivity of the cellulose derivative. Values of CAC for aqueous solutions of the cellulose ethers and SDS have been determined by a fluorescence probe and a dye solubilization technique. The ratio $I_1/I_3$ of the first ($\lambda$ = 373 nm) and third ($\lambda$ = 384 nm) vibronic peaks in the pyrene emission spectrum is known to be a monitor of the pyrene microenvironment polarity (Kalyanasundaram & Thomas, 1977; Thomas, 1980). 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 formation both in the absence (Kalyanasundaram & Thomas, 1977; Thomas, 1980) and presence of polymer (Turro *et al.*, 1984; Zana *et al.*, 1985; Nilsson *et al.*, 1995). Figure 6 shows a typical example of the fluorescence probe technique applied to one of the systems under study. The dye solubilization technique is a classical method to study and confirm interaction between surfactants and polymers (Goddard, 1986; Saito, 1957; Lange, 1971). It is based upon the ability of micellar surfactant solutions to solubilize hydrophobic substances such as dyes, drugs, hydrocarbons etc. Figure 7 gives a typical example of the dye solubilization technique applied on one of the systems studied. CMC of the binary SDS–water system

**Table 4. Surface tension (against air) and CAC results at 20 °C for aqueous solutions of the set of non-ionic cellulose ethers investigated.**

| Substance | CP (°C) | $\gamma^*$ (mN/m) | CAC$^1$ (mM) | CAC$^2$ (mM) |
|---|---|---|---|---|
| A. EHEC | | | | |
| CST-103 | 28 | 37 | 1.5 | 2.0 |
| DVT-87014 | 28 | 40 | 1.5 | 1.5 |
| E230G | 65 | 48 | 3.9 | 4.1 |
| E411 | 58 | 52 | 3.7 | 4.1 |
| B. Others | | | | |
| HPMC | 55 | 47 | 3.9 | 4.3 |
| HPC | 42 | 42 | 2.0 | 2.0 |
| MC | 65 | 47 | 4.1 | 4.5 |
| HEC | > 100 | ~63 | 7.0 | 7.5 |

CP - Refers to 0.5% (w/w) aqueous solutions.

CAC$^1$ - Critical aggregation concentration for the system polymer/SDS/water as determined by the ratio $I_1/I_3$ in the pyrene emission spectrum.

CAC$^2$ - Critical aggregation concentration for the system polymer/SDS/water as determined by a dye solubilization technique.

was determined to 7.0 and 7.5 mM with the fluorescence probe and dye solubilization technique, respectively. These values are in fair agreement with the literature (Handbook of Pharmaceutical Excipients, 1986).

Table 4 summarizes values of CAC, surface tension ($\gamma^*$) and CP for the set of nonionic cellulose ethers investigated. The results show that there is a good correlation between the surface activity of the polymers, the cloud point (CP, essentially hydrophobicity) and reactivity with the surfactant SDS, the latter expressed as CAC. The least surface active and most hydrophilic cellulose ether in the set, HEC, does not interact noticeably with SDS. It has recently been shown that reactivity towards surfactants can be conferred upon HEC by introducing hydrophobic substituents to the cellulose backbone (Tanaka *et al.*, 1990; Dualeh & Steiner, 1990) which should also enhance its surface activity. A corresponding pair is, as Goddard & Leung have indicated (Goddard & Leung, 1992), polyacrylamide, which is surface inactive and not reactive toward surfactants, and poly(*N*-isopropylacrylamide) which has been shown to be both surface active and reactive. The most surface active of the cellulose ethers CST-103, DVT 87014 and HPC have the lowest CP and the highest reactivity (lowest CAC values). To further illustrate the relation between surface activity of the cellulose ethers and their reactivity, Fig. 8 is presented. Here the surface activity of a given polymer is presented as $\gamma_{H_2O} - \gamma^*$ and plotted as a function of the CAC value determined by the fluorescence probe technique described above. An approximately linear relation between the quantity $\gamma_{H_2O} - \gamma^*$ and the corresponding CAC value is found with an intercept indicating some sort of a limiting surface activity for these cellulose ethers of approximately 40 mN/m. At this value interaction starts already upon addition of the first SDS monomer. As can be seen in Fig. 8 and in Table 4, there are three samples in the set which are very surface active (CST-103, DVT-87014 and HPC). They have a surface activity comparable to the surfactant SDS. Aqueous solutions of SDS at concentrations equal to CMC (≈8 mM) or slightly higher have a surface tension of approximately 35 mN/m (as determined by us and also in accordance with the literature (Neumann & Tanner, 1967)) which gives a surface activity ($\gamma_{H_2O} - \gamma_{SDS}$) of 37.8 mN/m. It can also be noticed, as a comparison, that aqueous solutions of these three cellulose ethers give surface tensions that are almost comparable even to the surface tension of organic solvents such as benzene (29 mN/m) and *n*-octanol (27 mN/m) (Florence & Attwood, 1988). The fact that the onset of interaction (CAC) between polymer and SDS is sampled at slightly lower surfactant concentrations by the hydrophobic index as compared to other methods has been observed and reported earlier for related systems (Kalyanasundaram & Thomas, 1977; Ananthapadmanabhan *et al.*, 1985; Nilsson *et al.*, 1995).

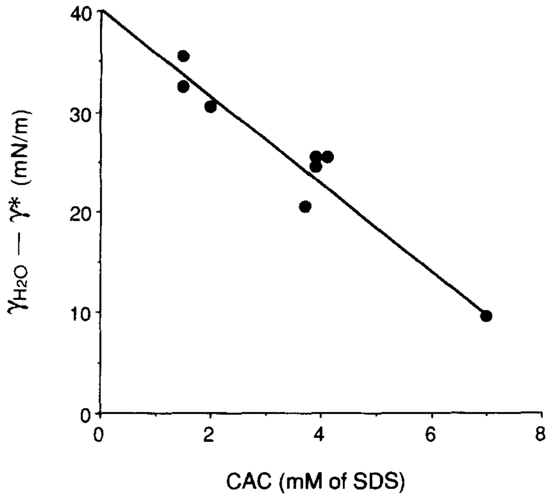

**Fig. 8.** Surface activity ($\gamma_{H_2O} - \gamma^*$) of the different cellulose ether samples investigated as a function of the CAC value in the interaction with SDS determined by the hydrophobic index of pyrene ($I_1/I_3$) at 20°C.

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