Colloid Polym Sci (2004) 283: 33–40
DOI 10.1007/s00396-004-1083-6

ORIGINAL CONTRIBUTION

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Preparation of substituted ionic carbohydrate polymers and their interactions with ionic surfactants

Received: 3 December 2003
Accepted: 10 February 2004
Published online: 24 March 2004

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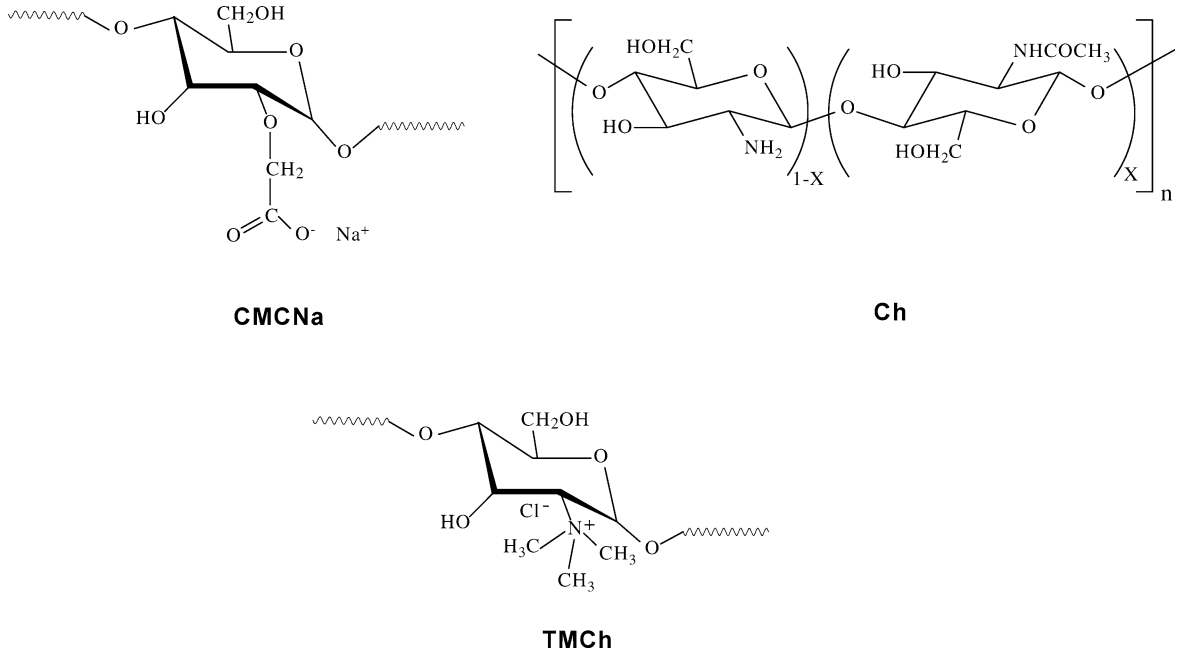
Abstract The formation of micelles of hexadecyltrimethylammonium chloride (CTAC) and sodium dodecylsulfate (SDS) in aqueous solutions containing charged polysaccharides was studied by steady-state and time-resolved fluorescence measurements using pyrene as a photophysical probe. Micropolarity studies using the I_1/I_3 ratio of the vibronic emission bands of pyrene and the behaviour of the I_E/I_M ratio between the excimer and monomer emissions show the formation of hydrophobic domains. The interactions between the polyelectrolytes and surfactants of opposite charge lead to the formation of induced pre-micelles at surfactant concentrations lower than the critical micellar concentration (cmc) of the surfactants. At similar concentrations, the I_E/I_M ratio shows a peak. This aggregation process is assumed to be due to electrostatic attractions. At higher surfactant concentrations, near the critical micellar concentration, micelles with the same properties as those found in pure aqueous solution are formed. On the other hand, systems containing polyelectrolytes and surfactants of the same charge do not show this behaviour at low concentrations. The presence of long alkyl chains bound to the polyelectrolytes also induces the formation of free micelles at concentrations somewhat below the aqueous cmc.

Keywords Carboxymethylcellulose · Chitosan hydrochloride · *N*,*N*,*N*-Trimethylchitosan chloride · Pre-micelles · Surfactants · Pyrene · Hydrophobic microdomains

Introduction

Carboxymethylcellulose (CMCNa) (Scheme 1a) and chitosan (Ch) (Scheme 1b) are polysaccharide-derived polyelectrolytes obtained by derivatization of cellulose[1] and chitin [2], respectively. The parent polymers play very important structural roles in living cells and are both homopolysaccharides composed of linear chains in which their monosaccharide units, D-glucopyranose (for cellulose) and 2-deoxy-2-acetamido-D-glucopyranose (for chitin), are bound through $\beta(1 \rightarrow 4)$ glycosidic bonds. Carboxymethylation of cellulose with chloroacetic acid in the presence of excess sodium hydroxide leads to the alkylation of some of the available hydroxyl groups [1, 3]. Thus, CMC is generally obtained as a sodium salt, a water-soluble polymer widely used in many industrial fields. The partial deacetylation of chitin results in chitosan, a copolymer of $\beta(1 \rightarrow 4)$-linked 2-deoxy-2-acetamido-D-glucopyranose and 2-deoxy-2-amino-D-glucopyranose in which the latter unit prevails [2]. Chitosan is soluble in slightly acid aqueous solutions due to the protonation of the amino groups present in the major part of its units, but it is insoluble in strong acid and in neutral and alkaline



Scheme 1 *CMCNa* carboxymethylcellulose; *Ch* chitosan, where *X* represents the degree of acetylation; *TMCh* *N*,*N*,*N*-trimethylchitosan

media. Chitosan is usually modified chemically to overcome its limited solubility in aqueous media by extensive alkylation of the amino groups. The reaction of chitosan with excess iodomethane in *N*-methyl-2-pyrrolidone results in *N*,*N*,*N*-trimethylchitosan (TMCh) [4] (Scheme 1c), a strong polyelectrolyte (i.e. a polymer that is permanently charged when dissolved in adequate polar solvents). Amphiphilic chitosan derivatives with tensoactive properties can be prepared by *N*-alkylation with long hydrophobic alkyl chains [5].

Spectroscopic techniques have become very successful in investigating phenomena that occur in polyelectrolyte–surfactant systems [6, 7]. All investigations indicated that many similarities exist between binding of surfactants to polyions and micelle formation in polymer-free solutions. The surfactant–polymer systems in aqueous solution are also intriguing from both fundamental, as well as practical points of view. These complex mixtures find extensive industrial applications in areas related to mineral processing, foaming control, medicine, food, detergency, enhanced oil recovery etc. They are also of interest in formulation and conditioning of cosmetics, biological, pharmaceutical and fine chemistry applications [8, 9, 10, 11].

The understanding of the nature of the surfactant–polymer interactions that lead to the formation of these complexes and their physical structure and stability are not clearly established yet. Thus, the interactions between surfactants and polymers have been the subject of active research for the last three decades and the focus of some recent reviews [12, 13].

The joint self-assembly of polymers and surfactants usually starts at a well-defined surfactant concentration, the critical aggregation concentration (cac). One of the most consistent experimental observations in polymer–surfactant systems is that the cac is found to be lower than the critical micellar concentration (cmc) of the polymer-free surfactant solution. Consequently, polymer–surfactant systems are commonly divided into two categories: i) polyelectrolyte and oppositely charged ionic surfactant for which the cac can be several orders of magnitude lower than the cmc; ii) neutral polymer and ionic surfactant for which the cac is lower than, but of the same order of magnitude as the cmc. Less common are systems containing a polyelectrolyte and a non-ionic surfactant [14, 15], which can be included in the second category as their cac is comparable to the cmc. Systems where both species are neutral exhibit a very weak interaction [16]. It is generally accepted that polyelectrolytes do not bind surfactants of similar charge, and few studies of such systems have been reported. However, the surfactant properties are affected by polyelectrolytes in the same way as by low molecular weight salts (i.e. the cmc will decrease and the aggregation number increases) [17, 18].

This research is a follow-up of the work performed previously [19, 20]. In the present contribution we use fluorescence emission spectroscopy [18] to determine the cmc and cac for systems involving interactions between surfactants and carbohydrate derivatives such as carboxymethylcellulose, chitosan hydrochloride and *N*,*N*,*N*-trimethylchitosan chloride. We put emphasis on

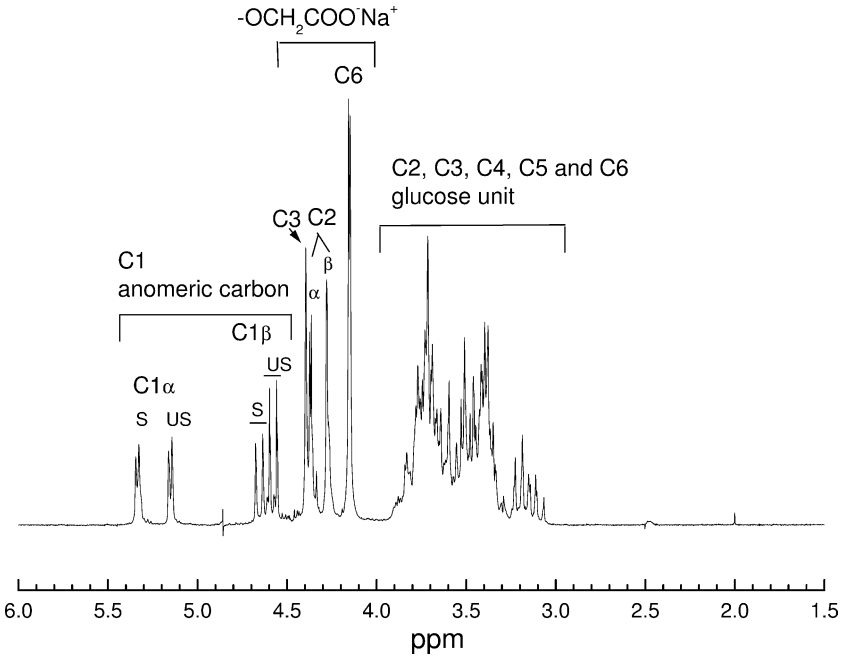


Fig. 1 ^{1}H NMR spectrum of sodium carboxymethylcellulose after hydrolysis in D_2SO_4/D_2O. Symbols *S* and *US* stand for substituted and unsubstituted carbon, respectively, for the anomeric carbon atom (C1)

cac values determined with pyrene as a fluorescence probe. Solubilization of this aromatic photophysical probe within the self-assembled surfactant aggregates offers a very sensitive way to study the onset of cooperative association between the polyelectrolyte and the surface-active agent.

Experimental

Chemicals

The charged surfactants hexadecyltrimethylammonium chloride (CTAC, Kodak, 99%) and sodium dodecylsulfate (SDS, Sigma, 99%) were used as received. The carbohydrate-derived polyelectrolytes were prepared as described below. Pyrene (Aldrich) was recrystallized twice from ethanol before use. Deionized (Milli-Q apparatus) water was used throughout.

Synthesis of the carbohydrate polyelectrolytes

Sodium carboxymethylcellulose (CMCNa)

CMCNa was prepared from the bleached pulp obtained from sugar cane bagasse [21]. Thus, 68 g of an aqueous solution of NaOH (40%) and 48 g of a solution of monochloroacetic acid in isopropanol (1:1 m/m) were added to 10 g of the pulp suspended in 261 mL of isopropanol. The temperature was raised to 55°C and the reaction proceeded under mechanical stirring for 210 min. The product was purified by dissolution in distilled water followed by the addition of enough NaCl to result in a clear solution, with polymer and salt concentrations of 1 g L^{-1} and 0.1 M, respectively. The resulting solution was filtered, and absolute ethanol was added to precipitate the polymer. Following extensive washing with distilled water/ethanol mixtures of increasing alcohol content, the sodium carboxymethylcellulose was dried at room temperature. The average degree of substitution ($\overline{DS}$) of the purified CMCNa was determined from the ^{1}H NMR spectrum shown in Fig. 1, as described elsewhere [22], resulting in $\overline{DS} = 1.1$.

Chitosan hydrochloride (Ch) [23]

One gram of commercial chitosan (Fluka/Biochimika) was dissolved in 150 mL of acetic acid aqueous solution (1%), followed by filtration of the resulting solution, dialysis against 0.2 M NaCl for 3 d, dialysis against deionized water for 2 d and freeze-drying. The average degree of acetylation ($\overline{DA}$) of chitosan hydrochloride was determined by ^{1}H NMR spectroscopy, as described elsewhere [23], and resulted in $\overline{DA} = 22.3\%$.

N,*N*,*N*-Trimethylchitosan chloride (TMCh)

Three grams of commercial chitosan (Fluka/Biochimika) were dispersed in 150 mL of 1-methyl-2-pyrrolidone, followed by the addition of 25.8 mL of an aqueous solution of NaOH (1.4 M), 33.84 g (0.238 mol) of CH_3I and 5.4 g (0.036 mol) of NaI. The reaction was carried out with magnetic stirring for 180 min at 60°C. The product was purified by dialysis against water, followed by dialysis against 0.1 N NaCl for 3 d to exchange the iodide counterion for chloride. Finally, the derivative was dialyzed for 3 d against deionized water (renewed every 12 h) and freeze-dried.

The ^{1}H NMR spectra of chitosan and *N*,*N*,*N*-trimethylchitosan are shown in Figs. 2 and 3, respectively. In the spectrum of chitosan (Fig. 2) the following attributions are made [24]: a) the signals at $4.5 < \delta < 5.0$ correspond to hydrogen atoms bonded to the anomeric carbon 1; b) the signals at $3.4 < \delta < 4.0$ correspond to hydrogen atoms bonded to carbon atoms 3–6 of the glucopyranose unit; c) the signal centred at 3.18 ppm corresponds to the hydrogen atom bonded to carbon 2 of the ring; and d) the signal centred at 1.99 ppm corresponds to the hydrogen atoms of the methyl moieties pertaining to the acetamido groups. From this spectrum the average degree of acetylation of the purified chitosan was determined as $\overline{DA} = 22\%$.

Evidence for the occurrence of *N*-methylation can be drawn from the signals appearing in the 2.47–3.37 ppm region. Only the

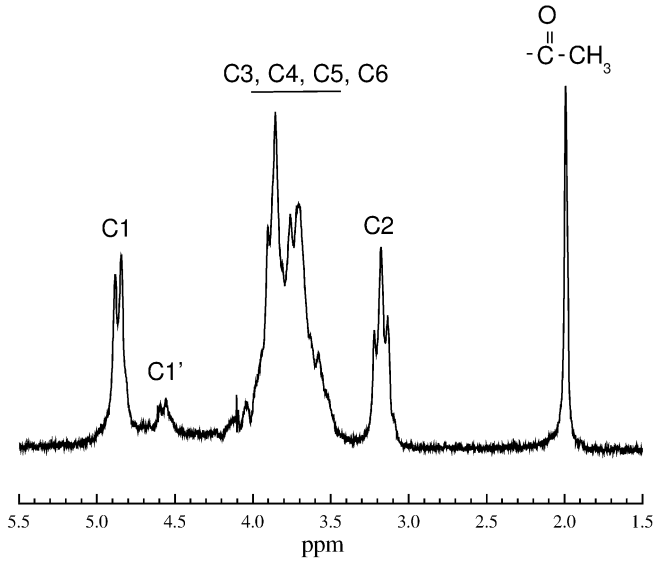


Fig. 2 ^{1}H NMR spectrum of chitosan in D_2O/HCl, where *C1* and *C1′* stand for the signals due to the hydrogen atoms bonded to the anomeric carbon of the deacetylated and acetylated glucosamine units, respectively

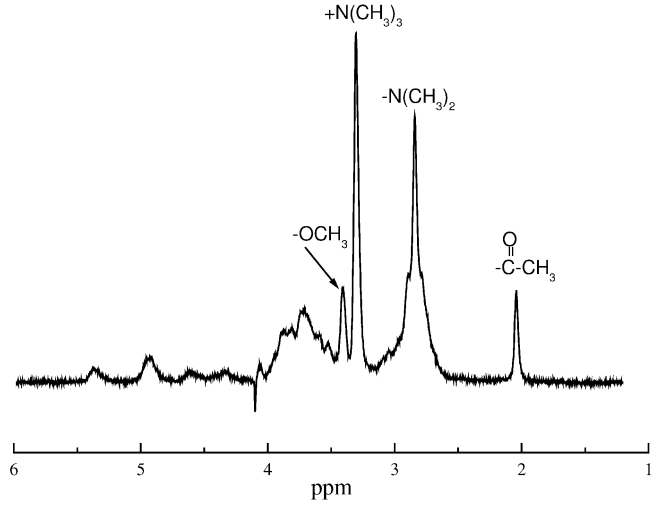


Fig. 3 ^{1}H NMR spectrum of *N*,*N*,*N*-trimethylchitosan in D_2O

signal at the lower magnetic field, centred at 3.31 ppm, corresponds to quaternized sites, while the signal centred at 2.76 ppm is attributed to *N*, *N*-dimethylated sites [25]. This spectrum also shows two signals in the $3.37 < \delta < 3.56$ region, both of them corresponding to *O*-methylated sites [26]. The average degree of quaternization determined from the ^{1}H NMR spectrum [4] was calculated as $\overline{DQ} = 25\%$.

Amphiphilic alkyl chitosan (C12Ch) [5]

Four grams of commercial chitosan (Fluka/Biochimika) were dispersed in 220 mL of 0.2 M acetic acid aqueous solution. After complete dissolution, 150 mL of ethanol were added. The pH was adjusted to 5.1, and an excess of sodium cyanoborohydride, $NaCNBH_4$, (3 moles per chitosan monomole) was added. An

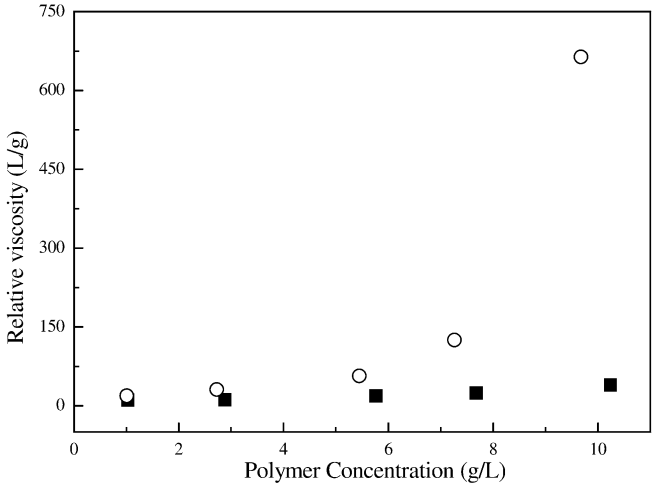


Fig. 4 Variation of the relative viscosity of (■) chitosan and (○) alkylated chitosan with concentration (in acetic acid 0.2 M at 20°C)

appropriate amount of dodecylaldehyde ($C_{12}H_{24}O$) in ethanol was then added to attain a 1:0.1 chitosan/aldehyde molar ratio. The mixture was stirred for 24 h at room temperature, and the amphiphilic alkyl chitosan derivative was precipitated by addition of ethanol. The pH was adjusted to 7.0 with sodium hydroxide aqueous solution, and the compound was washed with ethanol/water mixtures of increasing ethanol content (70–100%), filtered and dried at room temperature.

The success of this alkylation reaction could be verified by the increase of the relative viscosity in 0.2 M acetic acid with increasing polymer concentration, compared with that of chitosan (Fig. 4). This effect is attributed [5] to the hydrophobic groups that associate to form physical aggregates, which cause an increase of the viscosity.

Fluorescence measurements

Steady-state fluorescence measurements of pyrene were recorded on air-equilibrated solutions using an Hitachi F-4500 spectrofluorimeter at room temperature. A 1.0-cm-path-length quartz cuvette was used throughout. The vibrational fine structure of the fluorescence bands of pyrene was used to determine the critical aggregation concentration (cac) and the critical micellar concentration (cmc) values of the polyelectrolyte–surfactant solutions. Emission spectra of pyrene were recorded from 340 to 550 nm with excitation at 334 nm. The detection wavelengths were 373 nm for I_1 and I_M, 384 nm for I_3, and 475 nm for I_E. The excitation and emission slits were 2.5 mm and 5.0 mm, respectively, and the scan rate was 240 nm min^{-1}.

Fluorescence lifetimes were measured by a time-correlated single-photon counting method using an Edinburgh CD-900 instrument. Samples were excited at 334 nm, and the detection was made at 374 nm. The fluorescence decay profiles were analysed with a non-linear least-squares iterative reconvolution method. All samples were examined at room temperature (25 ± 0.5°C).

The solutions containing the probe were prepared by transferring a sufficient amount of a methanolic stock solution of pyrene to a flask under a stream of nitrogen, after which the polymer solution was added and the total volume diluted to 3.0 mL with water. Afterwards, the surfactant was added in very small portions. The final pyrene concentration was approximately 1.0×10^{-6} M for the steady-state and time-resolved fluorescence measurements, corresponding to an absorbance of 0.015 at 334 nm. Consequently, the concentration and the optical density were always low enough not to interfere with the system or affect it otherwise.

The solutions of the amphiphilic alkylchitosan (C12Ch) were prepared in 1% v/v acetic acid as a result of the insolubility of this polyelectrolyte in neutral pH solutions. The solutions of all the other polyelectrolytes (CMCNa, ChCl and TMCh) were prepared at pH 6.5.

Results and discussion

Interactions of CMCNa and TMCh with surfactants

Charged polysaccharides such as CMCNa and TMCh interact strongly with oppositely charged surfactants. A highly cooperative binding is usually accompanied by the formation of large surfactant clusters. The behaviour of the I_1/I_3 ratio of the emission peaks of pyrene and the ratio between excimer and monomer emissions of pyrene (I_E/I_M) in aqueous solutions of sodium carboxymethylcellulose (CMCNa) and *N*,*N*,*N*-trimethylchitosan (TMCh) with added CTAC and SDS can be deduced from the results shown in Fig. 5. When the components of the systems have opposite charges, the I_1/I_3 ratio shows an initial decay from values near 1.8 to about 1.6 at low surfactant concentrations. This decrease corresponds to the probe being displaced from a practically "aqueous" microenvironment around the polyelectrolyte to a more hydrophobic domain. These hydrophobic domains are attributed to the formation of pre-micelles induced by interactions between the surfactant and the polyelectrolyte molecules.

The I_1/I_3 ratio remains constant up to concentrations around 8.0 mM and 0.7 mM for the TMCh/SDS and CMCNa/CTAC systems, respectively. After this, the ratios fall again. The second decrease of the ratio is attributed to the formation of free micelles in the bulk of the solution, and characterizes critical micellar concentrations (cmc) of the surfactants of about 1.5 mM (CTAC) and 8.0 mM (SDS). These values are similar to the cmc found for the same surfactants in pure aqueous solutions [27]. Finally, the I_1/I_3 ratios reach a new plateau at around 1.2, typical of pyrene in surfactant micelles [28]. For the systems where the polyelectrolyte and the surfactant bear charges of the same sign, no pre-micelle formation was detected. The different stages of the interaction between the polyelectrolytes and oppositely charged surfactants are illustrated in Scheme 2for the TMCh/SDS system. Values for the I_1/I_3 and I_E/I_M ratios and lifetimes are also shown. For species with the same charge, the steps leading to pre-micelles are not present.

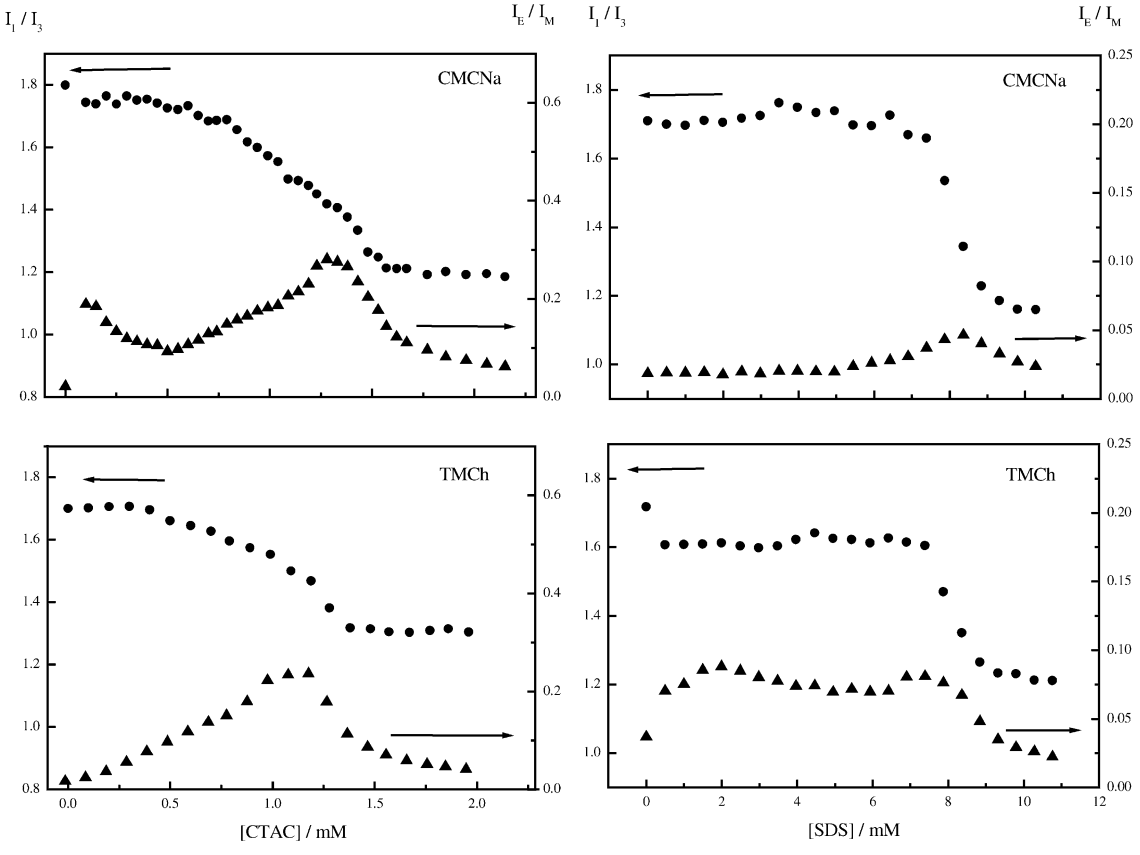


Fig. 5 Dependence of the I_1/I_3 and I_E/I_M ratios of pyrene with CTAC and SDS concentration in the presence of CMCNa and TMCh (2.0 mg L^{-1}).$\lambda_{exc} = 334$ nm. Detection wavelengths: $I_1 = I_M$, 373 nm; I_3, 384 nm; I_E, 475 nm

Medium	SDS/mM	effect	I_1/I_3	I_E/I_M	lifetime/ns
Aqueous solution			1.70	0.04	138 (Py in water)
little SDS	0.3	Py in SDS vicinity	1.60	~0.07	
pre-micelle formation (cac)	2	Py in hydrophobic aggregates.	1.60	0.10. More than one Py per aggregate	138 and 52 (Py in pre-micelles quenched by multioccupancy)
	4	more hydrophobic aggregates	1.60	0.75. Decrease due to redistribution of Py	137 and 2 (Py quenched in multioccupied micelles)
formation of free micelles (cmc)	8		1.40	0.10. Migration of Py to more hydrophobic environments	169 and 0.5
	>8	many micelles	1.20	0.05. Decrease due to Py redistribution between free micelles	180 and 0.6

Interactions of chitosan with surfactants

Although chitosan does not bear any effective charge on its structure, the marginal positive charges created by hydrolysis when dissolved in water, seem to be sufficient to induce the formation of pre-micelles in the presence of the negatively charged SDS (Fig. 6a). Before the addition of surfactant, the I_1/I_3 ratio is around 1.80 as expected for aqueous solutions without hydrophobic aggregates [18, 29, 30, 31, 32]. When about 0.5 M of SDS was added to the solution, the I_1/I_3 ratio quickly decreases from 1.8 to 1.6 and remains constant until the formation of the free micelles around 8.0 mM, indicating a formation of the pre-micelle aggregates. This behaviour is also accompanied by a peak of the I_E/I_M ratio. Afterwards, the I_1/I_3 ratio decreases again and remains approximately constant at a value around of 1.20, indicating constant polarity of the local environment sensed by the probe. This value is the same as found for pyrene solubilised in surfactant micelles [20, 32, 33] and supports the idea of micelle-like aggregation of the surfactant in the presence of a polyelectrolyte. On the other hand, when CTAC is added to the solution of chitosan (Fig. 6b), a steady decrease of the I_1/I_3 ratio is observed owing to the redistribution of the probe molecules from the polysaccharide environment to the more hydrophilic environment of the surfactant. The steady decrease and the absence of a plateau of the I_E/I_M ratio indicate that no pre-micellar aggregation occurs in this case. Again, in the vicinity of the cmc of CTAC (≈1.5 mM) an indication of the formation of real micelles is obtained from the behaviour of both ratios.

Interactions of a hydrophobically substituted chitosan with surfactants

At low surfactant concentrations the modified chitosan incorporating a C12 alkyl chain [34] showed practically the same behaviour as unmodified chitosan (i.e. the formation of pre-micellar aggregation in the presence of

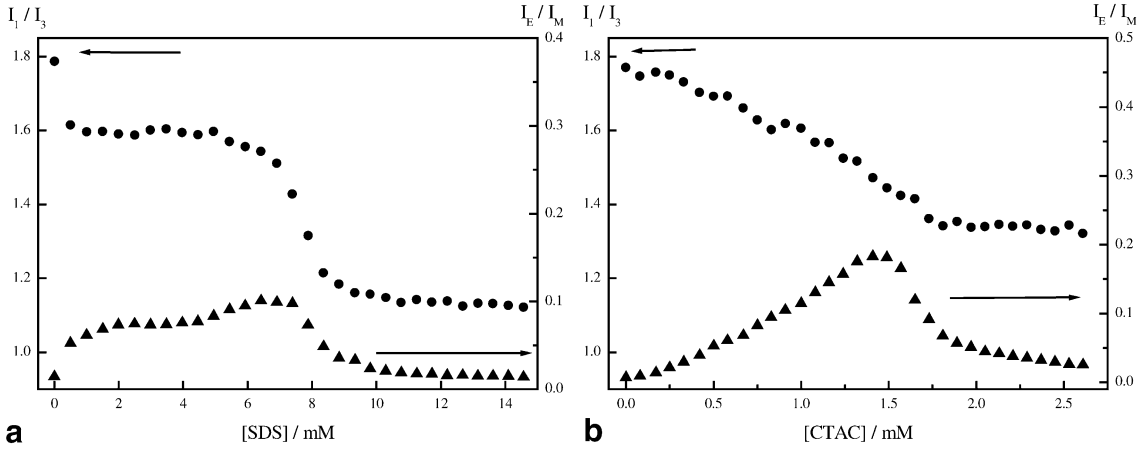


Fig. 6a,b Dependence of the I_1/I_3 and I_E/I_M ratios of pyrene with SDS and CTAC concentration in the presence of chitosan (2.0 mg L^{-1}). $\lambda_{exc} = 334$ nm. Detection wavelengths: $I_1 = I_M$, 373 nm; I_3, 384 nm; I_E, 475 nm

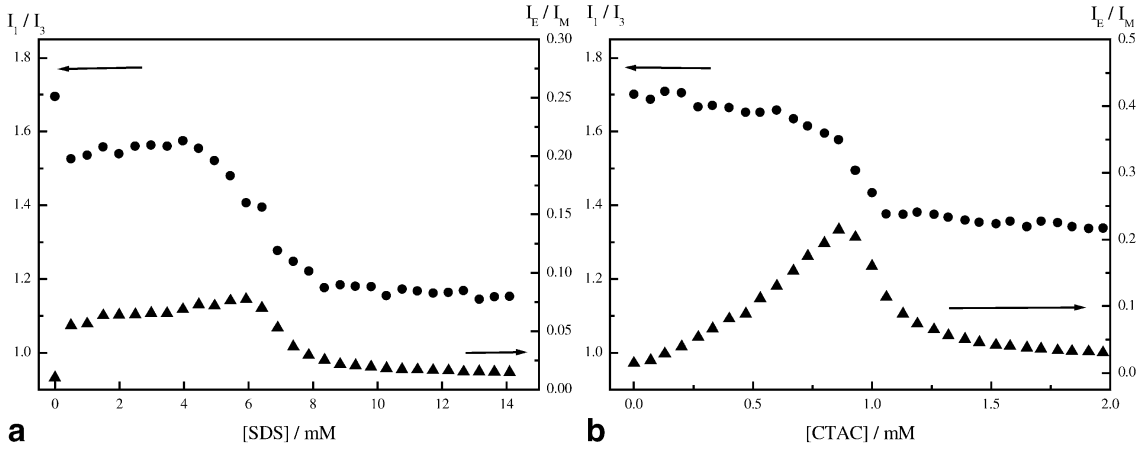


Fig. 7a,b Dependence of the I_1/I_3 and I_E/I_M ratios of pyrene with SDS and CTAC concentration in the presence of C12Ch (2.0 mg L^{-1}). $\lambda_{exc} = 334$ nm. Detection wavelengths: $I_1 = I_M$, 373 nm; I_3, 384 nm; I_E, 475 nm

SDS and no pre-micelles with CTAC: Figs. 7a and 8b, respectively). This behaviour can be traced to the fact that the degree of C12 substitution on the polysaccharide is not very high.

On the other hand, the onset of the formation of real micelles is displaced towards lower concentrations than those corresponding to the cmc in aqueous solutions. For C12Ch/SDS these micelles start to be formed at about 6.5 mM as compared with 8.0 mM in water, whereas for C12Ch/CTAC the value found is approximately 1.0 mM against 1.5 mM in water. The interaction between the large hydrophobic chains with the surfactants may induce the early formation of micellar aggregates.

Lifetime measurement in TMCh systems

The different microenvironments in the solutions of the polyelectrolytes were also identified by the lifetime of the pyrene probe. In pure TMCh a mono-exponential decay of the pyrene emission is observed, with lifetime around 138 ns, compatible with the lifetime of pyrene reported for aqueous solutions [35]. After addition of surfactant the decays can be approximated by a bi-exponential function. The lifetimes and the I_1/I_3 ratios of pyrene in the presence of TMCh with various amounts of SDS are shown in Fig. 8, and the corresponding lifetimes are collected in Table 1.

As can be observed in Fig. 8, the behaviour of the I_1/I_3 ratio parallels that of the first (τ_1) and second lifetimes (τ_2) of pyrene. The shorter lifetime τ_2, should be assigned to the quenching of pyrene molecules placed in multi-occupied pre-micelles. It presents a maximum at the surfactant concentrations where the I_1/I_3 ratio shows the first plateau, indicating the creation of new micelle-like microdomains. These microdomains will have a higher

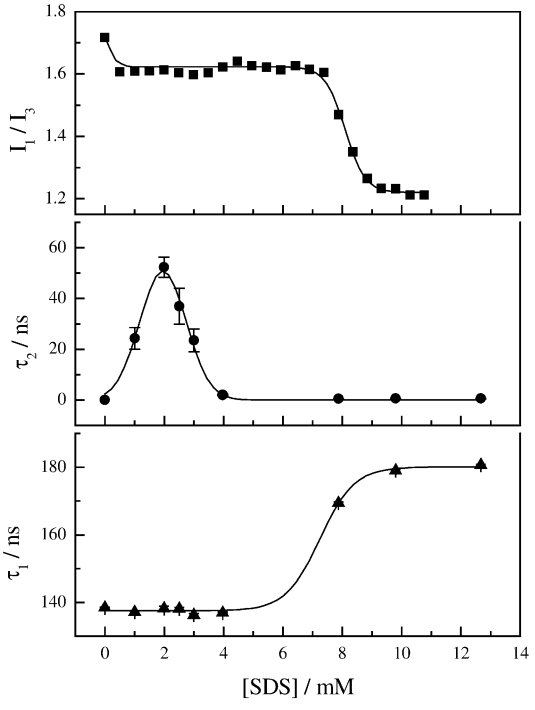


Fig. 8 Dependence of I_1/I_3, τ_1 and τ_2 of pyrene with SDS concentration in the presence of TMCh (2.0 mg L^{-1}). $\lambda_{exc} = 334$ nm

Table 1 Pyrene lifetime in the presence of TMCh (2 mg L^{-1}) and SDS

[SDS] (mM)	τ_1(ns)	B_1	τ_2(ns)	B_2	CHISQ
0	138.4	0.426	–	–	1.059
1.00	137.1	0.319	24.27	0.023	1.052
1.99	138.2	0.364	52.30	0.075	1.136
2.50	138.1	0.319	36.93	0.023	1.061
3.00	136.2	0.308	23.43	0.026	1.133
3.97	136.9	0.279	1.990	0.296	1.334
7.87	169.4	0.261	0.504	0.831	1.271
9.80	179.0	0.305	0.566	0.647	1.176
12.67	180.6	0.314	0.570	0.602	1.165

B_1 and B_2 correspond to the weight factors of each lifetime in the decay

hydrophobic character and the probe molecules will migrate to them preferentially (this characterizes the critical aggregation concentration). The second decrease of the I_1/I_3 ratio, which indicates the formation of free micelles, is also concomitant with the increase of the longer lifetime τ_1, characterizing the critical micelle concentration.

Conclusions

Fluorescence measurements of systems containing carboxymethylcellulose or *N*,*N*,*N*-trimethylchitosan chloride in the presence of surfactants like CTAC and SDS, respectively, show the formation of induced micelles at concentrations smaller than those needed to form free micelles in aqueous solution. The interaction of an alkylated chitosan (C12Ch) with SDS and CTAC presented some changes when compared with chitosan hydrochloride. The different microenvironments present in the solutions of polyelectrolytes were identified by fluorescence intensity and lifetime measurements by using pyrene as a probe. The formation of pre-aggregates was first deduced from the behaviour of the I_1/I_3 and I_E/I_M ratios, and later confirmed by the measurements of the emission lifetimes of pyrene. The single mono-exponential decay of the probe in pure TMCh corresponded to a lifetime of around 138 ns, compatible with the decay time of pyrene in aqueous solutions. The addition of surfactant to any of those systems turns the decays bi-exponential, with one of the lifetimes remaining around 138 ns. A shorter lifetime (possibly corresponding to the quenching of pyrene by other pyrene molecule present in the same microdomain) appears at low surfactant concentrations, indicating the formation of induced micelles.

Acknowledgment The authors thank CNPq and FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for financial support. E.T.I. and D. de B. also thank the same agency for a Graduate Fellowship.

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