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A fluorescence study of the interactions between sodium alginate and surfactants

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Abstract

The interactions between the polysaccharide alginate with charged ionic surfactants (anionic and cationic) in aqueous solution have been investigated using pyrene as a photophysical probe. Static fluorescence determinations have been used to obtain information about the new microenvironments arising by these interactions. Micropolarity studies using the I_1/I_3 ratio of the vibronic bands and I_E/I_M ratio between the excimer and monomer emissions of pyrene shows the formation of hydrophobic domains. The interactions between the natural polyelectrolytes and the oppositely charged surfactants lead to the formation of pre-micelles at surfactant concentrations lower than the CMC of the surfactants. The aggregation process is assumed to be due to electrostatic attraction. On the other side, systems containing an anionic surfactant do not show the same behaviour at low concentrations. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Alginates; Surfactants; Pre-micelles; Hydrophobic microdomains

1. Introduction

In the last two decades[1,2] many studies related to polymer/surfactant interactions have dealt either with interactions between polyelectrolytes and oppositely charged surfactant monomers, or with the association of non-ionic polymers with ionic surfactant micelles. In the former case electrostatic forces are the main driving force in these interactions, although hydrophobic forces may play a secondary role.[3,4] Polyelectrolytes interact with oppositely charged surfactant micelles so strongly that in many cases irreversible macroscopic phase separation occurs. Dubin and co-workers[5–7] showed that such strong electrostatic interactions could be attenuated by 'diluting' the surface charge of ionic surfactant micelles with non-ionic surfactants leading to the formation of soluble polyelectrolyte complexes.[8,9]

Fluorescence methods have been increasingly employed to examine polymer/surfactant interactions partly because of their inherent sensitivity. In general, for the study of polyelectrolyte/surfactant systems, fluorophores have been used in two ways. In the first case, monomeric fluorophores such as pyrene are used as fluorescence probes. The key feature in the photophysical properties of pyrene (Py) is its solvent-dependent variation in the ratio of fine structure emission band intensities, which can be correlated with the polarity of the probe's immediate environment.[10] Additionally, at relatively higher concentrations, pyrene presents a very characteristic excimer emission that is used to evaluate its concentration in the environment in which the emitting probe is placed.[11]

Biodegradable polymers, like the alginates (a binary linear heteropolymer containing 1,4-linked α-L-glucuronic acid and β-D-mannuronic acid) are used for various applications in medical, agriculture, drug-carrying and release, and packaging fields. One other widespread use is related to the encapsulation of herbicides, microorganisms and cells. Alginates have also been studied extensively for their ability to form gels in the presence of divalent cations.[12–17] Their interaction with surfactants may form microdomains with hydrophobic characteristics that might be important factors to be considered in the design of systems as those described above.

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In this study we want to extend recent studies on the interactions between surfactants and synthetic polyelectrolytes (like poly(styrene sulfonate) and some of its copolymers)[18] to a natural polymer (Alginate) in order to ascertain the differences due to their structures. The latter will have –COO$^-$ and –COOH groups along the chain conferring different charge densities depending on the pH. PSS copolymers do not have intrinsic pH-dependent configurations, as the hydrophilic part of the polyelectrolyte carries the sulfonate group that is practically completely dissociated at all conditions.

2. Results and discussion

The dependence of the I_1/I_3 ratio of the pyrene emission as a function of alginate concentration at pH 6 is shown in Fig. 1. It can be seen that this ratio, which measures the hydrophobicity of the medium, decreases steadily with the alginate concentration. At 3.0 g/L its value reaches approx 1.60. This value is smaller than that found for pyrene in aqueous solution (1.75–1.80). This behaviour suggests that over the concentration range studied, the pyrene molecules are partitioned between the hydrophobic microdomains of the polymer chain and the aqueous solution. When the concentration of alginate is increased, a larger number of polymeric hydrophobic microdomains will be present, to which the highly hydrophobic pyrene molecules will migrate. At even higher concentrations (~ 2.5 g/L) probably most of the probe molecules will accommodate in the hydrophobic microdomains. The high viscosity of more concentrated alginate solutions precludes the experimental determination of this parameter at concentrations above ~ 3.0 g/L.

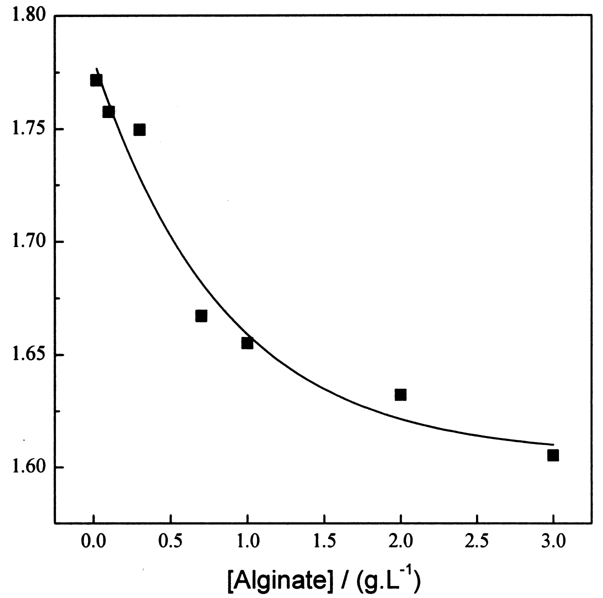

Fig. 1. Dependence of the I_1/I_3 ratio of pyrene in different concentrations of sodium alginate. $\lambda_{exc} = 334$ nm; detection wavelengths: I_1, 373; I_3, 384 nm. $[Py] = 1.0 \times 10^{-6}$ M.

The behaviour of aqueous solutions of the polyelectrolyte when the surfactant CTAC is added can be deduced from the results shown in Fig. 2, which illustrate the evolution of the I_1/I_3 ratio of the peaks of the vibronic structure of pyrene and the ratio between the monomeric and excimer emissions of pyrene, I_E/I_M, in the presence of alginate. The I_1/I_3 ratio shows an initial rapid decay from values near to 1.8, corresponding to the probe placed in an 'aqueous' microenvironment, to values around 1.6, attaining a first plateau at surfactant concentration of ~ 0.1 mM. This slightly more hydrophobic domain is ascribed to the formation of pre-micelles induced by the interactions (probably electrostatic) between CTAC and the alginate carboxylate groups. This decrease is due to the solubilization of the probe in the micelle-like aggregates which gradually start to form along the polymer chain. The onset of the process is defined as the ~ critical aggregation concentration (CAC).[19,20] A second decrease of I_1/I_3 observed between 0.5 and 1.5 mM is due to the formation of free micelles in the bulk of the solution, as probably the capacity of placing induced micelles on the macromolecular chain is saturated at these concentrations. The concentrations were this process occurs characterize the CMC and are quite similar to the value found for CTAC in pure aqueous solution (1.27 mM).[21] The I_1/I_3 ratio at higher concentrations remains constant at 1.20, typical of pyrene in CTAC micelles.[10,21–27]

On the other hand, as can be observed in the same figure, the I_E/I_M ratio shows a behaviour parallel to that of the I_1/I_3 ratio. The decrease of the I_1/I_3 ratio is concomitant with the peaks of the I_E/I_M ratio. Here, the CMC and CAC regions are more clearly characterized by two distinct peaks at about 0.4 and 1.2 mM. This proves that the initial addition of detergent to the alginate solution induces the formation of micelle-like microdomains with higher hydrophobic character, towards which the probes will migrate preferentially.

The second peak of the I_E/I_M ratio also accompanies the second decrease of the I_1/I_3 ratio. In this case, the probe molecules placed in the pre-micelle microdomains will tend to migrate to the more hydrophobic 'free micelle' environments, concentrating initially in a few micelles and giving place to an increase in the excimer emission. The ratio decreases again when the number of micelles is sufficiently large to redistribute the probes one-a-piece or less per micelle.

When using the shorter chain surfactant DTAC, the pre-micelles start being formed at higher concentrations than with CTAC. At the same time the I_1/I_3 ratio is higher than that with CTAC (1.7 vs. 1.6), and the I_E/I_M ratio is about half that found for the longer chain surfactant. Therefore, although in previous[ref] studies it

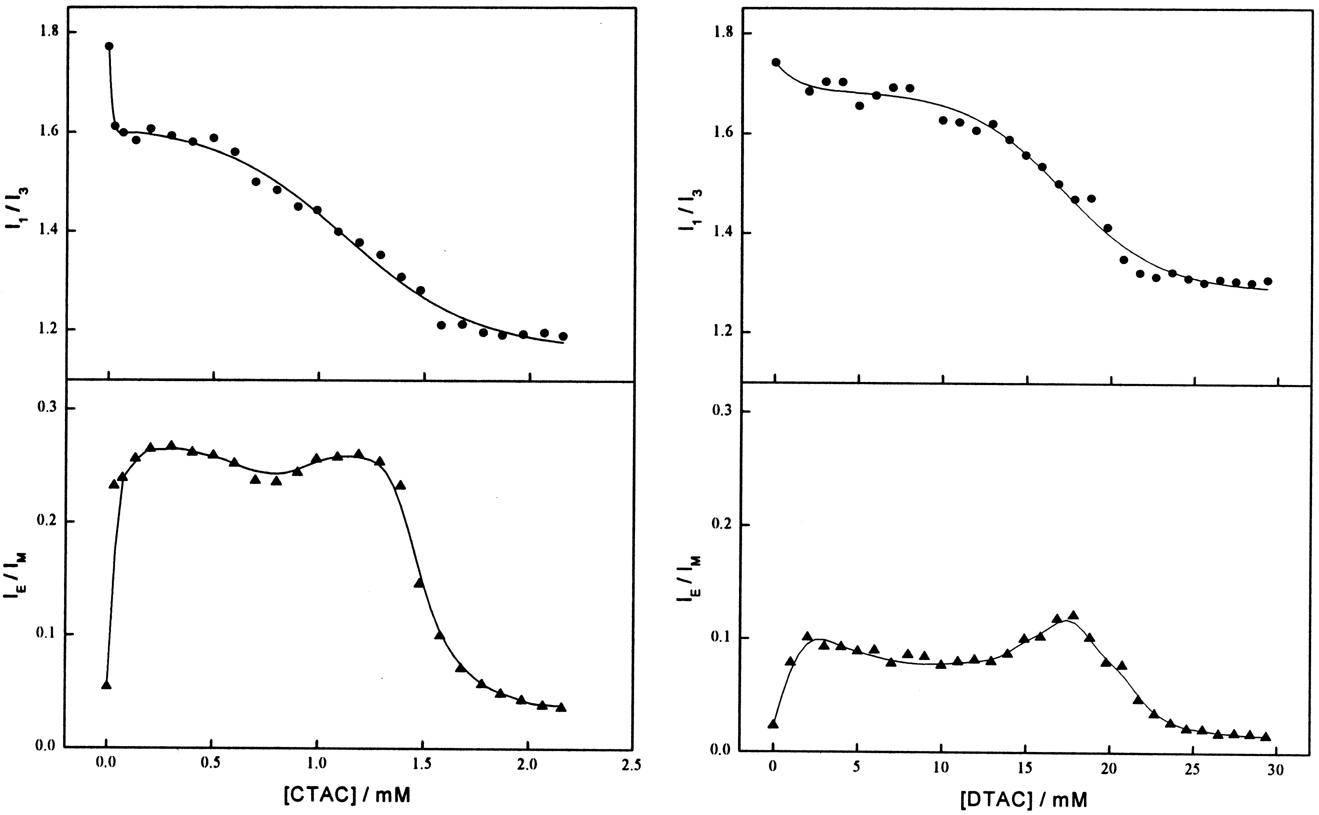

Fig. 2. Dependence of the I_1/I_3 and I_E/I_M ratios of pyrene in sodium alginate solutions (2.0 mg/L) containing CTAC and DTAC. $\lambda_{exc} = 334$ nm; detection wavelengths: $I_1 = I_M$: 373; I_3, 384; I_E: 475 nm.

could be proved that the initial interaction between surfactants and oppositely charged polyelectrolytes is predominantly electrostatic, some contribution from hydrophobic interactions can also be expected.

The behaviour of the system composed by alginate and a surfactant with the same charge (SDS) is shown in Fig. 3. For SDS concentrations up to approx 2 mM, a small and slow decrease of the I_1/I_3 ratio can be observed. The formation of these domains can be traced to the attraction of the hydrophilic sulfonate groups towards the microdomains formed by the hydroxyl groups on the polyelectrolyte chain. A hydrophobic interaction between the alkyl chain on the surfactant and the hydrophobic backbone of the alginate can be discarded in view of the small influence found for this effect when using a cationic surfactant with the same chain length. The interactions of SDS with PSS copolymerized with an hydrophobic monomer showed the same effects.[22,28,29] At higher surfactant concentrations the same behaviour is observed as with cationic detergents, i.e., the formation of normal micelles around the critical micellar concentration.

Overall, it can be said that the behaviour of the natural polyelectrolyte alginate in the presence of surfactants resembles that observed for synthetic polyelectrolytes like PSS and its copolymers with hydrophobic monomers.[18,30] In the presence of cationic surfactants (DTAC and CTAC), there is an initial electrostatic interaction which leads to the formation of pre-micelles attached to the polyelectrolyte backbone. This interaction is apparent at surfactant concentrations about an order of magnitude below the CMC of the surfactant in pure aqueous solution. Only a limited number of such aggregates can be bound to the polyelectrolyte chain. Eventually, above a certain surfactant concentration, a saturation point is reached when all the probe molecules will be solubilized in these microdomains. The polarity of these microdomains is quite different from the medium in which the probe is situated before the addition of the surfactant, and also from that found for the 'real micelles'. The values of the corresponding I_1/I_3 ratios are 1.6–1.7, 1.8, and 1.3, respectively.

The main effect of the chain length of the surfactants seems to affect the polarity of the induced micelle-like domains (lower I_1/I_3 ratio for CTAC than for DTAC, as well as higher emission intensity). Since induced micelle-like aggregates were not detected in systems involving hydrophobically modified polyelectrolytes, hydrophobic forces will have a second-order contribution in the formation of these pre-micelles.[31]

3. Conclusions

It has been proved, using pyrene fluorescence measurements methods, that alkyltrimethylammonium surfactants associate to alginate. Cationic surfactants like DTAC and CTAC form induced micelles at concentrations smaller than those needed to form micelles in aqueous solution. The main initial interaction between the alginate and the oppositely charged surfactant has electrostatic character, and probably proceeds between the charged centers on the macromolecular chain and the charged heads of the surfactant. The microenvironments formed by these aggregates are less hydrophobic than those of free micelles ($I_1/I_3 \approx 1.6$ against ~ 1.3 for normal micelles). At larger surfactant concentrations normal micelles are formed at CMC values slightly larger than those for aqueous solution.

Although the hydrophobic interactions do not seem to play the principal role in these systems, it was observed that the interactions are stronger for surfactants of longer chain. A contribution of these effects can also be present on the interactions between alginate and anionic surfactants.

On the other side, the interactions of polyelectrolytes and surfactants of the same charge seem to present only very weak interactions, which might be assigned to the solubilization of the hydrophilic heads on the surfactant in the domains formed by the hydroxyl groups of the polyelectrolyte.

4. Experimental

4.1. Chemicals

Alginic acid, sodium salt (Sigma), dodecyltrimethylammonium chloride (DTAC, Fluka, 99%), hexadecyltrimethylammonium chloride (CTAC, Kodak, 99%) and sodium dodecylsulfate (SDS, Sigma, 99%) were used as received. Pyrene (Aldrich) was recrystallized twice from EtOH before use. Milli-Q purified water was used throughout.

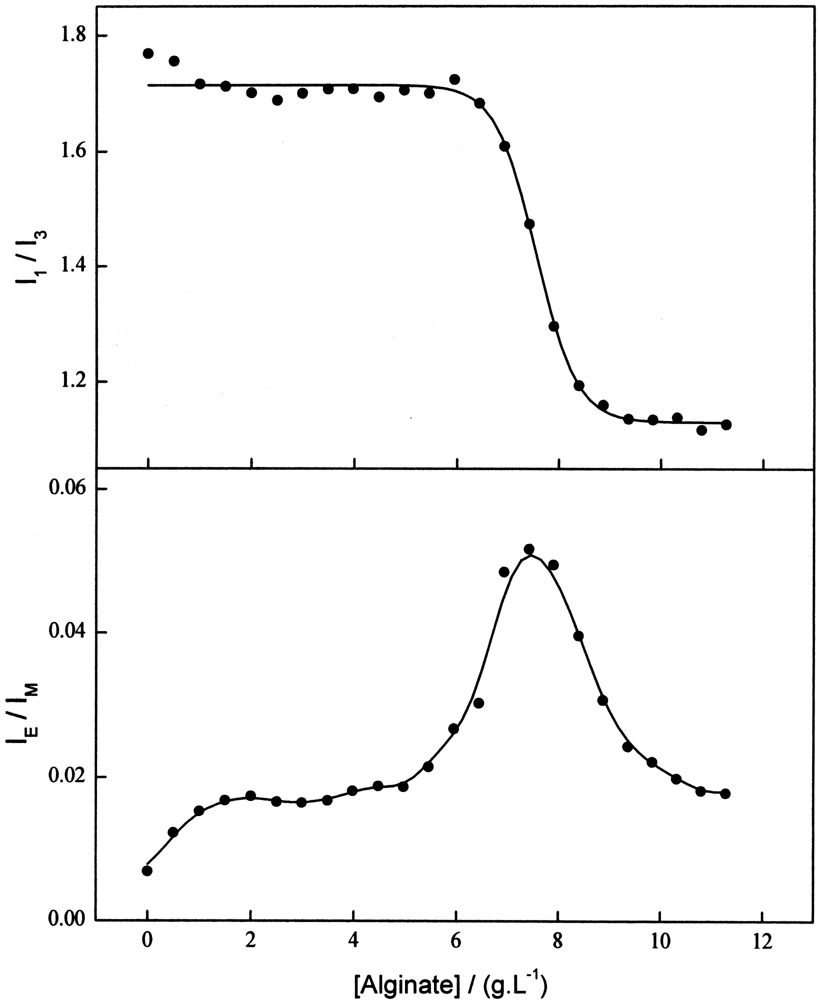

Fig. 3. Dependence of the I_1/I_3 and I_E/I_M ratios of pyrene with SDS concentration in the presence of sodium alginate 2.0 mg/L. $\lambda_{exc} = 334$ nm; detection wavelengths: $I_1 = I_M$, 373; I_3, 384; I_E: 475 nm.

4.2. Fluorescence measurements

Steady-state fluorescence measurements were performed on air-equilibrated solutions using a Hitachi F-4500 spectrofluorimeter. Pyrene was excited at 334 nm, and the detection wavelengths were $I_1 = I_M = 373$ nm, $I_3 =$ 384 nm, $I_E = 475$ nm. Excitation and emission slits were 5.0/2.5 nm, respectively. All samples were examined at pH 6.0 at room temperature.

The solutions containing the probe were prepared by transferring a sufficient amount of a methanol stock solution of pyrene to a flask under a stream of nitrogen, after which the alginate solution was added and the total volume completed to 3.0 mL with water. Afterwards, the surfactant was added in very small portions. The final pyrene concentration used for the measurements was $\sim 1.0 \times 10^{-6}$ mol/L, corresponding to an absorbance of 0.015 at 334 nm. The concentration and the optical density are low enough no to interfere with the system or affect it otherwise.

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