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ORIGINAL CONTRIBUTION

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Interaction of (hydroxypropyl) cellulose with anionic surfactants in dilute regime

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Abstract (Hydroxypropyl)cellulose (HPC) dilute aqueous solutions in the presence of sodium cholate (CS), sodium deoxycholate (DC), and sodium dodecylsulphate (SDS) were investigated. The hydrophobicity parameter (I_1/I_3) from fluorescence has shown a critical aggregation concentration (CAC) lower than the critical micellar concentration (CMC). One or two breakpoints were observed in the curve conductivity vs surfactant concentration. The thermodynamic parameters of aggregation (ΔG^0_{mic}, ΔH^0_{mic} and ΔS^0_{mic}) and the degree of counterion dissociation were calculated. Evidences for the secondary aggregation of CS/water system were found. The relative viscosity increases for HPC/bile salt solutions only at high surfactant concentrations, whereas for HPC/SDS, it passes through a maximum. The cloud points of both HPC/bile salt solutions at higher surfactant concentrations reach a temperature plateau value around 324 K, while for HPC/SDS, it exceeds 373 K at low SDS concentrations. Dynamic light scattering has demonstrated that the surfactants bind to HPC already at concentrations lower than CAC.

Keywords (hydroxypropyl) cellulose · Bile salts · Aggregation · Fluorescence · Light scattering

Introduction

The interactions between nonionic water-soluble polymers and surfactants are of technological importance and have been the subject of intense studies over the last three decades due to their wide range of applications [1–4]. The properties of polymer–surfactant complex are recognized in pharmaceutical formulations, food, cosmetics, ternary oil recovery, cleaning, as well as paint and coating products [5–7].

Through different techniques applied to polymer/surfactant mixtures in solution, such as fluorescence probe [8, 9], surface tension [10, 11], and conductivity [12, 13], it was observed that the ionic surfactants bind to nonionic polymers at a specific concentration, namely, critical aggregation concentration (CAC), below their normal critical micellar concentration (CMC). Bile salts are natural anionic surfactants that are polyhydroxy derivatives from cholesterol. In contrast to classical surfactants, formed by long alkyl chains with polar headgroups, the bile salts

exhibit a lipophilic surface, which is the convex side of the rigid steroid ring system, and a hydrophilic surface, which is the polyhydroxylated concave side of the molecule [14, 15].

We have been studying the aggregation of cellulose ethers as (hydroxypropyl)cellulose (HPC) with two bile salts, sodium cholate (CS) and sodium deoxycholate (DC), and the well-known sodium dodecylsulphate (SDS). The present work intends to study the aggregation characteristics of these bile salts in comparison with SDS in the presence of the semi-rigid polymer HPC. In a previous study, the aggregation of HPC with these surfactants was investigated in the presence of added sodium chloride [16, 17], and it was verified that the interaction of HPC with the bile salts is weak. To check if this interaction was not simply screened by the addition of inorganic salt, the present investigation was conducted in the absence of sodium chloride.

In the literature, the interaction flexible polymer/surfactant has been intensively investigated [2, 10, 11, 18]. Among the semi-rigid polymers, many studies with ethyl (hydroxyethyl)cellulose (EHEC) [19–24] and (hydroxypropylmethyl)cellulose [25–30] have been performed using various techniques. Investigations with HPC have been comparatively scarce [31, 32]. As for the surfactants, SDS has been frequently studied, whereas, up to our knowledge, there are only two published articles involving the interaction between a cellulose ether, namely, HPMC, and bile salts [26, 29]. In this way, the study of the interaction between bile salts and HPC may contribute to extend the comprehension about the role of surfactant and polymer structures in the formation of their aggregated systems.

Materials and methods

Materials The surfactants CS (99 %), DC (99 %), and SDS (98 %) were purchased from Acros Organics and used without further purification. HPC (Aldrich) presents molar substitution (MS)=4.5 (NMR), polydispersity M_w/M_n=3.5 (SEC) without previous treatment and M_w/M_n=2.5 (SEC) after dialysis. Also after dialysis, HPC presents M_w=145,000 g mol^{-1}, radius of gyration R_g=37.7 nm; second virial coefficient A_2=5.21×10^{-4} mol cm^3 g^{-2} (data obtained at 298 K through static light scattering by using Zimm plot extrapolation procedures) and refractive index increment dn/dc=0.1349 ml g^{-1} obtained by differential refractometry at 298 K. A stock aqueous solution of HPC was dialyzed 1 week (Membracel tubing, cut-off 12,000–16,000 g mol^{-1}, Polylabo) against Milli-Q grade water (Millipore), filtered subsequently through 8- and 0.45-μm membrane filters (Millipore) and kept under refrigeration. The HPC 0.25 % m/m/surfactant samples were prepared starting from the highest concentration in surfactant and subsequent dilutions with HPC 0.25 % m/m aqueous solution down to the desired surfactant contents. This polymer concentration is approximately five times lower than the overlapping concentration c^* calculated from the inverse of the product A_2M_w. Pyrene (Py, 99 % Aldrich) was recrystallized twice from ethanol (Aldrich) solution. All solutions were prepared with Milli-Q grade water (Millipore). The probe solution was prepared by evaporating the suitable volume of the ethanol stock solution, followed by dissolution of the remaining solid in the HPC/surfactant solution. All HPC/surfactant samples were stirred for 12 h at room temperature before the measurements.

Fluorescence The pyrene emission spectra were run on a Hitachi F-4500 Spectrophotometer in the corrected spectrum mode with excitation wavelength set at 336 nm and 2.5 mm slit in the range 350–500 nm with cell holder thermostated by a circulating ethylene glycol bath at 298±0.4 K. The Py concentration was kept as low as 5×10^{-6} mol l^{-1} to exclude the possibility of excimer formation that may occur when the concentration is higher than 10^{-4} mol l^{-1}.

Conductivity Conductivity was measured by using an Oakton Con 100 series conductivity meter. The solutions were thermostated at 298±0.1 K with a water bath for at least 10 min before the readings were taken. Milli-Q grade water had a specific conductivity value of 1.3 μS cm^{-1}.

Viscometry The viscometric measurements were performed with an ordinary Cannon-Fenske Capillary Viscometer (water flow time 83 s) thermostated at 298±0.1 K by a water bath. The relative viscosity, η_{rel}, was obtained by the relation $\eta_{rel}=t/t_0$, where t and t_0 are the flow times of the sample solution and solvent, respectively.

Turbidimetry and light scattering Turbidimetry and light-scattering measurements have been undertaken on a Brookhaven Instruments goniometer, with a He–Ne laser Spectra Physics at 632.8 nm. The cloud point of the solutions was measured by the intensity of the scattered light, I_s. The procedure involves the use of a constant heating rate of approximately 1.1 K min^{-1}, a value sufficiently slow for equilibrium to be achieved, as shown by the reproducible cloud points obtained. Before the measurements, also to obtain reproducibility, each sample was pre-heated above its cloud point and cooled to room temperature, taking at least 30 min to reach thermal equilibrium at this temperature. A BI-DNDCW Brookhaven differential refractometer was used to measure the refractive index increment of HPC in water at 298 K and 620 nm.

For dynamic light-scattering measurements, a 264-channel BI-9000 AT correlator covering seven decades in delay time was used. The samples were thermostated in a refractive-index-matching liquid (decaline). To characterize the hydrodynamic behavior of the aggregates, electric

field time correlation functions were analyzed by two-exponential fits [33] (Microcal Origin 5.0). Also performed was an inverse Laplace transformation to obtain the relaxation time distribution using the Repes Routine [34] incorporated in the Gendist [35] commercial software package. The apparent hydrodynamic radius, $R_{H,app}$, was obtained from the apparent diffusion coefficient at the fixed polymer concentration of [HPC]=0.25 % m/m and scattering angle θ=90° according to the Stokes–Einstein Equation [35]:

$$R_H = \frac{k_B T}{6 \pi \eta D}, \quad (1)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η the solvent viscosity. All experiments took place at 298 K. To remove dust from the solutions, they were filtered through 0.45-μm filter (Millipore) and centrifuged at 4,000 rpm for 90 min.

Results and discussion

At 298 K, Fig. 1 shows the ratio I_1/I_3 of the intensities of the first (372 nm) and third (384 nm) vibronic peaks of monomeric pyrene solubilized within HPC 0.25 %/surfactant mixed aggregates or surfactant/water micelles as a function of surfactant concentration. The ratio I_1/I_3 decreases sharply at the onset of mixed aggregates or free micelles formation, allowing to know the polarity of the probe environment [36, 37].

From water solution containing either only surfactant or both surfactant and polymer, it is possible to obtain CMC or CAC, respectively. The values for CMC or CAC were taken as the inflection points of the I_1/I_3 curves (Fig. 1). The results from fluorescence, as well as from conductivity, are summarized in Table 1 for all systems.

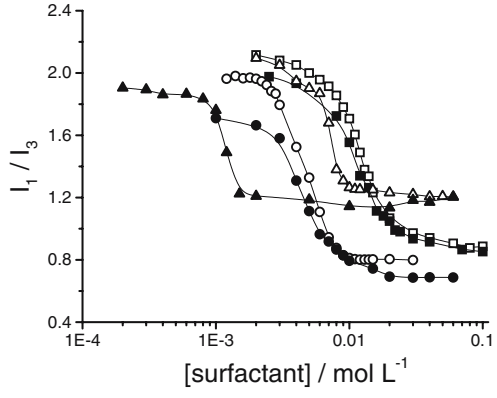

Fig. 1 Dependence of the ratio I_1/I_3 on surfactant concentration in the absence (*open symbols*) of or with HPC 0.25 % m/m (*full symbols*): CS (*squares*), DC (*circles*), and SDS (*triangles*). Temperature=298 K

Table 1 Critical concentrations from fluorescence and conductivity, as well as micropolarity (μP) from fluorescence measurements

System	CMC or CAC (mol $l^{-1}\times10^3$)		PSP or CMC_2 (See text) (mol $l^{-1}\times10^3$)	μP[(a)]
	Fluorescence	Conductivity		
SDS/water	7.4	8.3	–	1.21
HPC 0.25%/SDS	1.2	1.3	8.5	1.18
CS/water	11.8	11.5	23.1	0.89
HPC 0.25%/CS	10.1	–	24.7	0.86
DC/water	4.3	–	21.9	0.81
HPC 0.25%/DC	4.0	–	11.6	0.68

Temperature=298 K
[(a)]The uncertainty in μP values is approximately 2 %

The values of CMC obtained for each surfactant at 298 K are 11.8×10^{-3} mol l^{-1} for CS, 4.3×10^{-3} mol l^{-1} for DC, and 7.4×10^{-3} mol l^{-1} for SDS in agreement with literature data [5a, 14]. In the presence of HPC 0.25%, all CAC values decrease with respect to CMC, indicating an interaction polymer/surfactant. However, the pronounced decrease verified to HPC/SDS system (from 7.4×10^{-3} mol l^{-1} to 1.2×10^{-3} mol l^{-1}) suggests a strong interaction in line with other techniques used in this work. This behavior may be understood as a decrease of the electrostatic headgroup repulsion on the surface of the micelle due to the reduction of the surface charge density because of the presence of the polymer.

Concerning the micropolarity, μP, measured as an average value of I_1/I_3 for a complete aggregation (bottom plateau, Fig. 1), one observes that the aggregates and free micelles present similar polarity. On the other hand, it can be inferred that the bile salts are more effective to solubilize the pyrene molecule (lower μP values) than SDS (Table 1). This finding is expected, as the bile salt micelles exhibit different aggregate structures if compared to classical surfactants, as SDS. For these compounds, pyrene is primarily solubilized in the palisade layer [38], denoting their surface active character. The μP values found to HPC/CS and HPC/DC systems, in turn, reveal a possible absence of the palisade layer, as a consequence of very distinct chemical structure between bile salts and surfactant with long alkyl chains. Also on the basis of low μP values, the absence of the palisade layer was suggested previously for CS and DC free micelles in water in the presence of sodium chloride [39].

Another approach applied to study the binding of CS, DC, and SDS to HPC was the measurement of the conductivity, a property widely used in this kind of investigation. In aqueous surfactant solutions, the profile of the curve conductivity vs surfactant concentration shows two linear regions connected by a breakpoint, which is related to the onset of the micellization process. In the presence of a polymer, many studies of the system PEO/SDS demonstrated the existence of three regions connected

by two breakpoints. According to the classical interpretations, the first breakpoint is attributed to the CAC and the second one, to the polymer saturation point (PSP) [40–42].

Löfroth et al. [26] investigated the systems HPMC/sodium cholate and HPMC/sodium taurocholate and did not detect the formation of aggregates by conductivity with or without polymer. Nevertheless, in our work, all plots of the systems containing the bile salts showed at least one breakpoint as well as for the systems containing SDS. Unexpectedly, for the system CS/water two breakpoints were found in spite of the polymer absence (Fig. 2).

The data obtained from the curves conductivity vs surfactant concentration, at 298 K, are also shown in Table 1. One observes that the CMC and CAC obtained from fluorescence and conductivity techniques are in accordance with each other for all systems in which the detection of CMC or CAC is possible. Concerning the CS/water system, one should point out that the aggregation mechanism of the bile salts is complex, involving the primary (denoted in this paper as CMC) and secondary (denoted in this paper as CMC_2) micelles [43, 44]. According to the traditional Small model [45], the primary micelles consist of two to ten molecules of surfactant. The bile salt molecules bind to themselves via hydrophobic interactions, while the hydroxyl and carboxylate groups are accessible to water. At higher concentrations, secondary bile salt micelles are formed by primary micelle associations through intermolecular hydrogen bonding between the hydroxyl groups and side chain groups of the primary micelles. In this way, one can infer that the second breakpoint presented by CS/water system plots may be related to the secondary aggregation. Moreover, the aggregation values found in DC/water systems pointed to the same direction. Although an evidence of aggregation (only one breakpoint) was found, its value is too high to be considered the ordinary CMC (primary aggregation). Besides that, the CMC_2 values for DC/water and CS/water are quite in the same range of concentration, similar to the behavior found in another study [44].

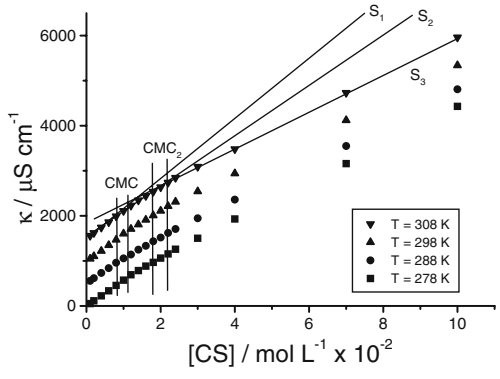

Fig. 2 Variation of the conductivity as a function of CS concentration at four temperatures. The plots have been shifted for a better visualization. The *parallel bars* indicate the region of both critical concentrations. S_1, S_2, and S_3 represent the different slopes of the *three straight lines* indicated in the *plot* for the measurement at 308 K

To determine the thermodynamic parameters of aggregation, the conductivity of all systems was measured at different temperatures (Fig. 2 exemplifies the study for CS/water system). It was considered the mass action model [46] for micelle formation of anionic surfactant. The standard free-energy change of micelle formation per mole of surfactant, ΔG^0_{mic}, is expressed by [47]

$$\Delta G^0_{mic} = (2-\alpha)\, R\, T\, \ln X_{cmc}, \tag{2}$$

where α is the degree of counterion dissociation obtained from the ratio of the slopes above and below the CMC, R is the universal gas constant, and X_{CMC} is the mole fraction of surfactant molecules at the CMC.

In turn, the enthalpy change, ΔH^0_{mic}, is given by

$$\Delta H^0_{mic} = -RT^2\left[(2-\alpha)(\partial \ln X_{cmc}/\partial T)_P - \ln X_{cmc}(\partial\alpha/\alpha T)_P\right] \tag{3}$$

If one considers that the parameter α varies slightly over the temperature range adopted in this study, Eq. 3 may be expressed as

$$\Delta H^0_{mic} = -(2-\alpha)RT^2(\partial \ln X_{cmc}/\partial T)_P \tag{4}$$

Thus, from ΔG^0_{mic} and ΔH^0_{mic} values, the entropic contribution $T\,\Delta S^0_{mic}$, may be determined as usual by

$$T\,\Delta S^0_{mic} = \Delta H^0_{mic} - \Delta G^0_{mic}. \tag{5}$$

The thermodynamic parameters of the systems CS/water, SDS/water, and HPC/SDS are displayed in Table 2. For the other systems, ΔG^0_{mic}, ΔH^0_{mic} and $T\,\Delta S^0_{mic}$ were not calculated once it was not possible to determine their CMC or CAC by breaks in the conductivity plots. At 278 K, there are no results found for SDS/water system, as the mentioned temperature is below the SDS Krafft point temperature [5b]. Table 2 lists the thermodynamic parameters obtained from the conductivity study at four temperatures, the critical concentrations, as well as the degree of counterion dissociation (α). Concerning the degree of dissociation, if one compares the α values between SDS/water and CS/water systems, it can be observed that the latter presents higher values than those for the systems containing SDS. This evidences that the SDS micelles have higher charge density than the CS micellles. On the other hand, comparing SDS/water to HPC 0.25%/SDS, the α parameter has increased in the presence of the polymer. This may be explained by a decrease in the charge density at the micellar surface due to a reduction in

the aggregation number of SDS micelles induced by HPC addition.

Taking into account the thermodynamic results, Table 2 shows that the free energy of micellization is negative and relatively independent of temperature for all systems. The ΔG^0_{mic} values between SDS/water and CS/water point out an aggregation more favorable to the alkylsulphate. The presence of HPC tends to diminish even more the free energy, denoting its influence on stabilizing the SDS micelles. This is correlated to the decrease of the CMC when HPC is added to a SDS solution (See Table 1). In turn, the ΔH^0_{mic} values are negative and seem to be temperature-dependent, while the entropic contribution $\left(T\ \Delta S^0_{mic}\right)$ is always positive and follows the free-energy trend related in terms of temperature dependence. Such ΔH^0_{mic} behavior indicates that London–dispersion interactions possibly play an important role in the aggregation processes [47].

The results from viscosity measurements on the HPC/surfactant/water systems, presented in this paper as relative viscosity, η_{rel} are shown in Fig. 3. The viscosity was measured in the presence of the actual level of surfactant, i.e., the solvent is taken as the surfactant solution of the same concentration as that in the polymer/surfactant system.

Firstly, considering the solutions HPC/bile salts, one realizes that the addition of CS or DC has little influence on the viscosity of HPC 0.25 % m/m. Along the surfactant concentration, the η_{rel} of these solutions is practically constant. In contrast, the viscosity profile for HPC/SDS shows a distinct feature from those for HPC/bile salt solutions. The η_{rel} curve passes through a maximum at 3×10^{-3} mol l^{-1} of surfactant and decreases to values below the pure polymer solution until 15×10^{-3} mol l^{-1}, increasing again after this point.

This behavior was earlier reported for other systems and may be attributed to an expansion of the polymer coil due to electrostatic repulsion between charged SDS aggregates along the polymer chain, reaching a maximum η_{rel} value. The subsequent decrease, with addition of surfactant, is related to the screening of the charge interactions by excess of counterions [48]. This maximum can be also attributed to the formation of interchain polymer–surfactant complexes. The subsequent decrease in the viscosity with increasing SDS concentration indicates that the aggregate formation possibly leads to a more compact polymer structure due to intrachain polymer–surfactant complexes [49, 50].

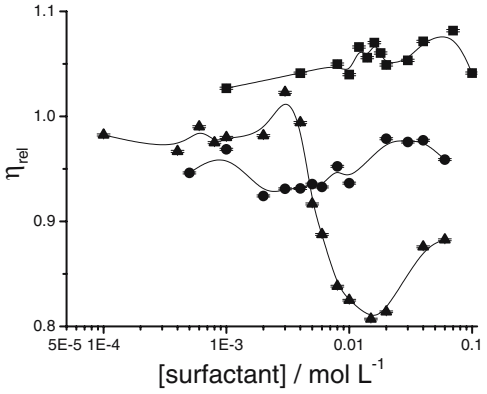

Fig. 3 Relative viscosity, η_{rel} of HPC 0.25 % as a function of surfactant concentration: CS (*squares*), DC (*circles*) and SDS (*triangles*). Temperature=298 K. The *lines* are guides to the eyes

If one considers now the range $5–20\times10^{-3}$ mol l^{-1}, the viscosity falls below the initial level, reaching a minimum about 15×10^{-3} mol l^{-1}. This may be an evidence of an increase of the degree of flexibility/mobility as a result of the polymer becoming more hydrophilic [50]. In accordance with this interpretation is the fact that the value of the micropolarity for HPC/SDS system is higher than those found of HPC/CS and HPC/DC systems.

The difference in the viscosity profile curves between HPC/SDS and HPC/bile salts may be explained from the

Table 2 Thermodynamic parameters and the degree of counterion dissociation (α) for some of the studied systems at different temperatures

System	*T*/*K*	α	CMC or CAC (mol $l^{-1}\times10^3$)	ΔG^0_{mic} (*kJ* mol^{-1})	ΔH^0_{mic} (kJ mol^{-1})	$T\ \Delta S^0_{mic}$ (kJ mol^{-1})
HPC 0.25%/SDS	278	0.43	0.78	−39.8	−27.2	12.6
	288	0.46	0.98	−40.9	−29.0	11.9
	298	0.44	1.3	−40.7	−30.7	10.0
	308	0.49	1.7	−40.2	−32.1	8.1
SDS/water	278	–	–	–	–	–
	288	0.34	8.7	−34.8	−4.4	30.4
	298	0.36	8.3	−35.7	−4.7	31.0
	308	0.38	8.6	−36.4	−4.9	31.5
CS/water	278	0.79	12.6	−23.5	−7.4	16.1
	288	0.85	8.7	−24.1	−7.5	16.6
	298	0.82	11.5	−24.8	−8.3	16.5
	308	0.82	12.6	−25.3	−8.8	16.5

Table 3 Cloud point values as a function of the surfactant concentration for HPC 0.25 %/surfactant systems

System	HPC 0.25%/surfactant[(a)]														
	SDS			CS				DC							
[Surfactant] (mol $l^{-1}\times10^3$)	3	5	10	16	20	30	40	70	100	10	16	20	24	30	40
Cloud point/K	327	340	360	323	323	325	323	326	325	321	326	326	321	323	324

[(a)]The cloud point temperature for HPC 0.25 % is 315 K

nature of their micelles: both CS and DC micelles are smaller in size and present smaller charge densities than SDS micelles, as can be concluded on the basis of the dissociation parameter values (Table 2). Thus, the η_{rel} is rather insensitive to changes in bile salt concentration due to the reduced micelle size, as shown by the little variation on the viscosity values for bile salts in contrast to SDS.

Cellulose ethers present a differentiated characteristic with respect to temperature effect on the solubility. While most of the substances have an increase in solubility with temperature, the cellulose derivatives tend to phase separation at high temperatures [28, 51].

This phenomenon may be attributed to the existence of a number of equilibrium bond configurations for the propylene oxide moiety, consisting of two C–C bonds and two C–O bonds [36, 52]. At low temperature and in polar solvents, the oxygens exhibit a gauche orientation about C–C bonds and a trans-orientation about C–O bonds. The latter presents a relatively large dipole moment. The increase in temperature may favor the bond configuration possessing a less dipolar nature. As a consequence, there may be a reduction of the propylene oxide group dipole moment, leading to phase separation.

The results obtained for cloud points (CP) by light scattering are displayed in Table 3. All solutions present concentrations above critical surfactant concentration and the CP of the pure polymer solution is 315 K. One observes that an increase in SDS content leads to a sharp increase in CP temperatures. The cloud point measurements to SDS samples above 10^{-2} mol l^{-1} indicated temperatures beyond 373 K (upper experimental limit). The analysis of the data suggests that the HPC/SDS aggregates are more efficient to shift the CP temperatures than HPC/bile salt aggregates. Besides, the cloud points of both HPC/bile salt systems increase smoothly from 315 K to about 324 K, reaching a maximum plateau value between 2×10^{-2} and 10^{-1} mol l^{-1} total surfactant concentration. This feature was also seen for the same systems but in the presence of sodium chloride [16, 17]. Once again, this behavior may be related to the reduced size and smaller charge density of the bile salt micelles.

Considering various nonionic polymer/anionic surfactant systems, the gradual increase in surfactant concentration tends to delay the onset of phase separation due to electrostatic repulsion between bond micelles adsorbed into polymer chain. However, being that the bile salt micelles charge density is relatively low in comparison with SDS micelles, at a given amount of surfactant, the repulsion effect between them is not strong enough to avoid the approach of a polymer chain. As a result, the solvent is expelled, leading to phase separation [6].

In dynamic light scattering, two modes were observed in the time correlation functions: a) a fast mode, related to single polymer chain, intrachain polymer/surfactant aggregates, or free micelles and b) a slow mode assigned to polymer clusters and interchain polymer/surfactant complexes. It is well-recognized that cellulose derivatives may show the presence of clusters in their aqueous solutions [53, 54]

Through DLS it was observed that the HPC/surfactant systems are diffusive [33]. The $R_{H,app}$ values for the polymer in the absence of surfactant are 10.9 and 73.0 nm for the fast and slow modes, respectively. The results of $R_{H,app}$ for the fast mode are shown in Fig. 4.

Initially, for the fast mode in the systems HPC/SDS, the $R_{H,app}$ increases with surfactant addition, reaching its maximum value about [SDS]=2×10^{-3} mol l^{-1}; after that, there is a continuous decrease of $R_{H,app}$ to about 1–2 nm at higher surfactant content. The slow mode for the same system showed similar profile. If one compares to viscosity data, the behavior is in good agreement: the maximum of $R_{H,app}$ corresponds to the maximum of viscosity, and at higher SDS contents there is a decrease for η_{rel}. This behavior was previously explained (see Viscosity results). In contrast, for the bile salt systems, the $R_{H,app}$ remains practically unchanged, within the experimental error, for

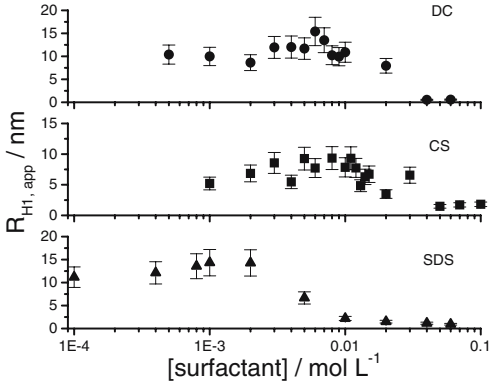

Fig. 4 Apparent hydrodynamic radius, $R_{H,app}$, of HPC 0.25 % as a function of surfactant concentration for the fast mode: CS (*squares*), DC (*circles*), and SDS (*triangles*). Scattering angle=90°. Temperature=298 K

both modes until [CS]=[DC]=10^{-2} mol l^{-1}, decreasing with the increase of surfactant concentration. For HPC/CS, this concentration limit coincides with its CAC, whereas for DC/HPC, it coincides with its PSP (See Table 1). In comparison with viscosity profile, this behavior of $R_{H,app}$ seems to be a discrepancy; once, at higher bile salt concentration, η_{rel} shows a little increase. However, this divergence is apparent, as the viscosity is sensitive to the number of particles.

The analysis of the ratio of the amplitudes of slow to fast mode (A_{slow}/A_{fast}) plotted as a function of the surfactant concentration may collaborate on the understanding of the aggregation of the systems (Fig. 5). The value for this parameter for HPC 0.25 % aqueous solution is 2.3. One verifies gradual increase of A_{slow}/A_{fast} for HPC/CS and HPC/SDS systems, reaching its maximum value in the vicinity of CAC. It can be also observed that the values of A_{slow}/A_{fast} are higher than the unity, indicating that the slow mode predominates over the fast one. On the other hand, the HPC/DC system shows an opposite trend, reaching a minimum value in the vicinity of CAC.

Nevertheless, at higher surfactant content, the ratio decreases to values below the unity for all systems, denoting a higher contribution of the fast mode on the dynamics of the systems. Moreover, for HPC/CS and HPC/SDS systems, such prevailing contribution of the fast mode becomes evident in the vicinity of the respective PSP. This can be correlated to the fact that for the fast mode, the $R_{H,app}$ values converge to corresponding values of the free micelles, about 1–2 nm. At this point, one believes that for [surfactant]≫[surfactant]$_{CAC}$ it occurs the formation of these free micelles. In addition, the study of the relaxation time distributions by means of Repes Routine corroborates the previous supposition.

Thus, the plots of the relaxation time distribution for the systems HPC/surfactant are displayed in Figs. 6, 7 and 8. Each group of curves is delimited by CAC, i.e., the first three curves HPC/surfactant (from bottom to top) are related to the pre-aggregation range, while the others refer to the post-aggregation range. The bottom curve is always pure HPC 0.25 % m/m.

A general feature of almost all curves is the absence of a second correlation mode, detected by two-exponential fit. This may be explained, considering that the relaxation time distributions are relatively large, extending over more than a decade. Also, in some cases, the correlation times found by the two-exponential method are comparatively close to each other in a logarithm scale. In this way, when the Repes Routine is applied to the intensity autocorrelation functions, both correlation modes would appear as a single one. In the plots, only one peak is detected with a broad distribution.

Another feature is that the addition of surfactant to the HPC 0.25 % m/m solution dissolves the highest molecular mass fraction of the polymer (seen as a "shoulder" in the curve), as well as widens the distribution reflecting a higher mobility of the aggregates. The changes in the profile of the curves appear already at low concentrations for all systems. These are evidences that the interaction between the surfactants and the polymer already starts below the CAC. The addition of DC changes the distribution more drastically than CS or even SDS. At [DC]=3×10^{-3} mol l^{-1}, the former single peak splits into two, being the dominant peak at longer correlation times, which corresponds to the slow mode. This behavior indicates that interchain HPC/DC complexes begin to form at a concentration close to CAC but lower than it. These interchain complexes keep being formed and constitute the dominant mode up to [DC]=7×10^{-3} mol l^{-1}. At [DC]=10^{-2} mol l^{-1}, which is not far from PSP of HPC/DC system (see Table 1), the right side of the distribution (longer times) is not dominant anymore, the left side prevails and indicates that faster structures dominate the dynamics. At [DC]=4×10^{-2} mol l^{-1}, the fraction at longer times has disappeared, and a peak at shorter times appears that can be assigned to free micelles, as discussed below. At [DC]=6×10^{-2} mol l^{-1},

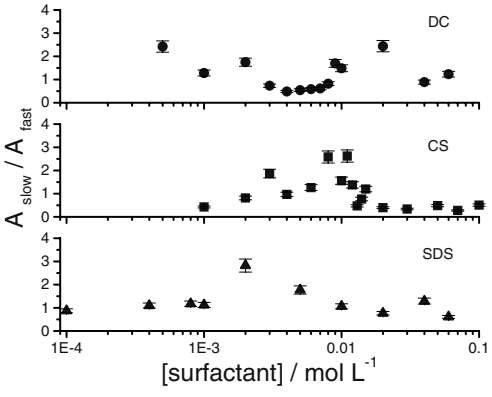

Fig. 5 Ratio A_{slow}/A_{fast} of the amplitudes of slow to fast correlation modes for HPC 0.25 % solutions as a function of surfactant concentration: CS (*squares*), DC (*circles*), and SDS (*triangles*). Scattering angle=90°. Temperature=298 K

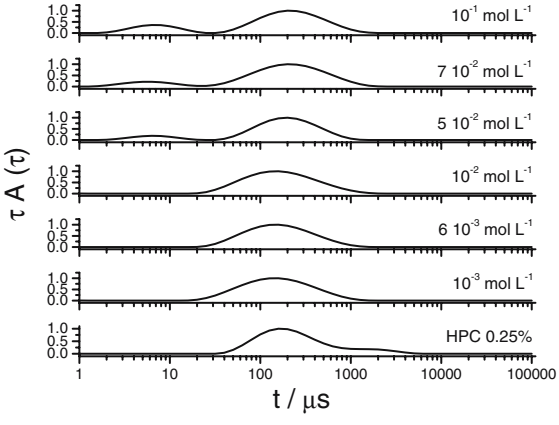

Fig. 6 Relaxation time distributions for the systems HPC 0.25 %/CS. The surfactant concentration is indicated in *each graph*. Scattering angle=90°. Temperature=298 K

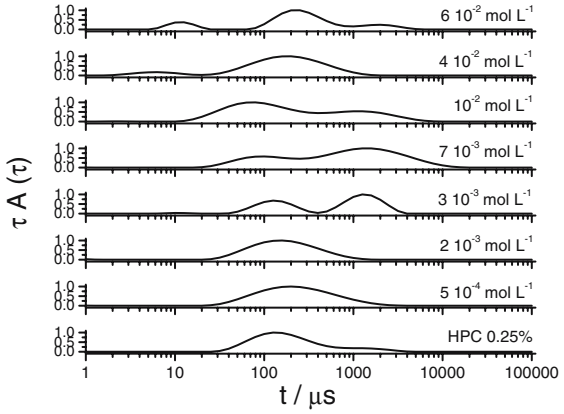

Fig. 7 Relaxation time distributions for the systems HPC 0.25 %/DC. The surfactant concentration is indicated in *each graph*. Scattering angle=90°. Temperature=298 K

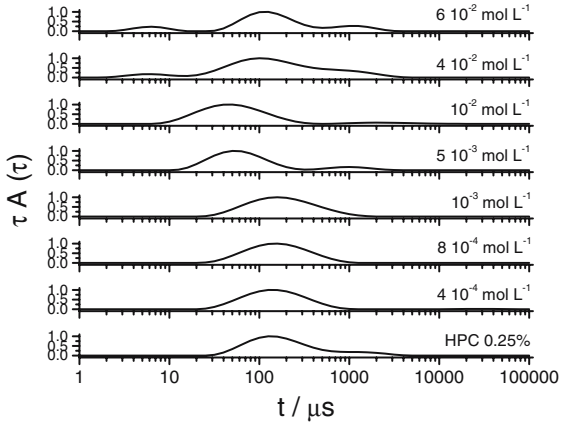

Fig. 8 Relaxation time distributions for the systems HPC 0.25 %/SDS. The surfactant concentration is indicated in *each graph*. Scattering angle=90°. Temperature=298 K

the distribution becomes more complex and the free micelle peak more evident.

As stated before, SDS binds to HPC at concentrations lower than CAC [shoulder in HPC distribution disappears, the relaxation time of the maximum peak is slightly shifted to shorter times and the polydispersity increases (Fig. 8)]. Above CAC, at [SDS]=5×10^{-3} mol l^{-1} and [SDS]=10^{-2} mol l^{-1}, the distribution is also shifted to shorter times. At SDS concentrations higher than 3×10^{-2} mol l^{-1}, the distribution becomes even wider and a high molecular mass fraction arises. All these evidences are in agreement with the viscosity behavior (Fig. 3). If one observes now the curves for [CS]=10^{-1} mol l^{-1}, [CS]=7×10^{-2} mol l^{-1}, [CS]=5×10^{-2} mol l^{-1}, [DC]=6×10^{-2} mol l^{-1}, and [SDS]=6×10^{-2} mol l^{-1}, it is possible to identify a peak at shorter correlation times that is found in about the same region in the scale. The calculated $R_{H,app}$ for these characteristic times is approximately 1 nm, corresponding to the value of the free micelles [55]. It is worth noting that Repes and the two-exponential methods give in general convergent results.

Conclusions

Fluorescence, conductivity, viscometry, turbidimetry, and light-scattering measurements have been employed to study the aggregation of different anionic surfactants (CS, DC, and SDS) in dilute solutions of (hydroxypropyl)cellulose (0.25 % m/m).

It is observed that the decrease of I_1/I_3 ratio for all surfactant systems, denoting the formation of micelles, is shifted in the presence of HPC to lower surfactant concentrations. This shift is more pronounced for HPC/SDS systems, indicating that the interaction HPC/SDS is stronger than HPC/bile salts studied in this paper. The turbidimetry results corroborate with this interpretation. The changes in the cloud points of HPC/surfactant systems are a balance between hydrophobic and electrostatic interactions, although the latter have little influence on the bile salts. In fact, the clouding behavior of HPC 0.5 %/CS/NaCl 0.1 mol l^{-1} or HPC 0.5 %/DC/NaCl 0.1 mol l^{-1} [16, 17] is similar to the results found in this paper, indicating that the electrostatic interactions may play a discreet role in the bile salt aggregations. The overall scenario for this behavior may be understood as an amphiphilic character of the polymer due to its hydrophobic and hydrophilic segments. In this way, the presence of HPC in aqueous surfactant solutions may screen the electrical density charges of the micelles, especially for SDS ones (hydrophilic character), in combination with a hydrophobic attraction, contributing to the formation of polymer/surfactant mixed micelles.

By conductivity, the values of ΔG^0_{mic} for the systems HPC/SDS pointed out an interaction between the alkylsulphate and HPC more favorable than the bile salts and HPC, as already demonstrated by fluorescence. The light-scattering data evidenced the influence on the dynamics of HPC when a surfactant is added. The electric field autocorrelation functions fitted by two-exponential method presented two correlation times (related to the slow mode and the fast mode), being both diffusive. At higher contents of surfactant, i.e., ≥PSP, the $R_{H,app}$ plots denoted the presence of free micelles in solution, verified by the low values of $R_{H,app}$. Such behavior was also observed in the relaxation time distribution curves in the region of shorter times. An important experimental evidence was the observation that the binding of the surfactants to HPC starts below its CAC, as may be seen in the Figs. 6, 7 and 8. Regarding the mechanism aggregation, one can infer from the overall results that the interaction between HPC and CS and DC and SDS may occur in two steps: 1) attachment of surfactant unimers to the HPC chain leading to the formation of aggregation nuclei; and 2) further binding of surfactant micelle-like aggregates on it.

The present study shows also that the strength of the polymer–surfactant interaction cannot be evaluated only by the decrease of CAC in comparison to CMC. As shown by the HPC/DC study, CAC is almost equal to CMC but the

relaxation time distribution is drastically changed already when the DC concentration is in the vicinity of CAC.

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References

1. Sundelöf LO, Nilsson S, Holmberg C (1995) Colloid Polym Sci 273:83 DOI:10.1007/BF00655678
2. Rodenas E, Sierra ML (1996) Langmuir 12:1600 DOI:10.1021/la9505778
3. Miguel MD (2001) Adv Coll Interf Sci 89:1 Sp. Iss
4. Berglund KD, Przybycien TM, Tilton RD (2003) Langmuir 19:2705 DOI:10.1021/la026429g
5. Ananthapadmanabhan KP (1993) Surfactant solutions: adsorption and aggregation properties. In: Goddard ED, Ananthapadmanabhan KP (eds) Interactions of surfactants with polymers and proteins, chapter 2. CRC, New York a) p. 22, b) p. 40
6. Holmberg K, Jönsson B, Kronberg B, Lindman B (2003) Surfactant and polymers in aqueous solution, 2nd edn. Wiley, United Kingdom, pp 197–201
7. Panmai S, Prud'homme RK, Peiffer DG, Jockusch S, Turro NJ (2002) Langmuir 18:3860
8. Neumann MG, Schmitt CC, Iamazaki ET (2003) J Colloid Interface Sci 264:490
9. Morimoto H, Hashidzume A, Morishima Y (2003) Polymer 44:943
10. Costa MFC, Froehner SJ, Ruzza AA, Santos SF, Zanette D (1998) Quim Nova 21:272
11. Zanette D, Soldi V, Romani AP, Gehlen MH (2002) J Colloid Interface Sci 246:387
12. Winnik MA, Bystryak SM, Chassenieux C, Strashko V, Macdonald P, Siddiqui J (2000) Langmuir 16:4495
13. Wang SC, Wei SC, Chen WB, Tsao HK (2004) J Chem Phys 120:4980
14. Roda A, Hofmann AF, Mysels KJ (1983) J Biol Chem 258:6362
15. Garidel P, Hildebrand A, Neubert R, Blume A (2000) Langmuir 16:5267
16. Martins RM, Silva CA, Becker C, Samios D, Bica CID, Christoff M (2002) Polímeros: Ciência e Tecnologia 12:109
17. Martins RM, Silva CA, Becker C, Samios D, Christoff M, Bica CID J Braz Chem Soc (in press)
18. Christoff M, Silveira NP, Samios D (2001) Langmuir 17:2885
19. Carlsson A, Karlstrom G, Lindman B, Stenberg O (1988) Colloid Polym Sci 266:1031
20. Karlstrom G, Carlsson A, Lindman B (1990) J Phys Chem 94:5005
21. Joabsson F, Rosen O, Thuresson K, Piculell L, Lindman B (1998) J Phys Chem B 102:2954
22. Kjoniksen AL, Nystrom B, Lindman B (1998) Macromolecules 31:1852
23. Nilsson S, Thuresson K, Lindman B, Nystrom B (2000) Macromolecules 33:6941
24. Lund R, Lauten RA, Nystrom B, Lindman B (2001) Langmuir 17:8001
25. Hammarstrom A, Sundelof LO (1993) Colloid Polym Sci 271:1129
26. Löfroth JE, Johansson L, Norman AC, Wettström K (1991) Prog Colloid & Polym Sci 84:73
27. Kulicke WM, Arendt O, Berger M (1998) Colloid Polym Sci 276:617
28. Nilsson S (1995) Macromolecules 28:7837
29. Avranas A, Tasopoulos V (2000) J Colloid Interface Sci 221:223
30. Sovilj VJ, Petrovic LB (2005) Colloid Polym Sci 284:334
31. Suto S, Iwasawa I (1993) J Polym Sci A 31:1599
32. Hormnirum P, Sirivat A, Jamieson AM (2000) Polymer 41:2127
33. Chu B (1991) Laser light scattering: applications of photon correlation spectroscopy. Academic, London, pp 84–134
34. Jakes J (1995) Collect Czechoslov Chem Commun 60:1781
35. Schillen K, Brown W, Johnsen RM (1994) Macromolecules 27:4825
36. Ahlnas T, Karlstrom G, Lindman B (1987) J Phys Chem 91:4030
37. Roy S, Mohanty A, Dey J (2005) Chem Phys Lett 414:23
38. Thomas JK (1980) Chem Rev 80:283
39. Zana R, Guveli D (1985) J Phys Chem 89:1687
40. Xia J, Dublin PL, Kim YJ (1992) J Phys Chem 96:6805
41. Chari K (1992) J Colloid Interface Sci 151:294
42. Chari K, Antalek B, Lin MY, Sinhá SK (1994) J Chem Phys 100:5294
43. D'Alagni M, D'Archivio AA, Galantini L, Giglio E (1997) Langmuir 13:5811
44. Santhanalakshmi J, Lakshmi GS, Aswal VK, Goyal PS (2001) Proc Indian Acad Sci 113:55
45. O'Connor CJ, Wallace RG (1985) Adv Colloid Interface Sci 22:1
46. Lee JN, Moroi Y (2004) J Colloid Interface Sci 273:645
47. Hiemenz PC, Rajagopalan R (1997) Principles of colloid and surface chemistry. Dekker, New York, pp 335–404
48. Mya KY, Sirivat A, Jamieson AM (2001) Macromolecules 34:5260
49. Wang G, Olofsson G (1995) J Phys Chem 99:5588
50. Singh SK, Nilsson S (1999) J Colloid Interface Sci 213:152
51. Thuresson K, Lindman B (1997) J Phys Chem B 101:6460
52. Karlstrom G (1985) J Phys Chem 89:4962
53. Schulz L, Seger B, Burchard W (2000) Macromol Chem Phys 201:2008
54. Wittgren B, Porsch B (2002) Carbohyd Polymer 49:457
55. Schurtenberger P, Mazer N, Kanzig W (1983) J Phys Chem 87:308