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STUDIES ON ANIONIC SURFACTANT STRUCTURE IN THE AGGREGATION WITH (HYDROXYPROPYL)CELLULOSE

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Fluorescence probing and light scattering measurements have been combined to study the aggregation of different anionic surfactants in dilute solutions (≤1% w/v) of (hydroxypropyl)cellulose (HPC MW 153,000). The set of surfactants includes some natural cholesterol derivatives, the bile salts sodium cholate (CS) and sodium deoxycholate (DC), and the well-known alkylsulphate, sodium dodecylsulphate (SDS). In moderate ionic strength, NaCl 0.1 mol.L^{-1}, the critical aggregation concentration (C_1) related to binding of the surfactant monomers decreases more significantly for SDS than to the bile salts. On the other hand, the cloud point temperature of HPC increases from 37^0C to 41^0C and 60^0C in presence of CS and SDS, respectively. Moreover, the hydrodynamic behavior indicates that also the electrostatic interaction with HPC is more effective as the highly charged SDS induces higher diffusion to polymer chain than the more hydrophobic bile salts

Introduction

Cellulose ether derivatives as (hydroxypropyl)cellulose (HPC) are water-soluble uncharged polymers that interact with anionic surfactants in solution resulting in special rheological properties to the system. The understanding of the mechanisms operating and structures formed in such solutions as well as the numerous applications of non-ionic polymer-ionic surfactant systems in the pharmaceutical formulations, cosmetics, enhanced oil recovery, paint and food products have contributed to several studies on these systems over the last 30 years. Interactions between nonionic polymers and ionic surfactants are a consequence of weak intermolecular forces, which allow for a wide variety and range of behaviors in these systems. The directed action of a number of weak interactions leads to the cooperative nature of the aggregation behavior usually characterized by a starting surfactant concentration termed the critical aggregation concentration (C_1). The stabilization of the interfaces between the hydrophobic core of the aggregates and water is the major driving force for polymer-surfactant.[1,2]

Different research groups have focused the relations between structure, charge and hydrophobicity of surfactants and polymers. Many studies have explored hydrophobic modifications in the polymers, but only a few types of surfactants have been investigated, most of them formed by long alkyl chains with polar head group.[3-6] We have recently studied different anionic surfactants with respect to the aggregation with low weight, non charged and flexible polymers as poly(ethylene oxide) and poly(vinyl pyrrolidone)[7,8]. These studies included some natural anionic surfactant bile salts, sodium cholate (CS) and sodium deoxycholate (DC), that are carboxylic polyhydroxy derivatives from cholesterol[9] and the well-known sodium dodecylsulphate (SDS) that is a long chain alkylsulphate. The molecular shape of the bile salts exhibits a planar polarity due to spatial distribution of lateral groups in their steroid backbone. The bile salt structures result in smaller and more rigid aggregates than the micelles formed by conventional alkylsurfactants, providing highly non polar microenvironments with chiral properties.[10] Indeed, the balance of hydrophobic and electrostatic forces in the polymer-surfactant interaction in moderate ionic strength was shown sensitive to different surfactant structures being the hydrophobic component more relevant to bile salt aggregation.[7,8]

The present work extends the studies with the same set of surfactants (CS, DC and SDS) to compare their aggregation behavior in the presence of the more rigid non-ionic polymer HPC at different temperatures. The HPC/SDS system has been shown as possessing the highest affinity between SDS and cellulose ether derivatives by different techniques including those used here.[7,8]

Experimental

The surfactants DC(Sigma), CS(Sigma), SDS(Fischer) were used as received. The HPC (Aldrich) presents

$M_w \cong 153{,}000$; $M_w/M_n = 2.5$ (GPC); MS = 4.5 (NMR). A stock aqueous solution of HPC was dialyzed one week (Membracel tubing, cut-off 12000-16000; Polylabo) and filtered subsequently through 8 and 0.45 μm membrane filters (Millipore). Pyrene (Py, Aldrich) and benzophenone (Bp, Vortec) were recrystallized twice from ethanol solutions. All solutions were prepared with Milli-Q grade water (Millipore). The probe or quencher solutions were prepared by evaporating the suitable volume of the ethanol stock solution, followed by dissolution of the remaining solid in the surfactant/HPC solution. All surfactant/HPC solutions were stirred for 12 hs at room temperature before the measurements. To remove dust for the light scattering experiments the solutions were filtered through 0.45 μm filter (Millipore) and centrifuged at 4.000g for 90 minutes. All the presented data are averaged from 3 experimental sets.

Results and Discussion

The steady-state fluorescence measurements employed a Hitachi F-4500 spectrofluorimeter with cell holder thermostated by a circulating ethylene glycol bath. The ratio I_1/I_3 of the first (372 nm) and third (384 nm) vibronic peaks in the Py (monomer $\leq 5x10^{-6}$ mol.L^{-1}) emission spectrum has been shown to be a sensitive function of local polarity in organized systems.(11) Indeed, the ratio I_1/I_3 from the Py fluorescence decreases for different systems as the total surfactant concentration increases reflecting the incorporation of Py in a hydrophobic site as the aggregate is formed. The critical surfactant concentration (C_1) was determined by the intercept from linear extrapolation on bottom and steep data or by the inflection point of the curve (Table 1). Both values confirm that HPC promoves a decrease in the C_1 for the SDS(12) aggregation as well for DC whereas no change is observed to CS. Since the closeness of the C_1 values is propotional to degree of the cooperativity in the aggregation process for each surfactant it is clear the opposite behavior between SDS and CS in presence of HPC, the later increasing the aggregation cooperativity. The micropolarity value (μP) corresponds to the ratio I_1/I_3 above C_1 where the full aggregate formation is assumed (Table 1). The μP shows small increase to aggregates in presence of the HPC for SDS and CS possibly due to the interaction with the polymer segment to result an aggregate more penetrable to water(13) similarly to absence of the salt screening effect.

Otherwise, the increment of the temperature implies more surfactant monomers to aggregate formation as the C_1 increases and mainly in the presence of HPC for all surfactants.

Table 1. Aggregation Parameters from Fluorescence Measurements[a]

	SDS		CS		DC	
	C_1[b]	μP[c]	C_1[b]	μP[c]	C_1[b]	μP[c]
T 25 ^{0}C						
W_0[f]	*8.3*[d] *5.5*[e]	*1.12*	*21*[d] *14*[e]	*0.83*	-	-
W	2.9[d] 2.4[e]	1.09	12[d] 5.3[e]	0.70	3.2[d] 2.3[e]	0.68
HPC[g]	0.58[d] 0.24[e]	1.12	11.7[d] 7.2[e]	0.72	1.1[d] 0.78[e]	0.67
T 39 ^{0}C						
W	3.0[d] 2.5[e]	1.02	12[d] 5.3[e]	0.70	-	-
HPC[g]	0.71[d] 0.24[e]	1.09	13.9[d] 7.0[e]	0.74	2.1[d] 1.1[e]	0.68

a)NaCl 0.1 mol.L^{-1}, error ± 10%; b) C_1 in mmol.L^{-1} is the critical aggregation concentration or micelle concentration (cmc);c) μP is the micropolarity obtained as the ratio I_1/I_3 from fluorescence of Py; d) C_1 is the intercept from linear extrapolation on bottom and steep data; e) C_1 is the inflection point of aggregation curves calculated from the minimum of its 1st derivative; f) No salt; g) MW 153,000, 0.5 g.dL^{-1}.

From the HPC point of view, the presence of SDS or CS reflects on increase of the cloud point temperature as shown by light scattering intensity in the Figure 1. Indeed, our preliminary results indicate that the HPC/NaCl 0.1 mol.L^{-1} solution starts the phase separation about 37^{0}C but when CS or SDS is added above C_1 the cloud point moves to 41^{0}C and 60^{0}C, respectively, indicating a more effective interaction for HPC/SDS than HPC/CS system

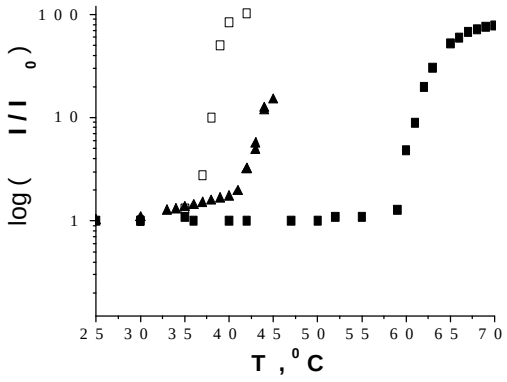

Figure 1 – Temperature dependence of light scattering intensity for (□) 0.5 g.dL^{-1} of HPC/NaCl 0.1 mol.L^{-1}; (s) with CS 40 mmol.L^{-1}; or (l) with SDS 5 mmol.L^{-1}.

Light scattering and photon correlating measurements have been undertaken on a Brookhaven Instruments spectrometer, with a He-Ne laser at 632.8 nm. Intensities were correlated by a 264-channel BI-9000

AT correlator covering 5 decades in delay time. The samples were thermostated in a refractive-index-matching liquid (decaline). In order to characterize the hydrodynamic behavior of the aggregates the multisampling time autocorrelation functions were analyzed by inverse Laplace transformation using the CONTIN[14] method to obtain the decay time distribution $A(\tau)$. For example, the Figure 2 shows the angle dependence for relaxation rate, Γ, from different HPC/NaCl 0.1mol.L^{-1} solutions with and without surfactants. Each system presents two components at assigned to polymer chain or polymer/surfactant aggregate (fast) and some polymer aggregate (slow) that is minimal due to dilute regime adopted. In despite of the different HPC concentrations of each surfactant system, the curves may confirm the effectiveness of SDS to modify the HPC aqueous behavior observed in the cloud point experiments.

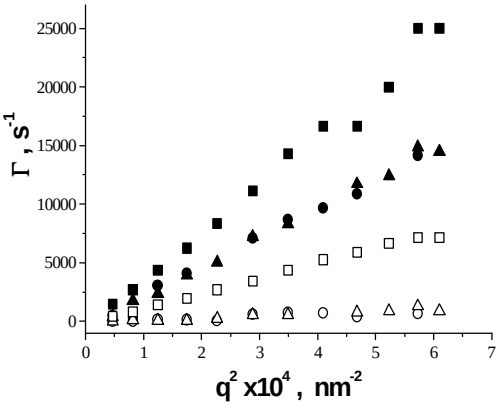

Figure 2 – Angle dependence of the relaxation rate, G, to fast (full symbols) and slow (open symbols) components for 1 g.dL^{-1} HPC (l , m) plus CS 40 mmol.L^{-1} (s, Δ), and 0.5g.dL^{-1} HPC plus SDS 5 mmol.L^{-1} (n,□). NaCl 0.1 mol.L^{-1}; T 20 °C.

Conclusions

The anionic surfactants SDS, CS and DC have shown different aggregate behavior in the presence of HPC. At this point, the interaction of SDS with HPC is being more effective than CS and possibly than DC. Besides the electrostatic interaction, favored to highly charged SDS micelles, the rigidity of HPC may play a role in order to expose the hydrophobic segments of the chain to interact with the more hydrophobic bile salts, CS and DC.

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