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New insights on the interaction between hydroxypropylmethyl cellulose and sodium dodecyl sulfate

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ABSTRACT

The interaction between an anionic surfactant (sodium dodecyl sulfate (SDS)) and an uncharged polymer (hydroxypropylmethyl cellulose) in aqueous solutions has been studied using conductivity, rheology and UV–vis transmittance methods.

The effect of hydroxypropylmethyl cellulose (HPMC) concentration on the critical association concentration (*cac*) of the surfactant and on the polymer saturation points (*psp*) was analyzed using an electrical conductivity technique, which allowed establishing association and micellization thermodynamic parameters at different polymer concentrations. The effect of temperature on these parameters was also investigated. It is seen that the free energy change in the association process is constant up to 0.5% HPMC, but increases after this point. A similar behavior is found for the bulk micellization process. It is also seen that the association process becomes more and more favorable as the temperature increases. Rheological measurements were performed to investigate the influence of surfactant concentration in the viscosity of HPMC hydrogels at room temperature. Three regimes were found: an initial decrease, up to the *cac*, followed by a drastic increase and a further decrease starting close to the *psp*. Studies with temperature ramps have been also conducted to assess the effect of SDS on the thermal gelation of HPMC, showing that SDS delays or even inhibits gelation. Optical transmittance studies were carried out in order to evaluate the behavior of the polymer chains (extension and compaction) as a function of SDS concentration. A model for HPMC–SDS interaction has been proposed, rationalizing the development of the system at different SDS and HPMC concentrations.

1. Introduction

Non-ionic cellulose derivatives comprise a broad group of biocompatible polymers. The respective aqueous solutions have gained a growing relevance in the last decades as a result of their interesting properties, which make them suitable to be used in several industrial applications such as cosmetics, drug formulations, detergents and food (Kennedy, Phillips, Williams, & Picullel, 1993). In many applications these aqueous solutions also contain ionic or non-ionic surfactants which are employed, among other reasons, to control the viscoelastic properties of these mixtures. The study of these systems is not only interesting from a perspective of industrial applications, but also for the fundamental understanding of polymer/surfactant interaction.

Some water-soluble cellulose ethers have use in many applications as viscosity modifiers as a consequence of their capability to self-assemble via hydrophobic interactions. Another interesting feature of this class of water-soluble polymers is their ability to form, in aqueous solutions, reversible three-dimensional networks with temperature, a process known as thermal gelation. The sol–gel transition is a desirable occurrence with many uses such as material processing (Cohen, Starosvetsky, Cheruti, & Armon, 2010; Gaweł, Gaweł, & Øye, 2010; Lind, Gates, Pedoussaut, & Baiz, 2010; Mujahid, Lieberzeit, & Dickert, 2010; Tseng, Lin, Chen, & Chu, 2010) and, particularly, a variety of bio-medical applications (Fadnavis & Koteshwar, 1999; Klonowski, 1988; Lee et al., 2010; Martin & Adolf, 1991; Satoshi, Naoto, & Hitoshi, 2009). There are different common strategies to induce gel phases (or at least phases of higher viscosity) and they comprise increasing polymer concentration above the overlap concentration (the so-called C^*), and the addition of surfactants or other associative species to promote bridging and association (Loyen, Iliopoulos, Audebert, & Olsson, 1995; Sarrazin-Cartalas, Iliopoulos, Audebert, & Olsson, 1994). Gel formation can also be achieved by tuning the temperature, either by cooling or heating, depending on the physicochemical characteristics of the polymer. The gelation temperature can therefore be adjusted by changing polymer architecture and/or molecular weight. This has been addressed in many interesting contributions, mainly

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dealing with three types of systems, including non-ionic polysaccharides such as ethyl (hydroxyethyl)cellulose (EHEC) (Carlsson, Karlström, & Lindman, 1990; Kjøniksen, Nyström, & Lindman, 1999; Lindell & Cabane, 1998; Ostrovskii, Kjoniksen, Nyström, & Torell, 1999; Thuresson, Lindman, & Nyström, 1997; Wang, Lindell, & Olofsson, 1997), poly(isopropylacrylamide) and its derivatives (Antunes, Gentile, Tavano, & Rossi, 2009; Eom, Oh, & Park, 1998; Hou, De Bank, & Shakesheff, 2004; Lu, Targonsky, Wheeler, & Cheng, 2007; Zeng, Liu, Tong, Yang, & Wu, 2000), and pluronics such as F127 (Barreiro-Iglesias, Alvarez-Lorenzo, & Concheiro, 2003a; Cappel & Kreuter, 1991; Lee et al., 2010; Schmolka, 1972). These systems exhibit an increase in viscosity above a critical temperature and are suitable for some biomedical applications, particularly for drug delivery systems (Derakhshandeh, Fashi, & Seifoleslami, 2010; Escobar-Chávez et al., 2006; Gilbert, Hadgraft, Bye, & Brookes, 1986; Lee, Lee, Baek, & Lim, 2004). Thermal gelation of polymers is ascribed to two different mechanisms: micellar-cubic phase transition, as observed in pluronics (Gentile, De Luca, Antunes, Rossi, & Ranieri, 2010; Lenaerts, Triqueneaux, Quartern, Rieg-Falson, & Couvreur, 1987; Vadnere, Amidon, Lindenbaum, & Haslam, 1984), or hydrophobization of some polymer segments, as in the case of hydroxypropylmethyl cellulose (HPMC) (Silva et al., 2008).

HPMC, in particular, can be seen as a hydrophobically modified cellulose derivative and it is frequently used in the food industry (Rosell, Rojas, & Benedito de Barber, 2001; Sanz, Salvador, & Fiszman, 2004), printing technology (Chen-Chao et al., 2006) and in many pharmaceutical applications (Siepmann & Peppas, 2001) because it is biocompatible, non-toxic and exhibits good mechanical properties. The usefulness of HPMC is essentially based upon different key attributes: efficient thickening, film forming ability, and surface activity (Pérez, Sánchez, Pilosof, & Rodríguez Patino, 2009). Furthermore, HPMC undergoes a reversible sol–gel transition which is today object of study of some research groups, using different approaches and techniques (Bodvik et al., 2010; Veríssimo, Pais, & Gomes, 2010). This transition is due to the increased hydrophobicity of the respective chains upon heating, which was discussed in a recent publication from our group (Silva et al., 2008). In that study, a fluorescent hydrophobic probe was added to a HPMC solution and monitored at different temperatures. Results clearly suggested that a polarity change occurs in some polymer segments, mostly composed of ethylene oxide groups. This is similar and compatible to what is observed for non-ionic surfactants containing such groups: while they are miscible in water at low temperatures, clouding and phase separation occur at higher temperatures. A thorough discussion on this topic has been recently published (Lindman & Karlström, 2009).

In the process of self-association of polymers, the presence of surfactants has a noteworthy effect (Nyström & Lindman, 1995). Surfactants are known to lower the interfacial tension between an aqueous solution and some other phase. In the case of ionic surfactants such as sodium dodecyl sulfate (SDS), the respective behavior is affected by the presence of a polymer in solution. The presence of surfactants may change the behavior of a polymer in solution. This can be exemplified by surfactant-induced thickening (Antunes, Marques, Miguel, & Lindman, 2009; Barreiro-Iglesias, Alvarez-Lorenzo, & Concheiro, 2003b; Cabane & Duplessix, 1982; François, Dayantis, & Sabbadin, 1985; Goddard & Ananthapadmanabhan, 1993; Holmberg, Jönsson, Kronberg, & Lindman, 2003; Lange, 1971; Lee, 1999), surfactant-induced swelling (Barreiro-Iglesias et al., 2003b) or compaction (Dias et al., 2004), surfactant-induced phase separation (Goddard & Ananthapadmanabhan, 1993; Holmberg et al., 2003), among other effects.

In an aqueous system containing both polymer and surfactant, there are clearly two important characteristic breakpoints in the interaction between these two entities. The first is known as the critical association concentration (*cac*) and represents the minimum surfactant concentration needed to start the polymer modulated surfactant association. The second breaking point is referred as the polymer saturation point (*psp*) and corresponds to the surfactant concentration at which the polymer chains become saturated of surfactant molecules. Subsequently, free micelles begin to form as further surfactant is added to the system. Various studies on this topic have been reported (Hammarström & Sundelöf, 1993; Sovilj & Petrovic, 2006).

In the present manuscript we will focus on the effect of the anionic surfactant, SDS, on the properties of aqueous solutions of HPMC. We present sets of electrical conductivity, rheological and optical transmittance data, which help to understand how polymer–surfactant interaction occurs at room temperature and upon heating, with emphasis on the thermal gelation. In addition, the effect of HPMC on the SDS association and micellization will also be addressed. The SDS–HPMC association is discussed not only based on the outcome of a thermodynamic analysis, but also supported by viscosity measurements and gel formation observables taken from rheological and optical transmittance tests. Models which allow the interpretation of SDS–HPMC interaction, at different concentrations of both components, are proposed from the experimental data.

2. Experimental

2.1. Materials and sample preparation

Hydroxypropylmethyl cellulose (METHOCEL K15M Premium), 19–24% methoxyl and 7–12% hydroxypropyl, $M_w = 4.3 \times 10^5$ Da was a kind gift from Dow Chemical. SDS was purchased from Fluka. Both reagents were used as received without further purification. Aqueous solutions of HPMC of different concentrations (0.1%, 0.25%, 0.50%, 0.75% and 1.0%, w/w) were prepared by adding dry polymer powder to Millipore water. The polymer solutions were kept stirring for 48 h before use.

2.2. Electrical conductivity studies

The electrical resistances of the solutions were measured using a Wayne–Kerr model 4265 Automatic LCR meter operating at 1 kHz. A dip-type conductance cell with a cell constant of $0.1002\,\mathrm{cm}^{-1}$, with an uncertainty of 0.02%, was used (Ribeiro, Valente, et al., 2004). Cell constants were determined from measurements with KCl (reagent grade, recrystallized, and dried) using the procedure and data reported elsewhere (Barthel, Feuerlein, Neuder, & Wachter, 1980). Solutions were studied within 24 h of preparation. Measurements were taken at different temperatures, 25.0, 37.0 and 50.0 (±0.1 °C) using a Grant thermostat bath. In a typical experiment, 40 mL of HPMC aqueous solution was placed in the conductivity cell and subsequently, aliquots of the SDS solution were added in a stepwise manner using a Methrom 765 dosimate micropipette. The conductance of the solution was measured and recorded after each addition once after the electrical resistance reached a stable value. House-made software was used both for programmed surfactant addition and acquisition of electrical resistance data after reaching equilibrium. The solution specific conductance value presented here, κ, was calculated from the experimental specific conductance and corrected for the experimental specific conductance of water or HPMC aqueous solution.

2.3. Rheological studies

All the rheological experiments were conducted using a controlled stress Reologica Stresstech rheometer equipped with automatic gap setting. All samples were allowed to equilibrate for

10 min before the measurements. A bob cup geometry (CC 15) with solvent trap was used to prevent sample evaporation. Temperature control was achieved using a water bath system coupled to the rheometer measurement system. The studies with temperature ramps were performed from 25 to 90 °C at a fixed heating rate of 1 °C/min. Dynamic viscosity was analyzed by rotational shear experiments at 25 °C. Flow curves were obtained by applying an increasing shear rate to the samples. Prior to this, a viscometry test was carried out for all samples in order to determine both Newtonian and non-Newtonian regimes and some useful parameters such as zero-shear viscosity (η_0) and infinite shear viscosity (η_∞).

In rheology, it is quite common to use equations that describe the shape of the general flow curves. These equations need at least four parameters. One of these examples and probably the most popular is the Cross equation (Eq. (1)), used to extract some significant parameters from the viscosity vs. shear rate profile (Cunningham, 2010)

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (C\dot{\gamma})^m} \quad (1)$$

which is equivalent to

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (C\dot{\gamma})^m} \quad (2)$$

In the Cross equation, η is the viscosity at any shear rate, $\dot{\gamma}$, η_0 and η_∞ refer respectively to the asymptotic values of viscosity at very low shear rates (zero-shear viscosity) and at very high shear rates (infinite-shear viscosity) respectively, C is known as the Cross rate constant parameter, with the dimension of time, and m is a dimensionless constant, indicating the degree of dependence of viscosity on the shear rate in the shear-thinning region. A value of zero for m indicates Newtonian behavior, while values of m close to 1 point to a shear-thinning behavior. The reciprocal of the time constant, $1/C$, corresponds to a critical shear rate ($\dot{\gamma}^*$) signaling the end of the Newtonian plateau and the onset of shear-thinning region. The rheological curves obtained, in terms of viscosity vs. shear rate, corresponding to the different formulations tested, were mathematically fitted using the Eq. (2).

Oscillation tests (25–90 °C) were conducted in order to determine both the storage modulus, (G') and the loss modulus (G''). Oscillatory measurements are particularly useful to study the structure of some sensitive materials because the deformation magnitude in these tests is very small. A test of linearity, the oscillation stress sweep, was performed prior to all oscillatory tests to make sure that all measurements are within the linear viscoelastic region, otherwise the results would depend not only on the frequency selected but also on the applied stress of deformation. In turn, the applied frequency (1 Hz) was chosen ensuring that, at the initial conditions, G'' is dominant. The complex viscosity modulus η^*, a mathematical representation of the viscosity in oscillatory tests, was also determined.

2.4. Optical transmittance measurements

A double-beam UV–vis spectrophotometer (Shimadzu UV-2450) was used for the optical transmittance measurements. The samples were placed in a cell with a dimension of 1 cm × 1 cm × 5 cm. Millipore water was used as reference. For temperature measurements, the cells were placed in a cell-holder connected to a water bath system with temperature control (Haake Phoenix II – Thermo Scientific). In addition to this regulator, an external temperature sensor (Pt 100) was placed in the sample cell. The absorption spectra (200–850 nm) confirmed that there were no UV-absorbing moieties in the solutions. The transmittance of the samples was measured at a wavelength of 800 nm as previously reported for a similar system (Xu, Song, Ping, Wang, & Liu, 2006).

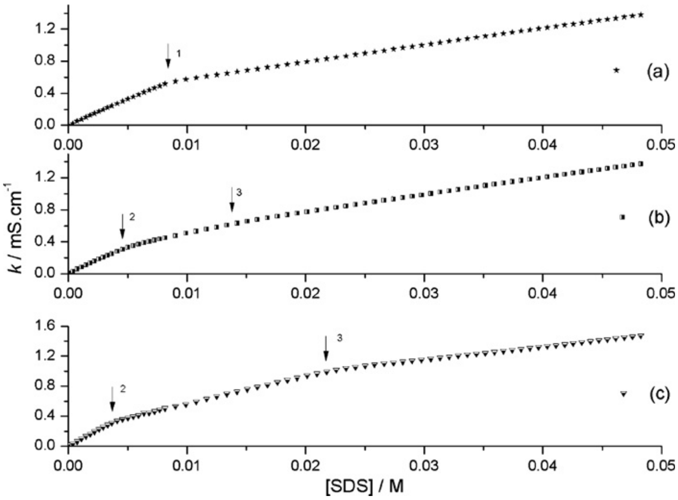

Fig. 1. Dependence of the specific conductance of aqueous solutions of SDS, at 25.0 °C, in the presence of HPMC with a concentration of (a) 0.0% (w/v), (b) 0.25% (w/v), and (c) 0.75% (w/v). Arrows indicate the *cmc* (1), *cac* (2) and *psp* (3).

3. Results and discussion

In what follows, we address firstly the results obtained by the different techniques, starting with the conductivity measurements. All the results will be subsequently integrated, discussed and rationalized.

3.1. Electrical conductivity studies to assess characteristic points and thermodynamics

3.1.1. Effect of HPMC on the electrical conductance of SDS

Electrical conductivity has been used to provide valuable information on the association between ionic surfactants and uncharged water-soluble cellulose derivatives, and several examples can be found in the literature (Kamenka, Burgaud, Zana, & Lindman, 1994; Zana, Binana-Limbele, Kamenka, & Lindman, 1992). Fig. 1 shows the effect of the presence of HPMC on the electrical conductance of aqueous SDS solutions. In the absence of HPMC (Fig. 1(a)), the SDS electrical conductance shows two different linear regimes as a function of surfactant concentration, corresponding to the behavior below and above the critical micelle concentration *cmc*). From these data, and by using the intersection of the data regression lines method (Ribeiro, Lobo, et al., 2004), the *cmc* and the degree of counterion dissociation (α), have been calculated yielding 8.34 (±0.09) mM and 0.331 (±0.002), respectively, in close agreement with the values reported in literature (Goddard & Benson, 1957; Valente et al., 2008).

In the presence of HPMC, a further transition point is observed on the conductivity of SDS/HPMC mixtures as a function of SDS concentration (Figs. 1(b) and (c)). The first point (2) in the presence of polymer corresponds to the critical association concentration (*cac*). The second transition point (3) corresponds to the onset of bulk micelle formation. This exceeds the polymer saturation point (*psp*), which represents the surfactant concentration needed to saturate the polymer. Up to the *psp*, it is likely to consider that SDS concentration in bulk is constant and equal to the *cac* value. After saturation of the polymer, bulk SDS concentration starts to increase and reaches the *cmc* value found in the absence of polymer, thus leading to the formation of micelles in the bulk. The *psp* and the onset of bulk micellization are, thus, in close proximity. In what follows, and for simplicity, transition point (3) will be denoted as *psp,* when extracted from conductivity measurements, but it constitutes in fact an upper limit (see below). It is

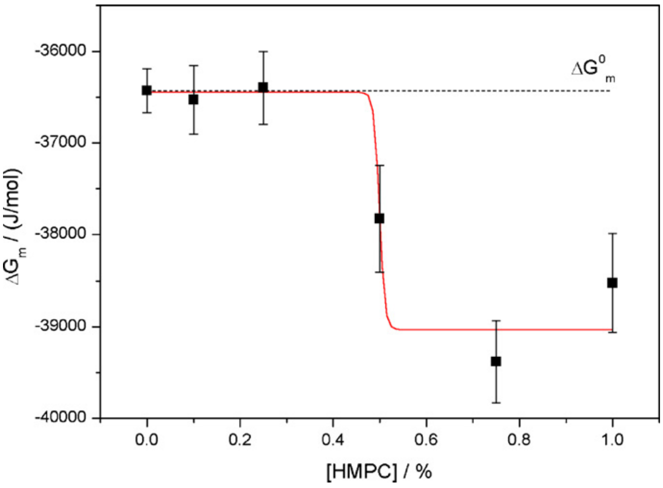

Fig. 2. Effect of HPMC concentration on the free energy of micellization of SDS, at 298.15 K, assuming that the polymer has only a spectator role on the equilibrium between SDS unimers and SDS micelles. The dashed horizontal line represents the free energy of micellization of SDS.

Table 1
Effect of HPMC concentration on the association and micellization of SDS as seen by electrical conductivity, at 25.0 °C.

[HPMC]/% (w/v)	*cac*/mM	ΔG°_a/kJ mol^{-1}	*psp*/mM	
0.0	8.34 (±0.09)[a]	−36.4 (±0.2)[b]		
0.1	5.4 (±0.3)	−33.1 (±0.8)	12.4 (±0.8)	11.6[c]
0.25	5.3 (±0.2)	−34.8 (±0.6)	15.6 (±0.8)	
0.5	5.2 (±0.3)	−35.05 (±0.03)	16.9 (±1)	22.6[c]
0.75	4.2 (±0.2)	−37.4 (±0.5)	22.7 (±0.3)	
1.0	2.6 (±0.4)	−37 (±1)	26.4 (±2)	

[a] Critical micelle concentration.

[b] In the absence of HPMC the free energy of association corresponds to the free energy change for SDS micellization.

[c] From Sovilj and Petrovic (2006).

worth noting that the slopes of $\kappa = f([\mathrm{SDS}])$ in the absence (above point (1)), and presence (above point (3)) of HPMC are very similar, which clearly confirms that for SDS concentrations above the *psp*, micellization takes place. For example, from data shown in Fig. 2, those slope values are $2.127(\pm 0.008) \times 10^{-2}$, $2.149(\pm 0.005) \times 10^{-2}$, $2.17(\pm 0.04) \times 10^{-2}$ mS cm^{-1} M^{-1}, for 0, 0.25 and 0.75% (w/v) HPMC concentration, respectively.

It is also worth noting that the *psp* increases linearly with HPMC concentration, following a straight line equation: $(psp/(\%\mathrm{w/v})) = 10.9\ (\pm 0.9) + 15\ (\pm 1) \times ([\mathrm{SDS}]/\mathrm{mM})$. The variation of *psp* with HPMC concentration is close to half of that has been reported elsewhere (Sovilj & Petrovic, 2006), which can probably be ascribed to different degrees of substitution in the modified cellulose polymers used.

We will now focus our discussion on the effect of HPMC on the association of SDS. The interaction between polymer and surfactant leads to an increase of the effective size of the ionic species and, consequently, the effect of the addition of SDS on the overall ionic mobility is smaller. The effect of HPMC concentration, at 25 °C, in the *cac* of mixed SDS/HPMC solutions is shown in Table 1. As usual in these systems, the value of the *cac* is lower than the critical micelle concentration, indicating that the polymer–surfactant complex formation induces a more favorable SDS association. It is seen that the *cac* value remains approximately constant up to ca. 0.5% HPMC, in accordance with previous observations (Sovilj & Petrovic, 2006). However, for HPMC concentrations higher than 0.5%, the association between HPMC and SDS becomes significantly more favorable. This probably indicates that, above this concentration, the hydrophobic domains start to grow as the degree of overlap between different HPMC molecules increases and the respective hydrophobic patches associate.

Table 2
Effect of the temperature on the polymer (0.5%) induced association properties of sodium dodecyl sulfate.

T/°C	ln$X$	$1-\alpha$	ΔG°_a/kJ mol^{-1}	ΔH°_a/kJ mol^{-1}	ΔS°_a/kJ mol^{-1}
25	−9.26	0.547	−35.05 (±0.03)	−23.15 (±0.02)	39.9
37	−9.08	0.552	−35.44 (±0.04)	−26.22 (±0.03)	29.7
50	−8.93	0.559	−37.04 (0±.04)	−28.73 (±0.03)	25.7

The free energy of association can be calculated from (Chatterjee, Moulik, Sanyal, Mishra, & Puri, 2001; Evans & Wennerstrom, 1999):

$$\Delta G^\circ_a = (2-\alpha)RT\ \ln X \tag{3}$$

where R is the gas constant, T the absolute temperature, X is the critical association concentration, or the *cmc* in the absence of polymer, in mole fraction units ($cac/[\mathrm{H_2O}]$). α is the degree of counterion dissociation, calculated as the slope ratio m_{2-3}/m_{0-2} (Zanette, Ruzza, Froehner, & Minatti, 1996), where the subscripts indicate the points that delimit the segment with each slope, with '0' for the axis origin (see Fig. 1). The degree of dissociation of SDS counterions in the presence of the polymer (ca. 0.55) is higher than that occurring for SDS micellization (ca. 0.33) and independent of the HPMC concentration. This can be justified by the occurrence of small (and less dense) aggregates (Prasad, Palepu, & Moulik, 2006; Zana, 1995). The calculated values of the free-energy indicate a SDS association process slightly less favorable for low polymer concentrations than SDS micellization. However, association and micellization values are very close, and conductivity focus on SDS association, probably only partially including the SDS-polymer interaction. The free-energy of association becomes more favorable at polymer concentrations higher than 0.5%.

To better understand the mechanism responsible for the association of SDS in the presence of HPMC, the effect of temperature on the thermodynamic association parameters of SDS was also studied. The dependence of the *cac* and α on the temperature (shown in Table 2), will allow us to compute the enthalpy of association (ΔH°_a), calculated by (Chatterjee et al., 2001)

$$\Delta H^\circ_a = -RT^2\left[(2-\alpha)\frac{d\ \ln X}{dT} + \ln X\frac{d(1-\alpha)}{dT}\right] \tag{4}$$

Assuming a linear dependence of ($\ln X$) and ($1-\alpha$) on T, with slopes m and m', respectively, Eq. (4) can be re-written as

$$\Delta H^\circ_a = -RT^2[(2-\alpha)m + m'\ln X] \tag{5}$$

Finally, the entropy of association (ΔS°_a) was evaluated from

$$\Delta S^\circ_a = \frac{\Delta H^\circ_a - \Delta G^\circ_a}{T} \tag{6}$$

Table 2 shows the different thermodynamic association parameters for SDS in the presence of HPMC. We can conclude that the association of SDS in the presence of HPMC is enthalpy-dominated ($|\Delta H^\circ_a| > |T\Delta S^\circ_a|$), but the entropy component is also significant. This is easily justified by a predominantly hydrophobic interaction. However, this process can only be seen if a concomitant dehydration of the surfactant chain and polymer takes place. It is known that the micellization of SDS is only enthalpy driven in the presence of ionic solutes (Pereira, Valente, & Burrows, 2010) and, consequently, the present results are in close agreement with both the presence of small SDS aggregates with low counterion condensation and also the amphiphilic character of HPMC (Lindman, Karlström, & Stigsson, 2010). Such behavior is also in agreement with the hypothesis that SDS aggregates are smaller than the corresponding micelles (Medeiros & Costa, 1996; Nilsson, 1995).

A more comprehensive analysis of the data shown in Table 2 allows us to point out that association is slightly favored upon heating. Quantifying this effect as $d\Delta G_a^\circ/dT$, a molar value of $-80\,\mathrm{J\,K^{-1}}$ is obtained, which is very close to the value reported to the micellization of SDS in water ($-82\,\mathrm{J\,K^{-1}}$) (Chatterjee et al., 2001). A deeper analysis of the effect of temperature on the ΔG_a° shows that the hydrophobic effect due to the interaction between the hydrocarbon tail (and probably the hydrophobic part of polymer) and water plays an important role in the HPMC–SDS interaction as can be inferred from the enthalpy–entropy compensation, which can be quantified by (Chen, Lin, & Huang, 1998)

$$\Delta H_a^\circ = \Delta H^* + T_c \Delta S_a^\circ \qquad (7)$$

where the slope T_c is the compensation temperature, closely related with solute–solute and solute–solvent interactions and ΔH^* is the intercept of the compensation plots which gives the heat effect belonging to $\Delta S_a^\circ = 0$, and can be interpreted as a measure of solute-solute interactions. By fitting the experimental data, shown in Table 2, to Eq. (7), the following values for T_c and ΔH^* have been obtained: 368 (±58) K and −38 (±2) kJ mol^{-1}, respectively. Despite a rather low correlation coefficient ($R^2 = 0.951$), the T_c value is within the range (280–450 K) found for micellization processes (Phillips, 1985) and ΔH^*, although more exothermic than what is observed for the SDS micellization: −29 kJ mol^{-1} (Pereira et al., 2009), can be considered as indicative that hydrophobic interactions play a major role in the association process.

Following further addition of SDS on aggregate-containing solution a second mechanism of association occurs, as pointed out before. The thermodynamic parameters for the micellization of SDS in the bulk, in the presence of different concentrations of HPMC at 298.15 K, were estimated assuming that the micellization of SDS can be treated also in the framework of the mass-law action model. The free energy of association is now calculated from an expression corresponding to Eq. (3), but in which the estimate of the variation in ion condensation is given by the slopes after the *psp* and before the *cac*, the bulk concentration value of SDS is considered the *cmc* (Holmberg et al., 2003).

$$\Delta G_m = (2-\alpha)RT\,\ln\left(\frac{cmc}{[\mathrm{H_2O}]}\right) \qquad (8)$$

The use of Eq. (8) in the terms described is based on the approximation that the equilibrium between bulk unimers and micelles is not affected by the presence of the surfactant saturated chains.

Fig. 2 summarizes the results obtained for the free energy of micellization in the bulk. This is independent of polymer concentration, up to a critical value. After this point (ca. 0.5%) micellization becomes more favorable. A possible interpretation of this data is that for saturated, scattered HPMC–SDS aggregates, the behavior is well described by the unimer–micelles equilibrium, being this equilibrium very similar to that observed in the absence of HPMC. However, for higher values of the HPMC concentration, partially formed micelles of a few unimers may be released from the HPMC–SDS aggregates, thus facilitating micelle formation. The analysis of Fig. 2 also highlights the importance of the degree of dissociation of counterions on the SDS micellization process, for HPMC concentration higher than 0.5% (w/v). The use of Eq. (8) in the conditions above would thus not be, strictum sensum, justifiable (see Fig. 3 for a pictorial description of these remarks).

3.2. Viscoelastic properties of HPMC–SDS solutions

When discussing the association between a polymer such as HPMC and an ionic surfactant such as SDS that affects the polymer behavior in solution, it is relevant to study and discuss their rheological behavior. The insight obtained from rheological data is crucial to build up the picture of polymer–surfactant association at different conditions and compositions.

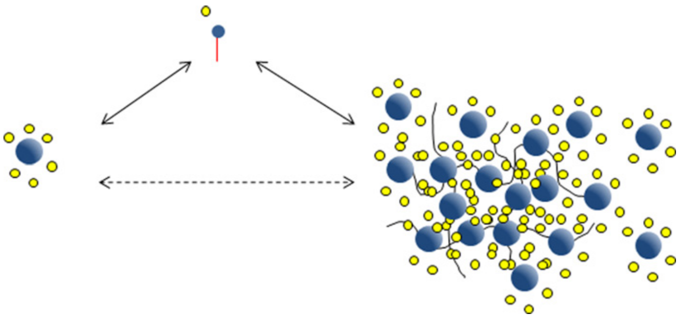

Fig. 3. Equilibrium scheme involving SDS unimers, SDS–HPMC aggregates and bulk SDS micelles. Solid black lines represent HPMC chains, blue and yellow spheres correspond to SDS micelles and counterions respectively. Surfactant unimer is represented as the small blue sphere connected to a red hydrophobic tail. While unimer-aggregate and unimer-bulk micelles can be regarded as independent equilibria, a large concentration of aggregates promotes a direct equilibrium of these aggregates with bulk micelles (indicated by the dashed double-arrow), without systematic disaggregation into unimers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 3
List of formulations tested in the rheological and optical transmittance studies and corresponding composition.

	HPMC K15M/% (w/w)	SDS/g/100 mL)	SDS/mM
S0.0	1.0	0.00	0.0
S1.7	1.0	0.05	1.7
S3.5	1.0	0.10	3.5
S5.2	1.0	0.15	5.2
S7.0	1.0	0.20	7.0
S8.7	1.0	0.25	8.7
S17	1.0	0.50	17
S26	1.0	0.75	26
S35	1.0	1.00	35
S43	1.0	1.25	43
S52	1.0	1.50	52

Table 3 shows the composition of the prepared polymer–surfactant solutions for a constant HPMC load of 1.0% (w/w).

3.2.1. Monitoring the association between polymer and surfactant

Dynamic viscosity was determined by rotational shear experiments, at 25 °C. Fig. 4 shows the dependence of zero-shear viscosity (η_0), mathematically obtained by fitting the viscosity vs. shear rate curves with the Cross model equation, on SDS concentration. Three different regions are visible, separated by two characteristic breakpoints, a local minimum and a local maximum, denoted as (1) and (2) in Fig. 4.

The rheological behavior of the mixed system is clearly sensitive to the association between HPMC and SDS. The profile obtained is in agreement with previous findings reported in the literature for cellulose ethers and SDS mixed systems (Hoff, Nyström, & Lindman, 2001; Holmberg, Nilsson, Singh, & Sundeloef, 1992).

Below the first point, the surfactant is already interacting to the polymer, as seen in Fig. 4 by a relatively small decrease in the zero-shear viscosity (ca. 40%) up to a minimum close to the *cac*. Different explanations may be invoked to justify this observation. The most accepted one is that there is a chain contraction due to the intense intramolecular hydrophobic association junctions (Hoff et al., 2001; Samii, Karlstroem, & Lindman, 1991; Torres, Müller, Szidarovszky, & Sáez, 2008). The binding of surfactant molecules to semiflexible polymers such as EHEC or HPMC may modify the respective stiffness and this may, in turn, induce a coil-to-globule

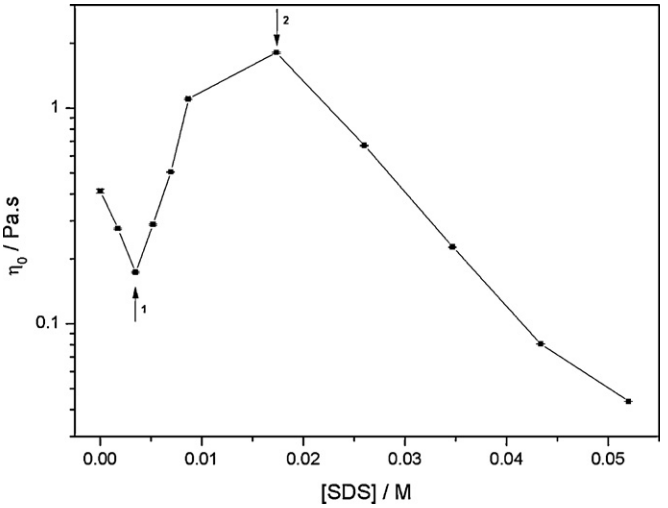

Fig. 4. Zero-shear viscosity as function of SDS concentration. Three different zones are visible. Before the first arrow is the pre-*cac* region. In the region between the two arrows, surfactant molecules start to form aggregates around hydrophobic moieties of the polymer, causing polymer swelling and leading to an increase in the viscosity. The second arrow indicates the maximum, which happens before the *psp*. After this concentration, surfactant molecules have saturated the polymer chains and start to form free micelles in solution, leading to screening of electrostatic repulsion and to an observable decrease in the viscosity. Solid lines are presented to guide the eye.

Table 4
Gelation temperature for HPMC–SDS solutions. Gel formation requires higher temperature as SDS concentration increase, not being detected (n.d.) in our oscillation tests (1 Hz) for concentrations of SDS above 5.2 mM. After a critical SDS concentration, gelation is totally inhibited, as can be seen in the oscillation tests.

Formulation	Gelation temperature/°C
S0.0	74
S1.7	81
S3.5	83
S5.2	87
≥S7.0	n.d.

transition. This phenomenon is ascribed to a balance between two forces: attractive hydrophobic association between the polymer and hydrocarbon tails of the surfactant, which bind to the polymer and make it less polar; and electrostatic repulsive forces between the polymer chains as the surfactant is added, therefore increasing the polarity of the polymer. Below the *cac*, electrostatic repulsion plays a minor role and a contraction of the polymer chains induced by the hydrophobic association inside the polymer is observed. For surfactant concentrations above the *cac* and below point (2), a significant increase in the viscosity upon surfactant addition is observed. At this stage micelle formation of SDS takes place along the HPMC chains and progressively converts the non-ionic polymer into a polyelectrolyte. Repulsion among the negative charges of the polymer–surfactant complex causes the polymer to swell leading to a consequent increase in the shear viscosity. Polymer chains reach their maximum extension at point (2), resulting in a six-fold enhancement in the viscosity from the minimum value read at *cac*. At this latter point, the polymer chains are virtually covered by surfactant micelles and further addition of the amphiphile causes an increase of free micelles in the bulk.

Above point (2), i.e., above the SDS concentration that promotes the maximal rigidity in the transient network, and with progressive addition of surfactant to the system, the viscosity starts to decrease and ultimately reaches values even lower than those obtained for the surfactant-free HPMC solution (S0.0). Within this region above the transition point (2), all the surfactant added will be placed in the bulk, firstly as unimers and, afterwards as free micelles (above the *cmc* value for bulk SDS concentration). Concomitantly, the presence of SDS in the medium increases the ionic strength and causes HPMC chains to shrink due to the screening of the electrostatic repulsion. At sufficiently high surfactant concentrations, the hydrophobic associations along HPMC chains are inhibited, the polymer contracts, and the viscosity reaches a global minimum, close to zero. In our view, the polymer saturation point, *psp*, is situated, in terms of SDS concentration, after transition point (2), but before the point where the viscosity in the presence of SDS equals that found in the absence of surfactant. The explanation is that (i) the destruction of the transient network provides additional room for surfactant associated upon the polymer, and (ii) HPMC chains associated with SDS are typically more extended than those in its absence, thus promoting a higher viscosity.

3.2.2. Modulating the thermal gelation of HPMC

Thermal gelation in cellulose based polymers requires a certain degree of insolubility of some polymer segments at sufficiently high temperatures. On the other hand, solubility can be enhanced by using a charged polymer instead, since the entropy of counterions favors the solubility. It would be interesting to check the dependence of the thermal gelation on the charge density of HPMC–SDS

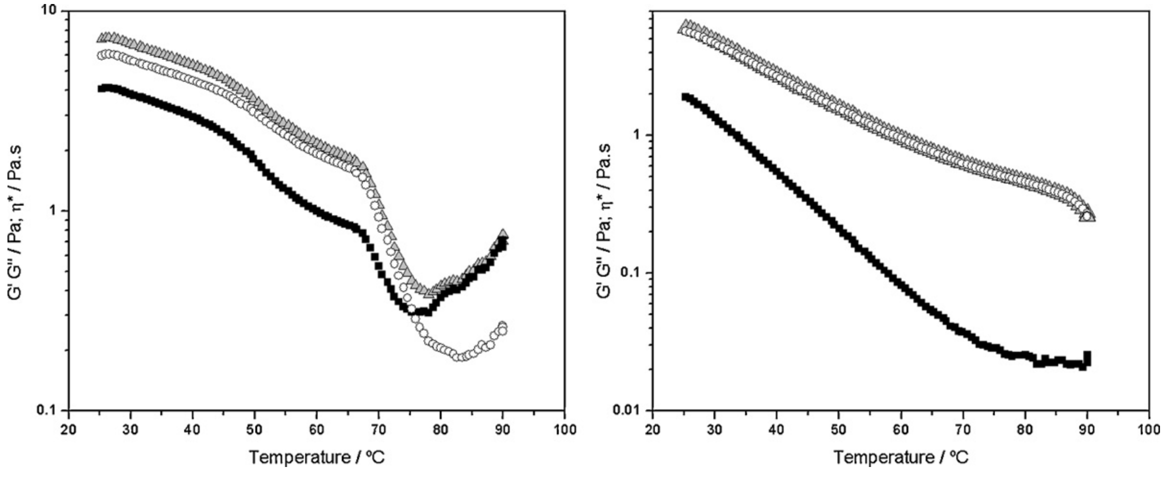

Fig. 5. Storage (*G*′, squares), loss (*G*″, circles) and the complex viscosity (η^*, triangles) modulus, as a function of temperature, for formulation S1.7 (on the left) and S17 (on the right). Frequency is chosen so as to impose a value of *G*″ higher than *G*′ at the initial conditions. Oscillation plots illustrate that gel formation occurs only for low concentration of SDS. For higher concentrations, the storage moduli *G*′ does not intersect the loss moduli *G*″ in the temperature range studied (25–90°C) indicating that gel formation is not detected. As the surfactant progressively ionizes the polymer inter-chain hydrophobic associations and thermal gelation become weaker or negligible.

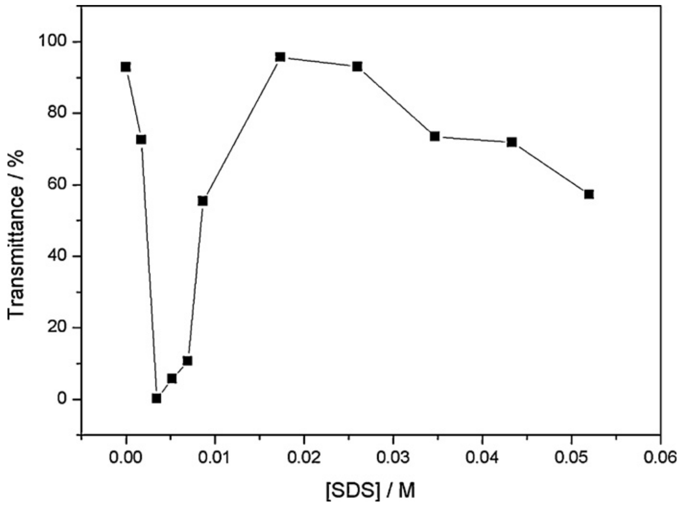

Fig. 6. Dependence of the optical transmittance (800 nm) at 25 °C of HPMC–SDS solutions on SDS concentration. Solid lines are a guide for the eyes.

complex by using different concentrations of SDS and therefore be able to adjust it.

For each solution (S0.0–S52) we have conducted a number of viscosity measurements to investigate the influence of the presence of surfactant on the thermal gelation of HPMC. Oscillation tests were carried out to determine both the storage modulus G', the loss modulus G'' and the complex viscosity (γ^*).

Following the same strategy used in a previous paper (Silva et al., 2008), we detected gel formation when the storage modulus G' intercepts the loss modulus G'' in an ascending trend.

Experimental data presented in Table 4 shows that the addition of very low amounts of surfactant to the system shifts thermal gelation to higher temperatures. Another interesting fact is that thermal gelation is only observed for surfactant concentrations lower than 7 mM. For higher SDS concentration thermal gelation is inhibited, as seen in the oscillation plots (Fig. 5).

The association of charged amphiphiles to HPMC brings a higher hydrophilic character to the polymer as result of a combined effect of the deactivation of polymer's hydrophobic regions and enhanced solubility due to the presence of charges along the chains. The hydrophobic association among polymer segments, which is the mechanism of thermal gelation of this type of polymers, is then inhibited. As the SDS concentration increases, thermal gelation is therefore shifted to higher temperatures and eventually inhibited, which is in agreement with previous studies analyzing the effect of ionic surfactants on the thermal gelation of other cellulose ethers (Kjøniksen, Nyström, & Lindman, 1998a; Kjøniksen, Nyström, & Lindman, 1998b; Nyström, Kjøniksen, & Lindman, 1996; Nyström & Lindman, 1995).

3.3. *Characteristic points revisited with light transmittance studies*

Optical transmittance studies were performed to gain additional insight on the mechanism of association between HPMC and SDS

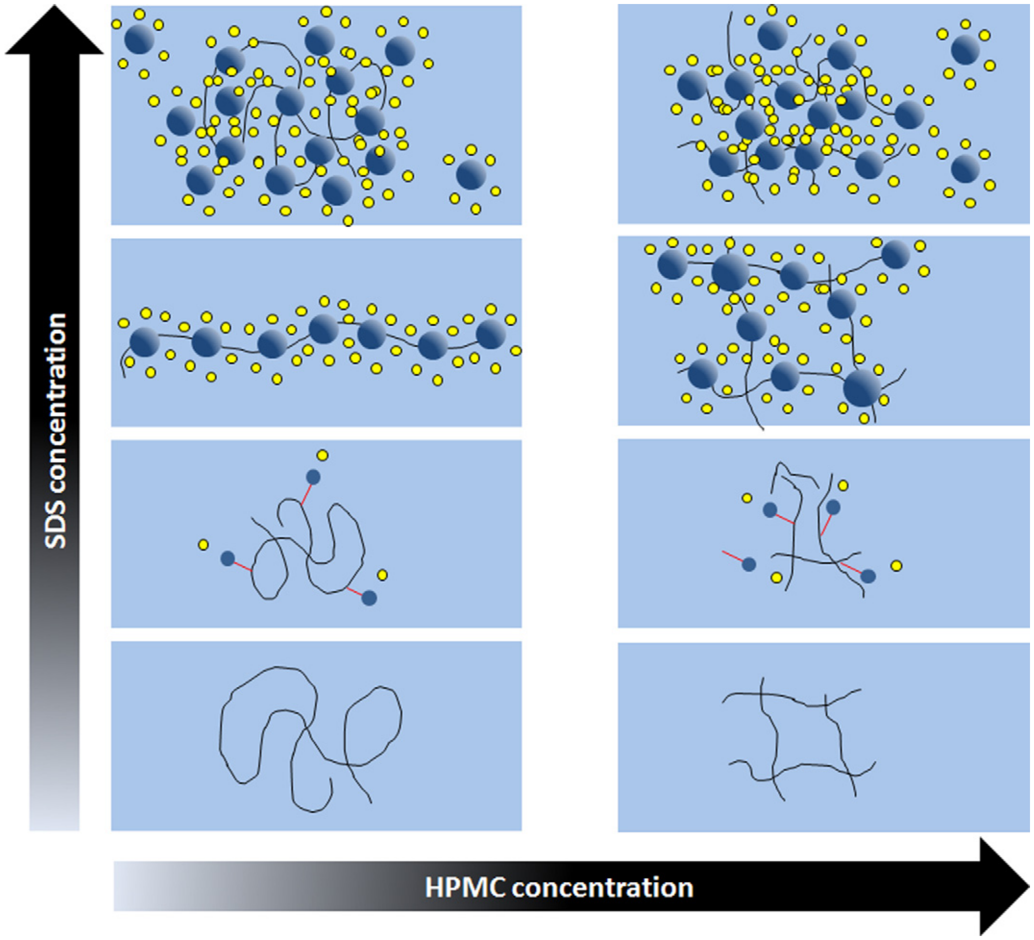

Fig. 7. Pictorial representation of the evolution of the SDS/HPMC/water system as a function of SDS and HPMC concentrations. Solid black lines represent HPMC chains, blue and yellow spheres correspond to SDS micelles and counterions respectively. The larger blue spheres indicate major hydrophobic association zones. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 5
Summary of *cac* and *psp* related values (mM) determined from conductivity, rheology and optical transmittance measurements are shown in the table above These were obtained by straight line interception at slope change (conductivity) and second degree polynomial fitting in the region of the minima (maxima) for rheological and optical transmittance measurements. The preceding inequality signs follow the considerations presented along the text.

	Conductivity	Rheology	Optical transmittance
cac (mM)	2.6	<3.4	<4.2
psp (mM)	<26	>16	21

at room temperature. Changes in the optical properties of the system can be used to monitor how it evolves as more surfactant is present. To achieve that, optical transmittance tests were carried out for the solutions S0.0–S52 (composition shown in Table 3). For sake of simplicity we considered the 1% HPMC hydrogel (S0.0) as reference i.e. 100% of transmittance at 800 nm. Fig. 6 shows that in the formulations containing low amounts of SDS (in the pre-*cac* region) it is observed a progressive decrease in the transmittance until the minimum transmittance point ($[\mathrm{SDS}] = 4.2 \times 10^{-3}$ M). This is in agreement with the mechanism we proposed above, explaining the decrease in the viscosity below the *cac* as a result of a salting-out-like effect. HPMC chains start to shrink leading to a lower entanglement level and consequently causing a decrease in the transmittance (Fig. 6) and in the viscosity (Fig. 4). The minimum in the optical transmittance is slightly above the values of *cac* determined by means of conductivity (as is that of the rheological studies). These observations indicated that the shrinkage of polymer chains slightly extends above the *cac*. The analysis of Fig. 6 clearly indicates that after the minimum, the transmittance increases sharply until a local maximum, indicating that the polymer swells for concentrations of SDS above the *cac*. This is caused by the adsorption of negatively charged micelles onto the polymer chain. The polymer is therefore converted into a polyelectrolyte and, due to charge repulsion, HPMC chains extend and swelling occurs. The swelling of the polymer allows a higher light transmittance because of the low optical contrast of the system, and thus the transparency increases at this stage up to a maximum, close to the *psp* ($[\mathrm{SDS}] = 2.1 \times 10^{-2}$ M). For surfactant levels above this point, i.e. above the concentration at which all the polymer chains are covered by surfactant micelles, additional surfactant unimers will be located at the bulk, forming micelles. Charged micelles and counterions now act as salt and screen electrostatic repulsion among negative charges of the HPMC–SDS complex. Such screening leads to polymer compaction, which is responsible for the reduction in the optical transmittance of the system observed.

3.4. *Rationale*

Table 5 compiles the significant breakpoints found in the interaction between HPMC and SDS, and relates them with the phenomenological *cac* and *psp* values.

Fig. 7 is a graphical representation of the information gathered by the various techniques employed in this work. On the left panel, corresponding to a dilute regime, there is an initial decrease in the chain extension when SDS is first added (pre-*cac* region). After SDS association, the chains expand again due to electrostatic effects. Finally, at even higher surfactant concentration (above the *psp*), bulk micelles promote the compression of the SDS saturated HPMC backbone. On the right, we see a corresponding evolution for higher polymer concentration, now for a semi-dilute regime. The random entanglement in the absence of SDS is slightly perturbed by the compaction of the chains. Upon SDS association, the chains expand again and connecting nodes resulting from hydrophobic intra- and inter-chain association are formed. These, with excess SDS, are finally solubilized.

4. Conclusions

In the present work we have shown that the addition of SDS to HPMC solutions affects both the behavior in terms of SDS self-assembly and that of the HPMC solution, but in a non-trivial way. For diluted HPMC solutions, the *cmc* is reduced by ca. 60% of the *cac* value, which remains constant up to 0.5% HPMC solutions. The calculated free-energy of SDS association (which only partially includes the polymer–SDS interactions) also remains approximately constant, and indicates that the process is slightly less spontaneous than in the absence of HPMC. Again, for concentrations of HPMC above 0.5%, there is an increase in the absolute value of the free-energy surpassing the one found in the absence of HPMC. The polymer saturation point, in contrast, increases monotonically with HPMC concentration, as could be expected. After the saturation point, the micellization process is very similar to that found in the absence of HPMC if the polymer solution is diluted, but becomes more favorable for higher concentrations.

For a constant (0.5%) concentration of HPMC, the SDS association process becomes more and more favorable as the temperature increases, in the range 25–50 °C.

Rheological measurements at room temperature also indicate three regimes as a function of SDS concentration. The first is characterized by a decrease in viscosity, up to the *cac* value, followed by a drastic increase until the proximity of the *psp* where it starts to decrease again (these trends are in close agreement with those obtained with optical transmittance measurements). SDS also promotes an increase in the gelation temperature and, for high concentrations, may completely inhibit gel formation.

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