



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.

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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 interest-

ing 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 & Koteswar, 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, Kjøniksen, 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 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

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