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Self-association of sodium deoxycholate with EHEC cellulose cooperatively induced by sodium dodecanoate

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ABSTRACT

Some aspects of ethyl (hydroxyethyl) cellulose (EHEC) aqueous behavior in the presence of ionic surfactants are described in the literature; however, most of the studies reported address moderately concentrated solutions. Few studies have been carried out in the dilute regime using mixtures of biosurfactants. The main purpose of this work is to investigate the interaction of EHEC in the dilute regime and to verify the mixture of two surfactants: sodium deoxycholate (NaDC) and sodium dodecanoate (SDoD). The parameters of the surfactant to polymer association processes such as the critical aggregation concentration (cac) and saturation of the polymer by surfactants (psp) were determined from the plots of surface tension and specific conductivity versus surfactant concentration in basic conditions. The cmc of NaDC–SDoD mixtures showed non-ideal behavior. However, EHEC added to mixtures of SDoD and NaDC acts as a stabilizer for the mixed aggregate during the association process.

1. Introduction

In recent decades, the interaction between ionic surfactants and neutral water-soluble polymers has been the subject of intense research to identify the physical properties in solutions and any possible mechanisms to help interpret the association of surfactants with polymers (Benrraou, Bales, & Zana, 2003; Bloor et al., 1995; Dal-Bó & Minatti, 2011; Dal-Bó, Schweitzer, Felippe, Zanette, & Björn, 2005; Dal-Bó, Laus, Felippe, Zanette, & Minatti, 2011; Goddard & Ananthapadmanabhan, 1993; Hoff, Nystrom, & Lindman, 2001; Modolon, Dal Bó, Felippe, Minatti, & Zanette, 2009; Zana, Binana-Limbele, Kamenka, & Lindman, 1992).

Anionic surfactants are associated strongly with polymers, and generally, the phenomenon starts at lower concentrations than in the absence of the polymer. The association is observed as being a phenomenon induced by the polymer (Dal-Bó & Minatti, 2011; Holmberg, Nilsson, & Sundelof, 1997; Nahringbauer, 1997; Nilsson, Holmberg, & Sundelof, 1995; Zanette & Frescura, 1999; Zanette et al., 1999). When in aqueous solutions, polymers and surfactants combine to form thermodynamically stable complexes with physical–chemical properties that are different from those observed in micellar solutions (Galant et al., 2005; Nilsson et al., 1995).

The study of the complex formation between polymers and surfactants is of particular interest in academic research because it is a mimetic model of associations and interactions that occur in vivo between proteins and cell membranes (Bu, Kjoniksen, & Nystrom, 2004; Dal-Bó et al., 2011). In addition to their use as models of biological systems, private industry has a wide selection of commercial products that involve mixed polymers and surfactants. Recently, a significant amount of research has focused on the molecular aspects of the interaction to understand the phase diagrams and rheological properties (Karlstrom & Lindman, 1992; Zanette & Frescura, 1999). The broader industrial applications are indisputable, extending into many important areas, such as foods, paints, cosmetics, textiles, microemulsions (as vehicles to dissolve components with different solubility) and even to the tertiary recovery of petroleum (Dal-Bó et al., 2011).

The effects that result from combining polymers and surfactants are synergistic; that is, the two associated components provide improved properties. For example, mixing reduces the critical micellar concentration (cmc) compared with the value for the pure surfactant (Bu et al., 2004; Holland & Rubingh, 1992). In general, a surfactant interacts cooperatively with a nonionic polymer, forming aggregates at a certain surfactant concentration, usually called

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the critical aggregation concentration (cac). This concentration is lower than the cmc of the pure surfactant. Several studies show that the value of the cmc is independent of the polymer concentration and that the polymer–surfactant mixed micelles form when the cac is reached. The polymer–surfactant interaction terminates after reaching a certain surfactant concentration that is known as the polymer saturation point (psp), and this concentration is directly proportional to the concentration of the polymer. After the psp, micelles are formed exclusively by the surfactant molecules (Hoff et al., 2001; Lund et al., 2001b; Minatti & Zanette, 1996).

Out of the large number of nonionic cellulose derivate polymers that have been investigated, the hydrophobically modified cellulose EHEC is the most relevant and studied polymer for rheological control in cosmetic formulations and in water-based paints. The interaction of EHEC with anionic surfactants has been extensively studied; it is governed by intricate forces between the chains and segments and aggregation between the chains and electrostatic forces (Dal-Bó & Minatti, 2011; Dal-Bó et al., 2005, 2011; Hansson & Lindman, 1996; Holmberg & Sundelof, 1996; Modolon et al., 2009).

In aqueous solution, the distribution of each micellar surfactant phase and the monomer phase varies depending on the structure of the surfactant and the composition of the solution. The simplest formation of mixed micellar aggregates occurs without interactions between micellar species surfactants (Dal-Bó & Minatti, 2011). This case occurs when two different surfactants are of the same class (i.e., mixtures of cationic with cationic or anionic with anionic), but different hydrophobic chains. In this case, the surfactants have properties that can be predicted from the properties of the individual components. These mixtures are called ideal system (Dal-Bó et al., 2011).

Dal-Bó and collaborators in other studies have shown that the process of self-association in the presence and absence of surfactants with different cellulose polymers is a highly spontaneous process and that the mixture has ideal behavior (Dal-Bó et al., 2005, 2011). Similar results were obtained by Zanette and collaborators for PEO complexes using sodium dodecyl sulfate (SDS) and sodium dodecanoate (SDoD) (Zanette & Frescura, 1999).

For mixtures that form non-ideal systems, the mathematical analysis becomes more complex. Examples of already widely studied non-ideal mixtures are composed of different classes of surfactants (hydrophilic and/or hydrophobic), such as anionic or cationic compounds with non-ionic surfactants.

For these non-ideal systems, the concepts used in the pseudophase model can also be applied, but in this case, the equations from the theory of regular solutions are used, which consider the interactions between monomers. Thus, the model requires empirical parameters to predict the behavior. The non-ideal mixtures generally show negative deviations from the ideal (Eising et al., 2008; Holland & Rubingh, 1992).

The main purposes of this paper are to investigate the interactions in the dilute regime, to check the ideality of a mixture of the surfactants sodium deoxycholate (NaDC) and SDoD and to monitor and interpret the variation in the properties of the solutions, such as the cac and psp (indicated by the presence of electrical conductivity) and the surface tension in the absence and presence of EHEC in basic conditions (0.020 mol L^{-1} borate/NaOH at pH 9.20 and 25.0 °C).

2. Experimental

2.1. Materials

Sodium deoxycholate (NaDC) with 99% purity was obtained from Sigma, Brazil and was used without previous purification. The sodium dodecanoate (SDoD) surfactant was prepared from the respective carboxylic acid with a purity of 99% (Sigma), which was dissolved in absolute ethanol, neutralized using a NaOH solution and used after recrystallization in acetone.

The EHEC comes from Bermocoll E 230FQ, lot No. 14770, donated by Akzo Nobel Surface Chemistry AB, Sweden. The sample shows a degree of substitution of 0.9–1.0 DSetil ethyl groups per anhydroglucose unit and a molar substitution of ethylene oxide groups from 1.9 to 2.2 MSEO per anhydroglucose unit. The EHEC molar mass, determined using light scattering, is of 330.000 g mol^{-1}. The polymer has a degree of polydispersity (M_w/M_n) lower than 2.

The experiments for determining the temperature of turbidity of the EHEC solutions in the absence and presence of the mixtures of the surfactants were carried out via visual observation in previously sealed Teflon-capped vials. The samples containing cellulose were preheated above the temperature of turbidity for 5 min and allowed to cool to room temperature followed by a waiting time to reach thermal equilibrium. We used a Schott ct52 water bath for temperature control.

The parameters of micellization of the surfactant mixtures were determined in the absence and presence of different concentrations of EHEC at conditions of 0.020 mol L^{-1} borate/NaOH at pH 9.2 and 25.0 °C.

Buffer stock solutions were prepared from deionized Milli-Q water and boric acid (Vetec). The pH of the solutions were adjusted to 9.20 using a standard NaOH solution.

The EHEC stock solutions were prepared by dissolving the polymer in a buffer solution using gentle stirring for 9–12 h. After the solutions were ready, they were centrifuged at 4500 rpm for 25–30 min and filtered using 0.45-μm (Sartorius) filters. These solutions were used to prepare the samples containing the NaDC and SDoD surfactants. This technique was employed because it keeps the EHEC concentration constant during the conductivity titrations, the surface tension experiments and the transmittance measurements; it keeps the solutions free of particles in suspension.

2.2. Methods

The surface tension measurements were carried out in borate buffer solutions (pH 9.20) at 25.0 °C. The former was measured using a Krüss GMBH interfacial tensiometer (model K8) equipped with a Pt–Ir–20 ring. The cmc, cac and psp values of the surfactants in the EHEC–surfactant solutions were obtained from the intersection of the two linear regions of the surface tension vs. the log surfactant concentration plot (Dal-Bó et al., 2011).

The electrical conductivity data were acquired using a water-jacketed flow dilution cell with an ATI Orion conductometry (model 170). Aliquots of a buffered surfactant stock solution containing the appropriate amount of EHEC were regularly added to the initial sample that had the same EHEC concentration to keep the concentration constant. The cac and psp in solutions containing EHEC and NaDC or SDoD were determined from the inflection points in the electrical conductivity vs. surfactant concentration plot.

3. Results and discussion

3.1. Turbidity measurements

It is common to observe phase separation in aqueous solutions of cellulose derivatives at higher temperatures, and this behavior was also observed recently in solutions of cellulose derivatives in polar organic solvents (Dal-Bó et al., 2005; Lund, Lauten, Nystrom, & Lindman, 2001). The temperature at which phase separation occurs

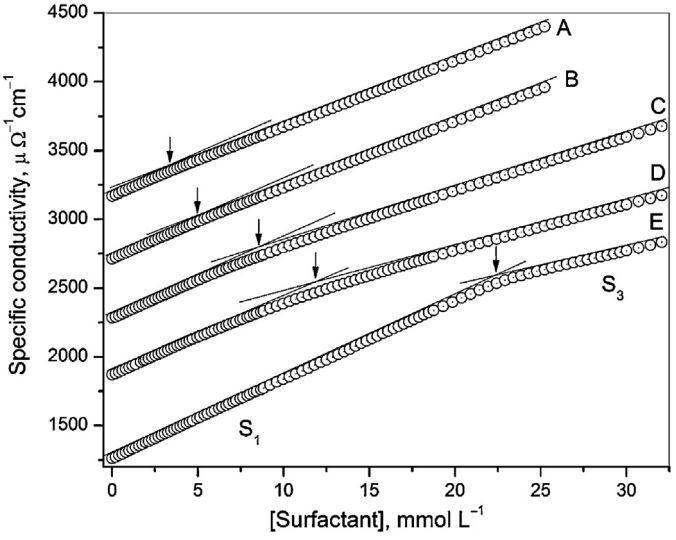

Fig. 1. Plots on a relative scale (except for plot A) of the specific conductivity in the absence of EHEC as a function of the NaDC–SDoD surfactant concentration at 0.020 mol L^{-1} borate buffer, pH 9.20, and 25.0 °C obtained for the following NaDC molar fractions: (A) 1.0; (B) 0.8; (C) 0.5; (D) 0.2; and (E) in pure SDoD. The arrows indicate the cmc.

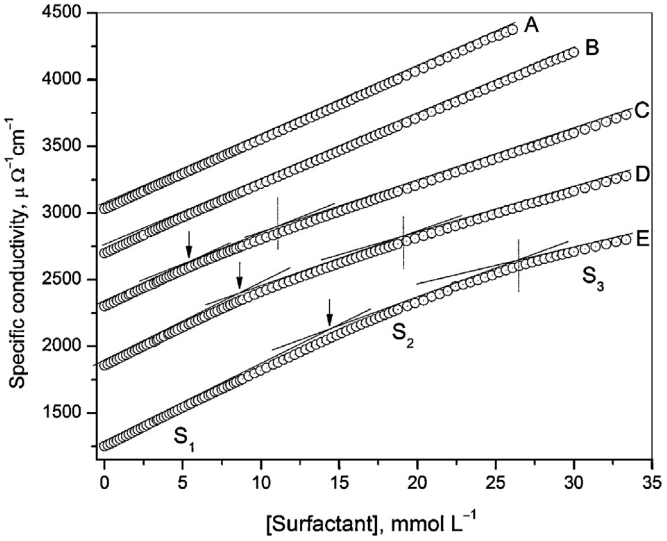

Fig. 2. Plots on relative scale (except for plot A) of the specific conductivity in the presence of 0.1 wt% EHEC as a function of the NaDC–SDoD surfactant concentration at 0.020 mol L^{-1} borate buffer, pH 9.20, and 25.0 °C obtained for the following NaDC molar fractions: (A) 1.0; (B) 0.8; (C) 0.5; (D) 0.2; and (E) in pure SDoD. The arrows indicate the cac, and the dotted lines indicate the psp.

is called the "clouding point" because of the drastic increase in the turbidity of the solution.

The solute–solute, solute–solvent and solvent–solvent interactions are responsible for the effects of temperature on the light scattering patterns of cellulose solutions. Therefore, measurements of turbidity are a useful experimental tool to study the phenomena.

The 0.1-wt% EHEC solutions in 0.020 mol L^{-1} borate/NaOH at pH 9.2 exhibited a clouding point at 65.5 °C, whereas solutions at 0.2 wt% of the polymer in the same solvent presented a clouding point at 67.3 °C. These values correlate with the values described in the literature (Dal-Bó et al., 2005; Lund et al., 2001).

The EHEC has a wide turbidity temperature range from 28 to 70 °C. This temperature range is associated with many factors, such as hydrophobicity, the structure of the substituents, polymer molar weight and the presence or absence of salt (Dal-Bó & Minatti, 2011; Dal-Bó et al., 2005; Lund et al., 2001). In the presence of anionic surfactants, the temperature values of turbidity above the cac tend to increase, making it more appropriate to use anionic cellulose–surfactant mixtures in the formulations and processes that require transparency at elevated temperatures.

For EHEC, the overlap concentration c^* varies within the range of 0.2–0.4 wt%. These values change with temperature, the technique used and the degree of substitution in the cellulose chain groups of the ethyl and ethylene oxide. The authors chose to work at temperatures below the point of turbidity of the polymer and at polymer concentrations lower than c^* for EHEC.

3.2. Electrical conductivity measurements

Electrical conductivity methods have been widely used to estimate the degree of ionization (α) of ionic micelles (Mukerjee & Mysels, 1971; Mukerjee, Mysels, & Kapauan, 1967). They have also been used during the process of micelle self-assembly (Mukerjee, Mysels, & Dulin, 1958), including the association of bile salts (Oakenfull & Fisher, 1977). The conductivity results are analyzed as profiles of the electrical conductivity vs. the surfactant concentration in the absence and presence of 0.1 wt% EHEC and varying molar fractions of the NaDC–SDoD mixture.

Fig. 1 shows the change in specific conductivity for NaDC and SDoD and their mixtures in the absence of EHEC. For SDoD (plot E), the results show a cmc at 22.5 mmol L^{-1} SDoD. The slopes of the linear conductivity regions below (S_1) and above the cmc (S_3) have values of 58 and 28 Ω^{-1} cm^2 mol^{-1}, respectively. Because the slopes represent the equivalent conductivities of ionic species in solution, S_1 can be correlated to the contribution of the Na^+, DoD^- or DC^- species and the buffer. For SDoD, S_1 can be represented by the sum of the two limiting equivalent conductivities of the anion and cation, i.e., $S_1 = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{DoD^-}$. Above the cmc, the explanation becomes more complicated because it is necessary to take into account the bound and ionized counterions plus the micelle contribution.

In contrast to the above SDoD behavior (Fig. 1E), the specific conductivity plot of NaDC is not sensitive to the cmc (Fig. 1A). Therefore, no defined critical micelle concentrations are observed for sodium deoxycholate aggregation. This conductivity behavior is consistent with a model that describes the process of aggregation as progressively changing from primary aggregates to larger structures as the concentration of bile salt monomers increase (Kawamura et al., 1989; Small & Penkett, 1969; Zana & Guveli, 1985).

The analysis in Fig. 1 clearly shows the profiles returning to the typical style, i.e., exhibiting a cmc discontinuity when the mixture is rich in SDoD. We can highlight the following points: First, with increases in the NaDC molar fraction, S_3 increases proportionally, leading to a slope equivalent to that of pure NaDC. Second, the addition of NaDC to the mixture is followed by a slight decrease of the cmc. Third, for all of the profiles in Fig. 1, the S_1 values are only slightly dependent on the surfactant composition. In a preliminary conclusion, the formation of mixed surfactant aggregates in the system can be suggested, similar to the already well-reported mixtures of a nonionic surfactant with sodium cholate (Ueno, Asano, Gotoh, Uchida, & Sasamoto, 1992; Ueno, Kimono, Ikeda, Momose, & Zana, 1987) and a nonionic surfactant with sodium deoxycholate (Yunomiya, Kunitake, Tanaka, Sugihara, & Nakashima, 1998). From Fig. 1, the experimental cmc values and the degree of micellar ionization (α_1) were obtained for mixed surfactants (Table 1).

The role of the EHEC in the NaDC–SDoD mixtures strongly depends on the molar fractions of the surfactant. Fig. 2 shows the specific conductivity versus the surfactant concentration for NaDC, SDoD and a mixture of the two in the presence of 0.1-wt% EHEC. We emphasize the general features of the EHEC–SDoD mixture

Table 1
Values of cmc or cac and psp and slopes of the linear region below the cmc or cac (S_1), between cac and psp (S_2) and above the cmc or psp (S_3) obtained from the profiles in Figs. 1 and 2 in the absence and presence of 0.1 wt% EHEC, respectively.

EHEC (wt%)	χ_{NaDC}	cmc (mmol L^{-1})	cac (mmol L^{-1})	psp (mmol L^{-1})	10^3 S_1 (Ω^{-1} cm^2 mol^{-1})	10^3 S_2 (Ω^{-1} cm^2 mol^{-1})	10^3 S_3 (Ω^{-1} cm^2 mol^{-1})	α_1 (Ω^{-1} cm^2 mol^{-1})	α_2 (Ω^{-1} cm^2 mol^{-1})
0.0	0.0	22.5			58		28	0.48	
0.0	0.2	12.0			57		32	0.52	
0.0	0.4	9.8			57		37	0.65	
0.0	0.5	8.5			56		39	0.70	
0.0	0.6	7.2			56		42	0.75	
0.0	0.7	5.8			55		46	0.84	
0.0	0.8	5.0			55		48	0.87	
0.0	1.0	3.5			54		52	0.96	
0.1	0.0		14.5	26.5	58	48	28	0.48	0.58
0.1	0.2		8.6	19.0	57	42	34	0.60	0.74
0.1	0.4		7.6	14.2	56	41	36	0.64	0.73
0.1	0.5		6.1	11.0	55	–	39	0.71	
0.1	0.6		5.6	–	55	–	45	0.82	
0.1	0.7		4.4	–	55	–	46	0.84	
0.1	0.8		–	–	55	–	49	0.89	
0.1	1.0		–	–	54	–	52	0.96	

(plot E), which are well-known, i.e., two breakpoints and linear regions below the first breakpoint, between the first and second breakpoints and above the second breakpoint (Dal-Bó et al., 2011). The first is interpreted to be the onset of a cooperative process of surfactant binding to the polymer and marks the critical aggregation concentration (cac), which occurs at surfactant concentrations below the cmc in this system. We note that a semi-quantitative analysis of the strength of the interaction between a polymer and surfactant can be characterized through the quantification of the cac/cmc ratio (Dal-Bó et al., 2011; Lissi & Abuin, 1985; Zanette & Frescura, 1999; Zanette, Ruzza, Froehner, & Minatti, 1996). Table 2 lists the values for the angular coefficients, S_1, which are practically independent of the composition of the mixture obtained in the absence and presence of EHEC. Considering the accuracy limit the technique, this fact indicates that below the cac, the first model of the mixture is formed by surfactant monomers, and in the polymer, there is no connection process; cooperative binding on the polymer occurs only at specific cac values. The second breakpoint can mark the saturation of the polymer by the surfactant, denoted here as the polymer saturation point (psp) (Dal-Bó et al., 2005, 2011; Lissi & Abuin, 1985; Zanette et al., 1996). The amount of surfactant exceeding this breakpoint forms regular aqueous micelles (Dal-Bó & Minatti, 2011; Dal-Bó et al., 2005; Zanette & Frescura, 1999; Zanette et al., 1996). This information is supported here by the conductivity plots with identical values for the slope (28 Ω^{-1} cm^2 mol^{-1}) obtained in the presence and absence of EHEC (Table 1). The region located between the points of discontinuity, cac–psp, is defined as a stage where aggregates are formed with various characteristics of the mixed micelles of NaDC–SDoD. It was noted that the linearity of this region is dependent on the experimental conditions, mainly the increase in polymer concentration, where there is a synergistic effect caused by the connection process and desorption (Froehner, Belarmino, & Zanette, 1998).

Based on the above conductivity descriptions of the typical features in the formation of polymer–surfactant complexes, Fig. 2 shows that their profile features are limited for high SDoD molar fractions at a molar fraction of approximately 0.2 SDoD; there is no evidence of the existence of a second breakpoint (Fig. 1B). Moreover, for molar fractions below ≈0.2 SDoD, the profiles in the presence (Fig. 2) and absence (Fig. 1) of EHEC exhibit the same tendencies and features. We conclude that the electrical conductivity technique is not adequate for this study when the molar fraction of NaDC is high.

Table 1 summarizes the effect of the NaDC molar fraction on the slopes S_1, S_2 and S_3 for mixtures of NaDC–SDoD and EHEC–NaDC–SDoD. Therefore, by comparing the S_1 values in the presence and absence of EHEC, it can be observed that the results are polymer independent, and the S_1 values decrease slightly as the NaDC molar fraction increases. This change can be rationalized in terms of the limiting equivalent conductivity of the DoD^- and DC^- anions and the Na^+ counterions; in fact, the reported value of $\lambda^{\circ}_{DoD^-} = 22.0\,\Omega^{-1}\,cm^2\,mol^{-1}$ (Zanette & Frescura, 1999) and deoxycholate anion $\lambda^{\circ}_{DC^-} = 14.8\,\Omega^{-1}\,cm^2\,mol^{-1}$ (Oakenfull & Fisher, 1977) can explain this result. In the measurement of the cmc for ionic surfactants, the main condition necessary for the application of the conductivity plot technique is that the interfaces of the micellar aggregates contain a structure and composition suitable to lead to an aggregate with a degree of ionization (α) other than unity. Therefore, the degree of ionization of ionic micelles can be evaluated from the ratio of the slopes of the linear regions in the

Table 2
Parameters obtained from the results of the surface tension measurements for the NaDC–SDoD mixtures in the absence and presence of 0.1 wt% EHEC in 0.020 mol L^{-1} borate buffer solution at pH 9.20 and 25.0 °C.

EHEC (wt%)	χ_{NaDC}	cmc (mmol L^{-1})	cmc_{Ideal} (mmol L^{-1})	cac (mmol L^{-1})	psp (mmol L^{-1})	S (mN m^{-1})	Γ (μ mol m^{-2})	A_m (Å^2)
0.0	0.0	22.0	22.0	–	–	−23.4	9.4	18
0.0	0.2	13.0	8.6	–	–	−6.9	2.8	59
0.0	0.4	9.4	5.3	–	–	−6.8	2.7	62
0.0	0.6	7.1	3.9	–	–	−6.6	2.7	62
0.0	0.8	4.4	3.0	–	–	−6.4	2.6	64
0.0	1.0	2.5	2.5	–	–	−4.8	1.9	88
0.1	0.0	–	–	10.0	24.4	–	–	–
0.1	0.2	–	–	8.3	16.4	–	–	–
0.1	0.4	–	–	5.0	12.0	–	–	–
0.1	0.6	–	–	4.1	8.8	–	–	–
0.1	0.8	–	–	3.1	6.8	–	–	–
0.1	1.0	–	–	1.2	4.0	–	–	–

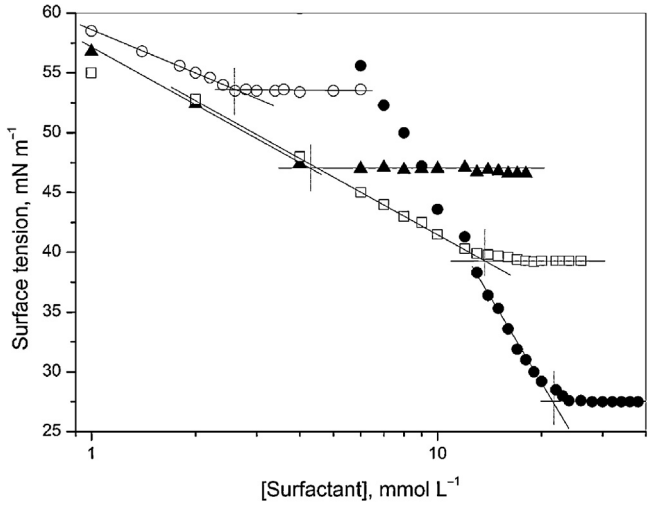

Fig. 3. Profiles of the surface tension in the absence of EHEC as a function of the NaDC–SDoD surfactant concentration at 0.020 mol L^{-1} borate buffer, pH 9.20, and 25.0 °C obtained for the following NaDC molar fractions: (○) 1.0; (▲) 0.8; (□) 0.2; and (●) in pure SDoD. The dotted lines indicate the cmc.

plots of Fig. 1, $\alpha_1 = S_3/S_1$. In the presence of EHEC, the ratio $S_2/S_1 = \alpha_2$ represents the degree of ionization of the polymer–surfactant complexes. This methodology has been applied to different surfactant systems in the presence and absence of polymers (Dal-Bó et al., 2005; Felippe et al., 2007; Froehner et al., 1998; Lima, Nome, & Zanette, 1997; Zanette & Frescura, 1999; Zanette, Felippe, Schweitzer, Dal Bó, & Lopes, 2006). We have found that the degree of ionization of mixed NaDC–SDoD micelles (α_1) increases from 0.48 for SDoD micelles up to nearly 0.96 for NaDC micelles. The most significant result of these data, however, concerns the fact that they depend on the NaDC molar fraction but not on the EHEC concentration. In fact, we found that the α_1 values obtained in the presence of EHEC are identical to those obtained in the absence of the polymer (Table 1).

Table 1 summarizes the parameters of the polymer mixtures with NaDC and SDoD obtained using electrical conductivity at 0.1 wt% of EHEC. The parameters α_1 and α_2 were determined using the slope method, i.e., the ratio between S_3/S_1 and S_2/S_1 estimated from the linear regions of the conductimetric profiles (Dal-Bó et al., 2005, 2011; Felippe et al., 2007; Zanette et al., 1996, 2006).

3.3. Surface tension measurements

Fig. 3 shows the results of the surface tension measurements in the absence of EHEC as a function of the NaDC–SDoD surfactant concentration at 0.020 mol L^{-1} borate buffer, pH 9.20, and 25.0 °C obtained for the different NaDC molar fractions. It can be observed that when the solution contains only NaDC, the surface tension at the cmc is 53.5 mN m^{-1} with a cmc = 2.5 mmol L^{-1}. For $\chi_{NaDC} = 0.8$, the break occurs at 47.0 mN m^{-1} with a cmc = 4.4 mmol L^{-1}. For $\chi_{NaDC} = 0.2$, the break occurs at 39.3 mN m^{-1} with a cmc = 13.0 mmol L^{-1}. The profile of the pure SDoD shows a break occurring at 27.4 mN m^{-1} with a cmc = 22.0 mmol L^{-1}. Above the cmc value, the surface tension is constant; it can be concluded that free micelles form. Above the cmc, the surface tension of a solution of pure SDoD (27.4 mN m^{-1}) is lower than pure NaDC (53.5 mN m^{-1}), which indicates that the SDoD has greater activity at the air–water interface than the NaDC and, therefore, is a more efficient surfactant in principle.

Fig. 4 shows the variation of the surface tension of NaDC in a borate buffer solution of 0.020 mol L^{-1} at pH 9.20 and 25.0 °C in the absence and presence of 0.1 wt% EHEC. The profile of pure NaDC

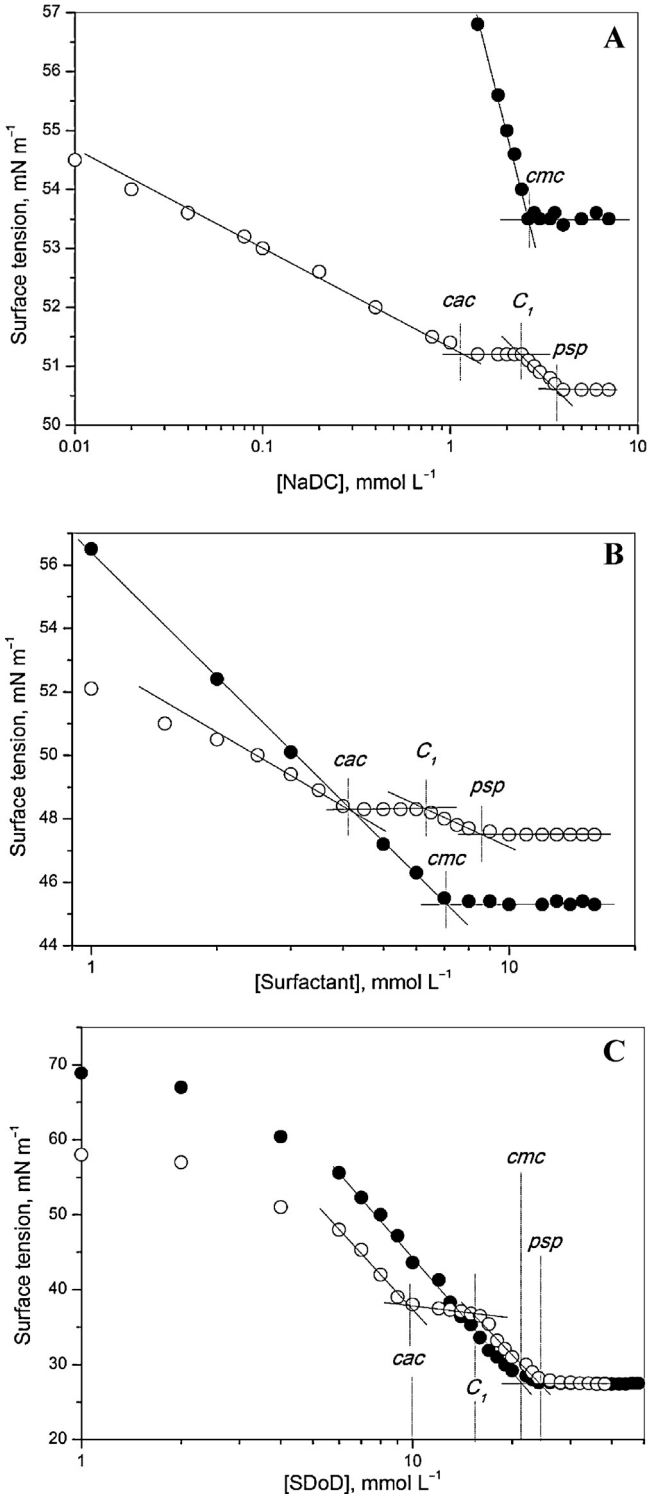

Fig. 4. Profiles of surface tension in the (●) absence and (○) presence of 0.1 wt% EHEC as a function of the NaDC–SDoD surfactant concentration at 0.020 mol L^{-1} borate buffer, pH 9.20, and 25.0 °C obtained for the following NaDC molar fractions: (A) 1.0; (B) 0.6; and (C) 0.0.

shows a break occurring at 53.5 mN m^{-1} with a cmc = 2.5 mmol L^{-1}. In the presence of EHEC, the profile exhibits the two classical breakpoints separated by a narrow surface tension plateau. The width of this plateau has been shown to be dependent on the polymer concentration (Goddard & Ananthapadmanabhan, 1993; Jones, 1967; Schwuger, 1973; Zanette & Frescura, 1999; Zanette et al., 1996; Zanette, Froehner, Minatti, & Ruzza, 1997;

Zanette, Soldi, Romani, & Gehlen, 2002). In the first narrow plateau, approximately 51.2 mN m^{-1} (whose width depends on the polymer concentration), the onset marks the beginning of NaDC micellar clusters binding on the polymer, called the cac, which occurs at 1.4 mmol L^{-1} NaDC. The plateau represents a step in which the surfactant concentration at the air–water interface is kept constant while the surfactant is added to the solution. This constant region ends at a NaDC concentration of approximately 2.4 mmol L^{-1} NaDC. Beyond this point, the surface tension decreases, and the association process must finish at the end of the second discontinuity, called the psp, which occurs at 4.0 mmol L^{-1} NaDC. The latter is interpreted as the NaDC concentration at which the saturation of the EHEC chain by the surfactant monomers is assumed (Jones, 1967; Schwuger, 1973). Note that the surface tension takes on a constant value of 50.6 mN m^{-1} at the NaDC psp in the presence of the polymer. This result implies the formation of only regular NaDC micelles above the psp, which are in equilibrium with EHEC–NaDC complexes.

Fig. 4B shows the variation of the surface tension of the mixture with χ_{NaDC} = 0.6 in the absence and presence of 0.1 wt% EHEC. The profile shows a break, which occurs at cmc = 7.1 mmol L^{-1}. In the presence of EHEC, the cac occurs at 4.1 mmol L^{-1}, and the psp occurs at 8.8 mmol L^{-1} NaDC. The profile of pure SDoD (Fig. 4C) shows the cmc occurring at 22.0 mmol L^{-1}, and in the presence of EHEC, the cac occurring at 10.0 mmol L^{-1}, and the psp occurring at 24.4 mmol L^{-1}. Table 2 summarizes the parameters of the polymer mixtures of NaDC and SDoD obtained from the surface tension measurements of 0.1 wt% EHEC at different molar fractions of the mixture.

In this study, the adsorption of the surfactants at the air–solution interface was investigated using surface tension measurements and as a function of the concentration of surfactant using a ring tensiometer.

The concentration of the excess surfactant monomers at the surface is a useful measurement of the effectiveness of surfactant adsorption because this concentration is the maximum that the adsorption can attain. There is an equilibrium between the surfactant molecules at the surface of the solution and those in the bulk of the solution, which is expressed by the Gibbs equation (Eq. (1)):

$$\Gamma = -\frac{1}{RT}\frac{\partial\gamma}{\partial \ln c} \quad (1)$$

where Γ is the surface excess concentration, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is temperature in Kelvin, and $\partial\gamma/\partial \ln c$ is the gradient of the plot of surface tension against $\ln c$ measured at a concentration just below the cmc.

The surface tension graphs were used to estimate the molecular area occupied by one molecule of surfactant at the air–water interface. The area of the monomeric surfactant is a measure of the degree of packing and orientation of the surfactant molecules at the air–water interface, indicating the effectiveness of the surfactant adsorption at the air–water interface [32]. The area A_m occupied by a surfactant molecule at the solution–air interface can be calculated from Eq. (2):

$$A_m = \frac{1}{N_A\,\Gamma} \quad (2)$$

where N_A is the Avogadro number (6.023×10^{23} molecules mol^{-1}).

According to the results in Table 2, the excess surface concentration (Γ) decreases as the fraction of NaDC in the mixture increases. Fig. 5 shows that the area occupied by each molecule on the surface is larger when the mixture has more NaDC. This behavior is most likely due to the rigid steroid ring structure of bile salts, which belong to the group of ionic detergents but do not possess a polar head group like other detergents. Instead, the polar groups are distributed in different parts of the molecule, all on one side of the molecule.

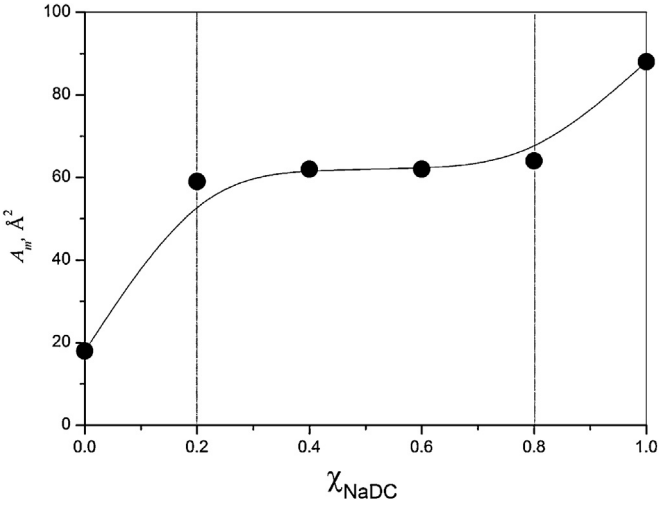

Fig. 5. Area occupied by each surfactant molecule at the air–water interface for different molar fractions of the NaDC–SDoD mixture.

Table 2 summarizes the parameters of the polymer mixtures with NaDC and SDoD obtained from the surface tension measurements.

3.4. Non-ideal mixing behavior of NaDC and SDoD in the absence and presence of EHEC

In a binary mixture formed by the surfactants A and B, the cmc of the mixture of an ideal system can be determined by the molar fraction of one of the components of the mixture (χ) and the cmc of the individual surfactants, as shown in Eq. (3).

$$\mathrm{cmc_{Ideal}} = \frac{\mathrm{cmc_A\,cmc_B}}{\chi_A\,\mathrm{cmc_B} + \chi_B\,\mathrm{cmc_A}} \quad (3)$$

where $\mathrm{cmc_{Ideal}}$ is the critical micellar concentration based on the theory of the optimal solution, $\mathrm{cmc_A}$ and $\mathrm{cmc_B}$ are the critical micellar concentration of the surfactants A and B, respectively, and χ_A and χ_B are the molar fractions of the surfactants A and B, respectively, in the solution.

Fig. 6 shows the variation of the cmc of the binary mixture of NaDC and SDoD in the absence of EHEC. It can be observed that the experimental values from the electrical conductivity and surface tension measurements are similar, but the mixture does not show good agreement with the curve representing an ideal system (dotted line), obtained using Eq. (3).

It is observed that the cmc values obtained experimentally using conductivity and surface tension are similar, but the mixture does not show good agreement with the curve representing an ideal system (dotted line), obtained by Eq. (3). The surfactants have the same counter-ion and similar values for the slope of S_1 in the electrical conductivity measurements, but the deviation from an ideal system was expected because the NaDC and SDoD surfactants have different hydrophobic groups, which hinders the typical hydrophobic interaction. The NaDC surfactant is composed of a steroid skeleton consisting of a rigid structure with a hydrophilic face and an opposite hydrophobic face; therefore, the association and aggregation processes differ considerably from classical anionic surfactants. At high concentrations of surfactant, the formation of primary and secondary bile salt micelles of NaDC is proposed in the literature. For biosurfactants made from bile salts, the literature suggests that micelles only form primary aggregates with up to 10 monomers that are presumably formed via hydrophobic interactions between

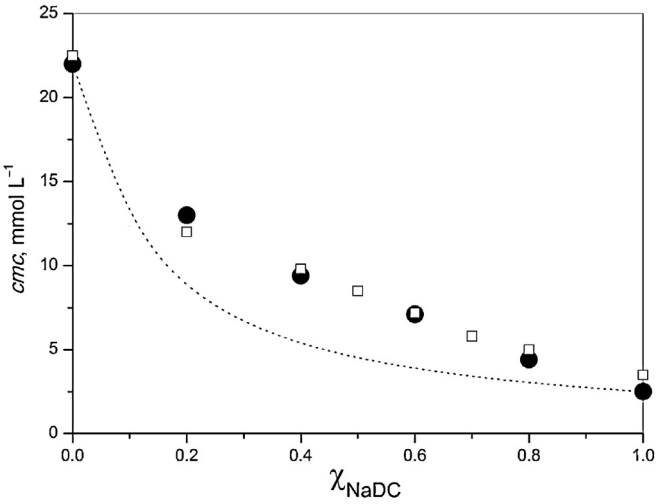

Fig. 6. Variation in the cmc of the NaDC–SDoD system as a function of the NaDC molar fraction obtained using surface tension (●) and electrical conductivity (□) measurements. The dotted line represents the variation of the cmc predicted by ideal mixing behavior.

the nonpolar parts of the monomers. With increasing concentration, secondary micelles are formed via hydrogen bonds between hydroxyl groups located on the external surface of the primary micelles (Ueno et al., 1987, 1992).

4. Conclusions

In solutions with sodium deoxycholate (NaDC), the results of the electrical conductivity measurements showed no discontinuity. The micellar aggregates are considered fully ionized, and the extent of formation of these aggregate is not clear.

When the ethyl (hydroxyethyl) cellulose (EHEC) solution is added, the results still do not present any discontinuities, which indicates that there is no formation of an EHEC–NaDC complex. However, when sodium dodecanoate (SDoD) is added to the system, the results show two discontinuities, the cac and psp, indicating the formation of EHEC–NaDC–SDoD complexes.

The addition of EHEC to the mixture of SDoD and NaDC acts as a stabilizer for the mixed aggregate during the association process. The results of the surface tension measurements, however, demonstrate that there is an interaction between NaDC and EHEC to form the EHEC complex. This fact is most likely because the NaDC and NaDC–EHEC micellar aggregates and complexes are small; therefore, their mobility becomes noticeable in the electrical conductivity measurements. The surface tension measurements are relevant because they differ from the electrical conductivity measurements; they examine the air–water interface. This measurement is more sensitive to the properties of micellar solutions.

The excess surface concentration (Γ) decreases with an increasing fraction of NaDC in the mixture. The area occupied by each molecule on the surface is higher when the mixture has more NaDC. This behavior is most likely due to the rigid steroid ring structure of bile salts.

The cmc of NaDC–SDoD mixtures showed non-ideal behavior because the values obtained experimentally differed from the values obtained from the theory of optimal solution.

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