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Thermodynamics of sodium dodecyl sulphate-salicylic acid based micellar systems and their potential use in fruits postharvest



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ABSTRACT

Micellar systems have excellent food applications due to their capability to solubilise a large range of hydrophilic and hydrophobic substances. In this work, the mixed micelle formation between the ionic surfactant sodium dodecyl sulphate (SDS) and the phenolic acid salicylic acid have been studied at several temperatures in aqueous solution. The critical micelle concentration and the micellization degree were determined by conductometric techniques and the experimental data used to calculate several useful thermodynamic parameters, like standard free energy, enthalpy and entropy of micelle formation. Salicylic acid helps the micellization of SDS, both by increasing the additive concentration at a constant temperature and by increasing temperature at a constant concentration of additive. The formation of micelles of SDS in the presence of salicylic acid plays the role of a stabilizer, and gives a pathway to control the three-dimensional water matrix structure. The driving force of the micellization process is provided by the hydrophobic interactions. The isostructural temperature was found to be 307.5 K for the mixed micellar system. This article explores the use of SDS-salicylic acid based micellar systems for their potential use in fruits postharvest.

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1. Introduction

Salicylic acid (SA) is a monohydroxybenzoic acid, a type of phenolic acid. SA is the pain-relieving ingredient found in aspirin, and a primary ingredient in many skin medications. It is found in plants, and helps protect the plants against bacterial and fungal infections. It also prevents inflammation in the body. Diseases, such as Type 2 diabetes, cardiovascular disease, cancer and Alzheimer's disease, are directly connected to chronic inflammation, and those who have a high intake of plant food have a lower risk for these chronic diseases. Some individuals are sensitive to SA and experience headaches, nausea, rashes, itching, swelling of the face or stomach pain when these foods are consumed; some may also experience anaphylaxis. Due to its relative toxicity and risk of bio-accumulation, its use has been limited in much the EU. The FDA has reviewed the safety of salicylic acid and methyl salicylate and permits their use as indirect food additive in food contact materials (FDA, 2012a). For instance, SA is authorised for use as preservative in adhesives and also as catalyst and cross-linking agent for epoxy resins. In addition, SA attracted much interest because several experimental studies have confirmed that SA could be used for postharvest handling of fruits and vegetables as a food additive. SA treatment was demonstrated to delay fruit ripening and/or reduce decay of several fruits and vegetables (Li & Han, 2000; Srivastava & Dwivedi, 2000; Wei, Liu, Liu, & Ye, 2011; Zhang, Chen, Zhang, & Ferguson, 2003), to alleviate chilling injury of tomato and cucumber storage at low temperature (Han, Li, & Feng, 2002) or to be used as anti-browning agent in fresh-cut Chinese water chestnut stored at low temperature (Peng & Jiang, 2006).

Micellar systems allow the coexistence of clear, isotropic and thermodynamic stable mixtures of water, oil and a surfactant, the presence of a co-surfactant being frequently necessary to ensure the stability of the system. These systems have notable industrial and food applications due to their capability to solubilise a large range of hydrophilic and hydrophobic substances (Cid et al., 2013; Esmaili et al., 2011; Fratter & Semenzato, 2011; Gaysinsky, Davidson, McClements, & Weiss, 2008; Kumar, Thakur, Mozumdar, & Patanjali, 2002; Sugiura et al., 2001). For instance, micellar systems provide an effective vehicle for solubilising some water-insoluble food flavours such as benzyl acetate, 2-phenyl ethanol and geraniol (Kumar et al., 2002), hydrophobic antimicrobials (Gaysinsky et al., 2008) or natural antioxidants (Esmaili et al., 2011) and also as an entrapment medium protecting precursor lipids from degradation, hydrolysis and oxidation (Jabeen, Chat, Rather, & Dar, 2013). Although the use of SDS as additive is not allowed for

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food application in the European legislation, it is included in the list of food additives permitted for direct addition to food for human consumption of the U.S. Food and Drug Administration as a "multipurpose additive" (FDA, 2012b). The aim of this work was then to evaluate the aggregation/micellar behaviour and interactions between sodium dodecyl sulphate (SDS) and SA. The influence of the temperature and the concentration of SDS and SA on the micellar properties were studied. SDS is widely used as a model for the study of micellar structures. The microstructure and properties of SDS micelles can be tuned for food applications by changing the concentration of salicylic acid, what produces changes in the packing and the air-water interface of the micellar system, and seems also to be helpful for reducing decay in postharvest handling of fruits and vegetables in comparison with SA treatments. The final goal would be to reduce the concentration of SA to be used both in delaying fruit ripening and/or reducing decay of several fruits and vegetables, and preventing browning and/or chilling injury in fresh-cut fruits and vegetables stored at low temperature.

2. Materials and methods

2.1. Thermodynamics of the SDS-salicylic acid micellar system

The following reaction shows the reaction mechanism between SA and the micellized surfactant (D_n) , where subscripts w and M denote aqueous and micellar pseudophases, respectively, and K_s is the binding constant that can be calculated from the Eq. (1).

$$SA_{w} + D_{n} \stackrel{\text{rs}}{\leftrightarrow} SA_{M}$$

$$K_{s} = \frac{[SA]_{M}}{[SA]_{w}[D_{n}]}$$
(1)

The concentration of the micellized surfactant is that of total surfactant less that of the monomer, which is assumed to be given by the critical micelle concentration (CMC) following Eq. (2).

$$[D_n] = [D_t] - CMC \tag{2}$$

The micellization degree (β) was calculated from the Eq. (3), where S_1 and S_2 are the slopes of the conductivity–concentration curve in the pre-micellar and post-micellar region (Nusselder & Engberts, 1992).

$$\beta = \frac{S_2}{S_1} \tag{3}$$

The standard Gibbs energy variation per mol of monomer (ΔG_m^o) in the aggregation process can be calculated using the Eq. (4) analogy to the model mass action (Mosquera et al., 1999; Suárez, López-Fontán, Sarmiento, & Mosquera, 1999) where *T* is the temperature, *R* a constant and X_{CMC} the CMC value expressed in mole fraction units.

$$\Delta G_m^o = (1+\beta) RT \ln(X_{CMC}) \tag{4}$$

The standard enthalpy (ΔH_m^o) and entropy (ΔS_m^o) of micellization process were obtained using the Eq. (5):

$$\Delta G_m^o = \Delta H_m^o - T \Delta S_m^o \tag{5}$$

2.2. Electrical conductivity determination

SDS and SA were both supplied by Sigma–Aldrich (Steinheim. Germany) and used without any further purification. Mill-Q system was used to purify water used to prepare all solutions.

Because of their high sensitivity (as any change in parameters, such as concentration of solution compounds, implies great

changes of the system) and high reproducibility, conductivity measurements provide a consistent method to determine the CMC of an ionic surfactant-additive colloidal system (García-Río, Leis, Mejuto, Mosquera, & Rodríguez-Dafonte, 2007). Conductivity measurements were developed as follows. Two Crison GLP-32 conductivimeters with a cell constant of 0.1 and 0.09 cm⁻¹, respectively, were used to obtain electrical conductivity (κ) measurements. Two KCl conductivity standard solutions supplied by Crison with $([KCl] = 0.0100 \text{ mol } L^{-1},$ well-known conductivity values $\kappa = 1413 \ \mu S \ cm^{-1}$ and [KCl] = 0.1000 mol L⁻¹, $\kappa = 12.88 \ mS \ cm^{-1}$ at 25 °C) were used to calibrate the conductivimeters. The electrical conductivity for SDS micellar systems containing the surfactant at concentrations from 0.1 to 0.001 M and salicylic acid from 1×10^{-5} to 15×10^{-5} M was determined at different temperatures between 298.15 and 323.15 K. Micellar systems were homogenised by stirring with a magnetic bar. During the measurements of electrical conductivity, temperature was regulated using a thermostatcryostat Teche TE-8D RB-5, with a precision of ±0.1 °C. The uncertainty of the electrical conductivity measurements was ±0.1%.

3. Results and discussion

3.1. Microstructure and properties of SDS-salicylic acid based micellar systems

The critical micelle concentration (CMC) in pure water at 25 °C is between 8.0 and 8.3 mM (Akbas & Taliha, 2003) and the aggregation number at this concentration is usually considered to be about 62 (Khan & Shah, 2008). The micelle ionisation fraction (α) is around 0.3% or 30% (Bales, Messina, Vidal, Peric, & Nascimento, 1998). The CMC of the SDS/SA system was determined from the plots of the specific conductance (κ) versus the concentration of SDS (0.001–0.1 M). The relationship between κ and [SDS] yields two straight lines with two different slopes, corresponding to the monomeric surfactant and surfactant aggregation zones, respectively. The CMC coincides with the intersection point between them. Thus, the zone below the CMC corresponds with a monomeric state of the surfactant, while the zone above the CMC corresponds to micellar aggregates and the ratio between both slopes corresponds with the micelle ionisation fraction. On the other hand, as the degree of micellization is a function of the temperature and the nature of the solvent (Sulthana, Rao, Bhat, & Rakshit, 1998), the influence of the temperature (between 298.15 and 323.15 k) and the concentration of SA (1 \times 10 $^{-5}\text{--}15$ \times 10 $^{-5}$ M) on the CMC was evaluated (Table 1). Representative plots of the specific conductance (κ) versus the concentration of SDS obtained at different temperatures are shown in Fig. 1.

As stated by other authors, there is a quite important effect exerted by the temperature upon the appearance of the CMC of ionic and no-ionic surfactants (Attwood & Florence, 1983; Sulthana et al., 1998). In this sense, when the temperature increases, the CMC of a non-ionic surfactant without additives decreases; whilst for ionic surfactants (e.g. SDS) the CMC decreases in the region of low temperature, declines to a minimum and then increases with the increase of temperature (Attwood & Florence, 1983). As it can be seen in Table 1 and Fig. 2, CMC values decrease linearly with increase in the temperature independently of the SA concentration $(R^2 > 0.88)$. Therefore, the behaviour showed by the SDS/SA micellar system agrees with the studies reported for non-ionic surfactant systems and confirms the non-ionic nature of the mixed micelles system. Hence, the hydrophobic interactions are the main reason of the appearance of the micelles. When temperature increases, the CMC values decrease as a consequence of the reduction of the hydration sphere of the hydrophobic groups (Attwood & Florence, 1983). With non-ionic surfactants, the CMC suffers an Download English Version:

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