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Synergistic interfacial properties of soy protein–stevioside mixtures: Relationship to emulsion stability

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ABSTRACT

The dynamic interfacial tension and dilatational rheology of soy protein isolate (SPI) and stevioside (STE) mixtures at the oil–water interface were investigated to study the underlying stabilization mechanism for emulsions. The physical properties and long-term stability of emulsions prepared by SPI–STE mixtures were also evaluated. With bulk concentration of SPI fixed at 0.5%, the interfacial dilational properties and emulsion characteristics were markedly affected by the presence of low STE concentration (0.1%), although the interface was still dominated by SPI. With increasing STE concentrations to intermediate level (0.25–1%), synergistic effects in interfacial tension decays and a plateau in the elasticity for mixed SPI–STE interfaces were clearly observed. The effects should be mainly attributed to the formation of SPI–STE complex, enhancing interfacial protein–protein and protein–STE interactions, thus resulting in the presence of a plateau in the elastic behavior. These interfacial properties were positively reflected in the emulsions prepared by SPI–STE mixtures. The emulsions exhibited a fine formation ability and long-term stability after 120 days, which was believed to be due to their better response to external deformations. At high STE content (2%), STE dominated the formation of interface mainly by the preferential adsorption of STE molecules, as evidenced by the results of interfacial properties and surface protein load of emulsions. These findings would provide a potential strategy for designing emulsified foods with long-term stability.

1. Introduction

The formation and stabilization of food emulsions, thermodynamically unstable systems, depend on the interfacial properties of surface active components in the system (Bos & Van Vliet, 2001; Dickinson, 2001). Mixtures of proteins and low molecular weight (LMW) surfactants are widely used in most emulsified foods. However, both types of molecules play different roles in the formation and stabilization of emulsions. LMW surfactants can quickly and effectively reduce interfacial tension, thus facilitating the process of emulsification (Bos & Van Vliet, 2001; Miller, Alahverdjieva, & Fainerman, 2008). In contrast, proteins are more effective for long-term stability of emulsions by forming highly elastic networks on the droplets surface (Bos & Van Vliet, 2001; Murray, 2011; Tcholakova, Denkov, Ivanov, & Campbell, 2006; Wilde, Mackie, Husband, Gunning, & Morris, 2004). These differences often result in synergistic or antagonistic effects on interfacial and emulsifying properties of protein–LMW surfactants mixtures due to competitive adsorption of two molecules at the oil–water interface (Alahverdjieva et al., 2008; Bos & Van Vliet, 2001; Cornec, Mackie, Wilde, & Clark, 1996, 1998; Dickinson, 1998; Ruíz-Henestrosa, Carrera Sánchez, & Rodríguez Patino, 2008).

The interactions between proteins and LMW surfactants have been of great interest to many researchers so far due to their strong influence on the formation and stabilization of emulsions (Bos & Van Vliet, 2001; Maldonado-Valderrama & Rodríguez Patino, 2010). Indeed, proteins can interact with LMW surfactants in the bulk and at the interface in different ways, which leads to the formation of complexes with different surface activities (Kotsmar et al., 2009; Krägel et al., 2003; Maldonado-Valderrama & Rodríguez Patino,

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2010). This interaction can be of hydrophobic and/or electrostatic nature and will change the conformation of protein molecules in the bulk and at the surface, respectively (Kotsmar et al., 2009; Maldonado-Valderrama & Rodríguez Patino, 2010). Generally, nonionic surfactants such as Tween 20, can form complexes with proteins mainly by hydrophobic interactions (Maldonado-Valderrama & Rodríguez Patino, 2010), whereas for ionic surfactants such as protein–SDS mixtures, the complexes mainly were formed by electrostatic interactions (Maldonado-Valderrama & Rodríguez Patino, 2010; Pradines, Kragel, Fainerman, & Miller, 2009). Increasing the amounts of LMW surfactants in the mixtures affects the complexation processes and interfacial layer composition, as the LMW surfactant will gradually displace the protein from the interface due to the competition adsorption. Finally, above a certain concentration of LMW surfactant, protein contributed little to the formation of the adsorption layer (Chen & Dickinson, 1995; Dickinson & Tanai, 1992; Wilde et al., 2004).

In recent years, most of the studies on proteins–LMW surfactants mixtures are focused on synthetic surfactants, mainly petroleum-derived. However, there has been increasing interest within the food industry in replacing synthetic surfactants with natural alternatives of biological origin (biosurfactants) due to their low toxicity and intrinsic biodegradability. Triterpenoid saponins, plant-derived biosurfactants, have exhibited strong surface activity and are widely used as efficient foamers and emulsifiers (Güçlü-Üstündağ & Mazza, 2007; Yang, Leser, Sher, & McClements, 2013). Recently, several authors reported high surface elasticities of saponin adsorption layers at the air–water interface, which attracted currently a lot of research interest (Golemanov, Tcholakova, Denkov, Pelan, & Stoyanov, 2012; Stanimirova et al., 2011). In addition, interfacial properties of mixtures of proteins and saponin have also been described in detail in recent studies (Piotrowski, Lewandowska, & Wojciechowski, 2012; Wojciechowski, Kezwon, Lewandowska, & Marcinkowski, 2014; Wojciechowski, Piotrowski, Popielarz, & Sosnowski, 2011).

Stevioside (STE), the most abundant component of steviol glycosides, has been mainly used as a noncaloric natural sweetener in food products due to its intense sweetness (250–300 times sweeter than sucrose). Moreover, STE also exhibits many biological effects on humans, such as antihyperglycemic, antihypertensive, antitumor progression, and immunomodulatory activities (Puri, Sharma, & Tiwari, 2011). STE is a diterpene ent-kaurene glycoside, which contains a hydrophobic part, composed of a diterpenoid or steviol backbone, and a hydrophilic part consisting of glucosyl and sophorosyl residues. The amphiphilic structure of STE molecules, similar to that of triterpenoid saponins, may determine their potential capability as natural surface-active substances (biosurfactants). In our previous study, we have found that STE possessed a notable surface activity and the emulsion prepared by the mixtures of soy protein isolate (SPI) and STE showed a remarkable physical stability with small oil droplet size ($\sim$220 nm) (Wan, Wang, Wang, Yang, & Yuan, 2013). However, the potential stabilization mechanism for emulsions still remains unclear.

Considering the fact that the interfacial properties of such mixed adsorbed layers, given by the protein and LMW surfactants mixtures and by their interactions, can strongly influence the emulsion formation and stability (Maldonado-Valderrama & Rodríguez Patino, 2010), therefore, it is of interest to study the interface properties of SPI–STE mixtures and their relation to the emulsion characteristics. Furthermore, no information is available about the interfacial interactions between protein and STE. Therefore, the objective of this study is to characterize the adsorption layers of SPI–STE mixtures at the oil–water interface by means of dynamic interfacial tension and dilational rheological studies. In addition, the physical properties (particle size distribution as well as surface protein concentration and composition) and long-term stability of emulsions prepared by SPI–STE mixtures were also evaluated. Finally, the underlying stabilization mechanism for emulsions was proposed.

2. Materials and methods

2.1. Materials

Defatted soy flour was provided by Shandong Yuwang Industrial and Commercial Co., Ltd., China. SPI was prepared according to a previously described protocol (Guo et al., 2013). The protein content of SPI was 88.79%, determined by using the Dumas method ($N \times 5.71$, wet basis) in a Rapid N Cube (Elementar France, Villeurbanne, France). STE (purity $>$ 95%) was purchased from Jining Aoxing Stevia Products Co., Ltd., China. Corn oil (purity $>$ 99%) was purchased from a local supermarket and purified with Florisil (60–100 mesh, Sigma Aldrich) to remove surface-active impurities as described elsewhere (Gaonkar, 1989). The interfacial tension of purified corn oil against the phosphate buffer (10 mM, pH 7.0) remained constant at a value of 24.5 $\pm$ 0.5 mN/m. All chemicals used in this work were of analytical or better grade without further purification.

2.2. Preparation of mixed SPI–STE systems

All samples were prepared in a 10 mM phosphate buffer (pH 7.0) using distilled water (18.2 MΩ cm) at room temperature (25 °C). The absence of surface active contaminants in the phosphate buffer solution was checked by interfacial tension measurements before sample preparation. No aqueous solutions with a surface tension other than that accepted in the literature (72–73 mN/m at 25 °C) were used. SPI dispersions were stirred for at least 1 h to ensure complete dissolution, and then they were left overnight at 4 °C to hydrate appropriately. All measurements were made at constant SPI concentration (0.5 wt%) and varying STE concentration (0–2 wt %) at pH 7.0. The mixed SPI–STE systems were obtained by mixing the appropriate volume of each double concentrated SPI and STE solutions up to the required concentration and stirring for further 30 min before any measurements.

2.3. Dynamic interfacial properties

The dynamic interfacial properties of SPI, STE, and SPI–STE mixtures at the oil–water interface were determined using an optical contact angle meter (OCA-20, Data-physics Instruments GmbH, Germany) equipped with oscillating drop accessory (ODG-20). Details of this apparatus are given elsewhere (Tamm, Sauer, Scampicchio, & Drusch, 2012). All the experiments were carried out at 25 °C. The solutions were placed in the syringe and were allowed to equilibrate for 30 min to reach the desired constant temperature before the interfacial measurements.

2.3.1. Dynamic interfacial tension

A drop of emulsifier solution (15 μL) was delivered into an optical glass cuvette containing purified oil, and allowed to stand for 180 min to achieve adsorption at the oil–water interface. An image of the drop was continuously recorded by a CCD camera and digitalized. The interfacial tension (γ) was calculated through the analysis of the droplet profile according to fundamental Laplace equation. The interfacial pressure is $\pi = \gamma_0 - \gamma$, where γ_0 is the interfacial tension of 10 mM phosphate buffer (pH 7.0) and γ is the time-dependent interfacial tension of the tested solutions. The average standard accuracy of the interfacial tension was roughly 0.1 mN/m. However, the reproducibility of the results was better than 0.5%.