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Investigation on complex coacervation between fish skin gelatin from cold-water fish and gum arabic: Phase behavior, thermodynamic, and structural properties

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ABSTRACT

The study is aimed to investigate phase behavior, thermodynamic, and structural properties based on complex coacervation between fish skin gelatin (FSG) from cold-water fish and gum arabic (GA). Phase separation behavior between FSG and GA was investigated as a function of pH through varying mixing ratios from 4:1 to 1:4 at 25 °C and 1.0 wt% of total biopolymer concentration. The turbidity of FSG-GA mixture reached the maximum (1.743) at the 1:2 of mixing ratio and pH_{opt} 3.5, and stabilized at zero. Then physicochemical properties of FSG-GA coacervates at pH_{opt} 3.5 and FSG-GA mixtures at pH 6.0 ($> pH_c$) were evaluated. Scanning electron microscope (SEM) and X-ray diffraction (XRD) showed that the interactions between FSG and GA occurred at pH_{opt} 3.5 and were very weak at pH 6.0 ($> pH_c$). The isothermal titration calorimetry (ITC) results including the negative Gibbs free energy change ($\Delta G = -18.71 \pm 1.300$ kJ/mol), binding enthalpy ($\Delta H = -41.81 \pm 1.300$ kJ/mol) and binding entropy ($T\Delta S = -23.10$ kJ/mol) indicated that the complexation between FSG and GA was spontaneous and driven by negative enthalpy owing to the electrostatic interaction and hydrogen bondings. The zeta potential (ZP) of FSG-GA coacervates at pH_{opt} 3.5 was -9.00 ± 0.79 mV that was not close to electrically neutral, indicating other interactions besides electronic interaction. Hydrogen bondings in FSG-GA mixtures at pH 6.0 and 3.5 were found to be stronger than pure FSG at pH 6.0 and 3.5 owing to that the amide II peaks shifted to high wavenumbers. Electronic interaction was proven to exist in FSG-GA mixtures at pH 6.0 through the vanishment of asymmetric $-COO^-$ stretching. However, the electronic interaction in FSG-GA coacervates at pH_{opt} 3.5 was obviously stronger than FSG-GA mixtures at pH 6.0, resulting from the vanishment of asymmetric and symmetric $-COO^-$ stretching vibration and the positively charged FSG and GA. The intrinsic fluorescence represented that the introduction of GA changed the microenvironment of tyrosine residues in FSG, which may be owing to the unfolding of the tertiary conformation. Moreover, the decrease of pH could promote the formation of random coils of FSG through circular dichroism (CD). Therefore the addition of GA into FSG and decrease of pH might enhance the conformation freedom of FSG, which would bring about favorable entropic effects and contribute to the complexation.

1. Introduction

Proteins and polysaccharides are the essential functional ingredients determining the texture, structure, and shelf-life of most food products (Dickinson, 2008; Doublier, Garnier, Renard, & Sanchez, 2000). Meanwhile, coacervates of proteins and polysaccharides, were the most widely used hydrocolloids in food industry (Schmitt et al., 2005). Coacervation is a fundamental physicochemical phenomenon that is of great importance to determine the structure and physical properties of formulated foods (Schmitt, Sanchez, Desobrybanon, & Hardy, 1998; Strauss & Gibson, 2004). Interplay between biopolymers can be divided into three behaviors, including co-solubility, thermodynamic in-compatibility, and complex formation (Vivian & Callis, 2001; Cgde & Tuinier, 2001). Biopolymers are co-soluble in dilute solutions because mixing is driven by entropy (Turgeon, Beaulieu, Schmitt, & Sanchez, 2003). The mixture of biopolymers may become unstable with increase in concentration. Effective repulsion between biopolymers or an asymmetry in biopolymer-solvent interaction may lead to thermodynamic in-compatibility or segregative phase behavior where each phase is enriched in one of the biopolymer components (Cao et al., 2015; Piculell & Lindman, 1992; Tolstoguzov, 1991). Effective attraction between biopolymers with opposite charges and separation into

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biopolymer-rich and solvent-rich phases bring about complex coacervation or associative phase behavior (Cao et al., 2015; de Kruif, Weinbreck, & de Vries, 2004; Piculell & Lindman, 1992; Tolstoguzov, 1991).

In recent years, a number of researchers have studied protein-polysaccharide complexes and coacervates to broaden possible food applications for development of bioactive delivery devices (Dong et al., 2015), gels (Huang et al., 2017), and emulsions (Ganzevles, Cohen Stuart, Tvan, & Hhjde, 2006). There have been many reports about biopolymer pairs, such as ovalbumin/gum arabic (Boudia, Louly, & Prins, 2015), carrageen/gelatin (Cao et al., 2015), sodium caseinate/gum arabic (Ye, Edwards, Gilliland, Jameson, & Singh, 2012), bovine serum albumin/flaxseed gum (Liu, Shim, Wang, & Reaney, 2015), canola protein isolate/chitosan (Chang, Gupta, Timilsena, & Adhikari, 2016), gelatin/chitosan (Wang, Wang, & Heuzey, 2016), and so on. The most classical biopolymer pair of complex coacervation is the gelatin/gum arabic (GE/GA) system in which GE and GA are used as positive and negative polyelectrolyte, respectively (Leclercq, Harlander, & Reineccius, 2010). GE can be acquired from bovine hide, cattle bones, pig skin, and marine sources (warm- and cold-water fish skins, bones, and fins) (Piacentini, Giorno, Dragosavac, Vladisavljević, & Holdich, 2013). Mammalian GE is expected to seek for alternatives, due to worldwide religious sentiments, vegetarian nutritional requirements, and the risk associated with the transmission of pathogenic vectors (Piacentini et al., 2013). Therefore GE obtained from marine sources has attracted growing attention from researchers in recent years (Karim & Bhat, 2009; Surh, Decker, & Mcclements, 2006).

Fish gelatin (FG), especially from cold water fish, possesses low gelling point (8–25 °C) that enables complex coacervation to happen at about ambient or slightly above-ambient temperature. FG has been blended with different polysaccharides including hydroxy propyl methyl cellulose (Chen, Lin, & Kang, 2009), chitosan (Kołodziejska, Piotrowska, Bulge, & Tylingo, 2006), pectin (Liu, Liu, Fishman, & Hicks, 2007), and GA (Anvari & Chung, 2016). GA is one of the mostly widely used industrial polysaccharides owing to its good surface activity and low viscosity (Burgess & Carless, 1984; Weinbreck, D.V., Schrooyen, & D.K., 2003). So many researchers focused on the interactions between FG from cold water fish and GA molecules in aqueous solution and the results are as follows: Yang, Anvari, Pan, and Chung (2012) studied the influence of pH, FG to GA ratio, and total biopolymer concentration on turbidity, methylene blue–GA interactions, zeta potential, and biopolymer complex size; Piacentini et al. (2013) focused on production of complex coacervate microcapsules of controlled size under mild shear stress conditions; Anvari et al. studied the influence of phase separation temperature (Anvari, Pan, Yoon, & Chung, 2015) and oxidized or non-oxidized tannic acid (Anvari & Chung, 2016) on the rheological and structural characteristics of FG–GA complex coacervate gels. But above all, the understanding of interactions between FG and GA in an aqueous environment is not enough. The characteristics such as thermodynamic and spectroscopic properties of FG–GA complex coacervate are still unclear.

The objective of this study is to investigate the interactions between fish skin gelatin (FSG) from cold water fish and GA as a function of pH at 25 °C. The interactions between FSG and GA were firstly found by the increase of turbidity and then verified by determining the structural properties of FSG–GA complex coacervates through scanning electron microscope (SEM) and X-ray diffraction (XRD). Finally, the mechanism of interactions between FSG and GA was clarified through isothermal titration calorimetry (ITC), electrophoretic light scattering, Fourier transform infrared (FTIR) spectroscopy, intrinsic fluorescence, and circular dichroism (CD) spectrometry. These experimental results can contribute to the understanding of interactions between FSG and GA. Moreover, the research results provide guidance on designing complex food systems based on complexes and coacervates.

2. Materials and methods

2.1. Materials

FSG (molecular weight 60 kDa) was purchased from Sigma-Aldrich (St. Louis, MO, USA). GA (molecular weight 250 kDa) was obtained from Shanghai Yuanye Biochemistry Co., Ltd. (Shanghai, China). All the chemicals used were of analytical grade and were purchased from Tianjin Damao Chemical Reagent Co., Ltd. (Tianjin, China).

2.2. Sample preparation

The mixture of FSG and GA was obtained by dissolving each powder in deionized water under 100 rpm stirring at 25 °C for 2 h to ensure biopolymer dissolution. The total concentration of a mixture of FSG and GA was fixed at 1.0 wt%. The mixing ratio of FSG and GA ranged from 1:4 to 4:1. Homogenous FSG and GA solutions were obtained according to the above method. The mixture of FSG and GA was initially adjusted to pH 10.0 using 0.1 M NaOH and then gradually acidified to pH 1.0 at an interval of 0.5 by the addition of HCl (0.05, 0.5, 1.0, 2.0 M) (Niu et al., 2015). The various concentrations of HCl could make dilution effects and changes to solution conductivity minimal, as described by Liu, Low, and Nickerson (2009). Critical pH values (pH_c: formation of soluble complexes, $pH_{\varphi 1}$: formation of insoluble complexes, pH_{opt}: maximum spectroscopic density, $pH_{\varphi 2}$: dissolution of complexes) associated with structure-forming events were determined graphically according to the methods of Weinbreck, Minor, and de Kruif (2004).

2.3. Turbidimetric analysis

The turbidity of a mixture of FSG and GA was measured via the absorbance using an UV/Vis spectrophotometer (UV-5200, Metash instrument Ltd., Shanghai, China) with a 1 cm path length spectroscopic probe at 600 nm (Harnsilawat, Pongsawatmanit, & Mcclements, 2006). All measurements were conducted at 25 °C and the turbidity was then measured as a function of pH. The turbidity (T) was defined as

$$(T) = -\ln(I/I_0)$$

where I is the spectroscopic density that passes through a volume of solution of 1 cm length and I_0 is the incident light intensity. All samples were measured in triplicate.

2.4. Lyophilization

The FSG (pH 6.0 and 3.5), GA (pH 6.0 and 3.5), and FSG-GA coacervates (1.0 wt%, 1:2 mixing ratio of FSG and GA, pH 3.5), FSG-GA mixtures (1.0 wt%, 1:2 mixing ratio of FSG and GA, pH 6.0) were lyophilized by a Scientz-10ND apparatus (Ningbo Scientz biotechnology co. LTD, Zhejiang, China) to obtain dry powder. The acidification of samples was referred to the method in Section 2.2. After the acid titration, the FSG-GA mixture solution at pH 3.5 was centrifuged at 10,000 rpm for 10 min and the sediment was dispersed with 3 mL deionized water in 8 mL glass vials. The FSG (pH 6.0 and 3.5), GA (pH 6.0 and 3.5), and FSG-GA mixture solution at pH 6.0 were directly lyophilized. The next lyophilization method was made some modifications according to Li, Zhao, Zu, and Zhang (2015). The samples were frozen at −20 °C overnight. Subsequently, lyophilization was underway at −50 °C for 24 h, followed by a secondary drying phase of 12 h at 20 °C. The obtained samples were used to conduct SEM, XRD, and FTIR tests.

2.5. Scanning electron microscope

The morphologies of FSG, GA, FSG-GA mixtures at pH 6.0 and FSG-GA coacervates at pH 3.5 were ascertained by scanning electron microscope (SEM, JSM-7800F, JEOL, Tokyo, Japan). The samples were directly deposited on aluminium stubs with double sided carbon tape

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