Food Hydrocolloids 74 (2018) 37–45

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Freeze-thaw stability of Pickering emulsions stabilized by soy protein nanoparticles. Influence of ionic strength before or after emulsification

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ARTICLE INFO

Article history:
Received 25 April 2017
Received in revised form
11 July 2017
Available online 21 July 2017

Keywords:
Pickering emulsions
Freeze-thaw stability
Soy protein nanoparticles
Electrostatic screening
Gel-like emulsions

ABSTRACT

There is still a debate about the influence of salts on the freeze-thaw stability of emulsions. In this research, the influence of the NaCl addition (before or after the emulsification; 100–500 mM) on the freeze-thaw stability of the Pickering emulsions stabilized by heat-induced soy protein isolate (SPI) nanoparticles, at a given protein concentration of 1.0% (w/v) and oil fraction of 0.4, was investigated. The addition of NaCl resulted in considerable changes in particle characteristics (including particle size, surface hydrophobicity and ζ-potential) of the SPI nanoparticles, with the extent of the changes varying with the applied ionic strength (μ). Despite the NaCl addition before or after the emulsification, the presence of NaCl remarkably improved the freeze-thaw stability against droplet coalescence and creaming of the emulsions, though the improvement was related to the applied μ. The improvement of the freeze-thaw stability would be largely attributed to the strengthening of the interfacial protein or protein nanoparticle films coating droplets, rather than the inhibition of ice crystal formation by the presence of NaCl. If the salt was introduced before the emulsification, a gel-like network might be formed in the corresponding emulsions, which would further provide an additional stabilization against the freeze-thaw treatment. Optimal freeze-thaw stability was observed in the presence of appropriate concentrations of NaCl (e.g., 100–200 mM). This is the first report to indicate the importance of the electrostatic screening to the improvement of the Pickering emulsions stabilized by charged particles. The findings would be of great importance for the formulation of food grade emulsions with excellent freeze-thaw stability.

1. Introduction

The freeze-thaw stability is an important attribute for many emulsion-based products that need to be frozen, e.g., sauces and mayonnaise. The freeze-thaw stability of an oil-in-water emulsion is generally affected by a number of variables, including emulsion composition (such as the type and nature of emulsifiers, biopolymers, salts and cryoprotectants, and even the type and nature of lipids), homogenization conditions, and freezing/thawing conditions (Degner, Chung, Schlegel, Hutkins, & McClements, 2014; Ghosh & Coupland, 2008). When an emulsion is freeze-thawed, it usually destabilizes in terms of oiling off, creaming, flocculation and coalescence. The destabilization of freeze-thawed emulsions has been recognized to come from two kinds of stresses: crystallization of water and/or lipid phases, and dramatic changes in pH, ionic strength, osmotic pressure and viscosity (around droplets) (Degner et al., 2014). Among all the destabilization mechanisms, coalescence seems to be one of the most important items for emulsions, since when coaescence of droplets occurs, it would lead to oilling off or phase seperation, and accelerate the flocculation and creaming processes. To date, many strategies using interfacial engineering have been proposed to effectively improve the freeze-thaw stability against coalescence of oil-in-water emulsions, e.g., fabrication of multilayered structure on the surface of droplets (Aoki, Decker, & McClements, 2005; Gu, Decker, & McClements,

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http://dx.doi.org/10.1016/j.foodhyd.2017.07.017
0268-005X/

2007; Mun, McClements, & Surh, 2010; Thanasukarn, Pongsawatmanit, & McClements, 2006), and the usage of particle-based emulsifiers or stabilizers (Marefati, Rayner, Tiumgren, Dewjmek, & Sjöö, 2013; Matsumiya & Murray, 2016; Zhu, Zhang, Lin, & Tang, 2017). In a recent work of ours, it was found that the Pickering emulsions stabilized by heat-induced nanoparticles of soy protein isolate (SPI) and whey proteins exhibited a much better freeze-thaw stability than those stabilized by unheated SPI or whey proteins (Zhu et al., 2017). In this previous work, it was proposed that the good freeze-thaw stability of the Pickering emulsions might be largely attributed to the formation of a gel-like network in the system.

A number of our previous works had indicated that the microstructure and rheological properties (e.g., a gel-like rheological behavior) of the Pickering emulsions stabilized by heat-induced soy protein nanoparticles can be well modulated by variation in protein or particle concentration (c) in the continuous phase and/or oil fraction (ϕ and even the choice of emulsification process (Liu & Tang, 2014, 2016a). For these emulsions, it is generally observed that increasing c and/or ϕ results in a progressively strengthening of the gel-like network, as a result of enhanced droplet flocculation. Due to these considerations, in our preliminary experiments, we investigated the influence of variation in c and/or ϕ on the freeze-thaw stability of the Pickering emulsions stabilized by heat-induced SPI nanoparticles at a specific ionic strength (μ) of 300 mM, and the results confirmed that the improvement of the freeze-thaw stability (especially against creaming) of these Pickering emulsions was closely associated with the enhancement of a gel-like network, rather than the inhibition of ice crystal formation in the aqueous phase (data not shown). However, it still remains uncertain how the gel-like network formation in these emulsions improves their freeze-thaw stability. To address this issue, the molecular basis for the gel-like network in these Pickering emulsions, e.g., the importance of nature of interfacial particle films, should be clarified.

For negatively charged protein particles (at pH above isoelectric point of proteins), their emulsification and interfacial properties are highly dependent on the pH and μ. Our previous work indicated that for heat-induced soy glycinin nanoparticles, the electrostatic screening by addition of increasing concentrations of NaCl (0–500 mM) remarkably improved their emulsification performance and interfacial packing at interface (Liu & Tang, 2016b). The improvement was largely due to the enhanced diffusion and/or adsorption at the interface (Liu & Tang, 2016b). If the c and/or ϕ are high enough and a high energy input of emulsification applied, the strength of the gel-like network of the resultant Pickering emulsions stabilized by heated soy proteins would be progressively improved by increasing the μ in the aqueous phase (Liu & Tang, 2016b; Tang & Liu, 2013). Thus, it can be reasonably hypothesized that the freeze-thaw stability of the Pickering emulsions stabilized by protein particles can be improved by the electrostatic screening, or addition of salts.

The presence of aqueous salts is expected to produce an inhibitory effect on the water crystallization during the freezing process, which seems to be favorable for the freeze-thaw stability of oil-in-water emulsions. However, there is still a debate in the literature addressing the influence of salt addition on the freeze-thaw stability of emulsions (Ghosh & Coupland, 2008). In fact, for the emulsions stabilized by charged emulsifiers (e.g., proteins), it is very important to mention whether the salt is introduced before or after the emulsification, when the freeze-thaw stability of the corresponding emulsions is evaluated. If the salt is added before the emulsification, the structural characteristics (including surface charge and surface hydrophobicity/hydrophilicity) of proteins will be affected by the presence of salts, and as a consequence, the interfacial film structure and stability of the droplets in the resultant emulsions would be affected. In this case, besides the influence of aqueous salts themselves, the freeze-thaw stability of the emulsions can be affected by the changes in interfacial film characteristics. If the salt is introduced after the emulsification, the presence of aqueous phase may also produce an influence on the freeze-thaw stability of the resultant emulsions, by changing the interfacial film structure of protein-coated droplets (through the electrostatic screening), in a different way from that with the salt added before the emulsification.

Based on our previous work addressing the freeze-thaw stability of the Pickering emulsions stabilized by heat-induced SPI or whey protein nanoparticles (Zhu et al., 2017), the present work was to investigate the influence of salt addition (before or after the emulsification; 100–500 mM) on the freeze-thaw stability of the Pickering emulsions stabilized by heat-induced SPI nanoparticles, with the aim not only to further confirm the importance of the gel-like network to the high freeze-thaw stability of these emulsions, but also to unravel the molecular mechanisms for the high freeze-thaw stability of the gel-like Pickering emulsions. In the first part, the influence of variation in μ (0–500 mM) on the particle characteristics of heat-induced SPI nanoparticles (formed at $c = 2\%$, w/v) was characterized, in terms of particle size, surface hydrophobicity (H_o) and ζ-potential. Then, the fluence of the NaCl addition before or after the emulsification on the characteristics of the resultant initial emulsions, formed at $c = 1.0\%$ (w/v) and $\phi = 0.4$, as well as their freeze-thaw stability, was characterized by visual and microstructural observations. Last, the influence of the salt addition (before or after emulsification) on the ice crystal formation and melting of these initial emulsions was evaluated using differential scanning calorimetry (DSC).

2. Materials and methods

2.1. Preparation of dispersions containing heat-induced SPI nanoparticles

The SPI applied in the current work was the same as in our previous work (Zhu et al., submitted for publication), which protein content was approximately 92.5% (dry basis), as determined by the Dumas method with a nitrogen conversion factor of 6.25. The stock SPI solution (2%, w/v) was prepared by firstly dissolving the SPI sample in deionized water (with the help of a magnetic stirrer) and subsequently storing overnight (for complete hydration of the proteins). If necessary, the pH of the SPI solution was adjusted to 7.0 with 1 M NaOH or 1 M HCl. NaN_3 (0.02%, w/v) was added as the antibacterial agent. The dispersions containing heat-induced SPI nanoparticles were prepared by heating the stock SPI solution (2%, w/v) in a water bath at 95 °C for 15 min, and then immediately cooling in ice bath to 25 °C. After that, NaCl powder was gradually added to the heated dispersions under the stirred conditions to reach an ionic strength (μ) value in the range 100–500 mM. Before being subjected to the particle characterization, all the dispersions at different μ values were equilibrated for at least 2 h. Soy oil was purchased from a supermarket in Guangzhou (China).

2.2. Characterization of heat-induced SPI nanoparticles

The particle characteristics, including particle size distribution (PSD) profile and z-average diameter, ξ-potential and surface hydrophobicity (H_o), of heat-induced SPI nanoparticles at various μ values of 0–500 mM were determined according to the same processes and devices as described in our previous work (Zhu et al., submitted for publication).