Current Opinion in Colloid & Interface Science 28 (2017) 63–73

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

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

The heat stability of milk protein-stabilized oil-in-water emulsions: A review

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ARTICLE INFO

Article history:
Received 13 September 2016
Received in revised form 13 March 2017
Accepted 15 March 2017
Available online 22 March 2017

Keywords:
Heat treatment
O/w emulsions
Milk proteins
Attractive/repulsive forces

ABSTRACT

The knowledge on the factors affecting the heat-induced physicochemical changes of milk proteins and milk protein stabilized oil-in-water emulsions has been advanced for the last decade. Most of the studies have emphasized on the understanding of how milk-protein-stabilized droplets and the non-adsorbed proteins determine the physicochemical and rheological properties of protein-concentrated dairy colloids. The physical stability of concentrated protein-stabilized emulsions (i.e., against creaming or phase separation/gelation after heat treatment) can be modulated by carefully controlling the colloidal properties of the protein-stabilized droplets and the non-adsorbed proteins in the aqueous phase. This article focusses on the review of the physical stability of concentrated milk protein-stabilized oil-in-water emulsions as influenced by physicochemical factors, interparticle interactions (i.e., protein–protein, and droplet–droplet interactions) and processing conditions. Emphasis has been given to the recent advances in the formation, structure and physical stability of oil-in-water emulsions prepared with all types of milk proteins, reviewing in particular the impact of pre- and post-homogenization heat treatments. In addition, the importance of common components found in the continuous phase of heat-treated nutritional emulsions that can promote aggregation (polymers, sugars, minerals) will be highlighted. Finally, the routes of manipulating the steric stabilization of these emulsions to control heat-induced aggregation—through protein–surfactant, protein–protein, protein–polysaccharide interactions and through the incorporation of protein based colloidal particles—are reviewed.

1. Introduction

Oil-in-water emulsions are the basis for many food products such as mayonnaise, dressings, coffee creamers, chocolate, whipped cream, infant formulae, meal replacement beverages and medical nutrition [1, 2••–4•]. Oil-in-water food emulsions are complex colloidal systems consisting of oil droplets and various aqueous phase components—such as biopolymers, carbohydrates, and salts—with different sizes and concentrations; their interactions determine the heat stability, creaming stability, viscosity and texture of the emulsions [5–7].

There is a strong interest in the food industry to develop protein-stabilized oil-in-water emulsion-based nutritional beverages especially at high protein content for medical use. The medical beverage is usually a complete nutrition and contains high level of proteins, carbohydrates, minerals and vitamins. The ingredient interactions are very complex, especially the heat-induced milk protein interactions which result in viscosity increase and physical instability at protein content >6% *w*/w [4•]. It is desirable to have good stability against environmental stresses (i.e., gravity, heat treatment, ionic strength) as well as an acceptable viscosity for specific processing, storage and consumption purposes [8–10] however, the necessary tuning of ingredients to achieve this is challenging.

The colloidal behavior of oil-in-water emulsions is determined by three types of interparticle interactions in the system: (i) the droplet–droplet interactions occurring within the dispersed phase; (ii) the interactions between the interfacial materials at the oil–water interface and between the interfacial material and the components in the continuous phase (i.e., proteins and polysaccharides); and (iii) the interactions within the continuous phase (i.e., protein–protein interactions) [5,6, 11]. It is important to understand the interfacial properties and bulk physicochemical properties well to be able to control the food emulsion functionality.

In the following, emphasis has been given to the recent advances in the formation, structure and physical stability of oil-in-water emulsions prepared with concentrated milk proteins. The behavior of emulsion

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http://dx.doi.org/10.1016/j.cocis.2017.03.007
1359-0294/

droplets in the presence of food-grade components are critically summarized for specific destabilizing or stabilizing mechanisms particularly upon heat treatment.

2. Milk protein-stabilized oil-in-water emulsions

Milk derived proteins have been extensively used in the preparation of food emulsions because of their amphiphilic nature, which allows them to adsorb and spread around the oil/water interface during homogenization [12–14]. The droplet size, interfacial composition, adsorbed protein conformation and emulsion stability have been found to be influenced by the type of protein [6,15–17]. Food emulsions prepared with milk proteins are generally divided into two classes according to their protein structure: caseins, which show flexible disordered conformations with little secondary structure [12,18] and whey proteins, which have a considerably ordered secondary structure with a compact tertiary structure linked together by intramolecular disulfide bonds [12,18].

2.1. Emulsifying properties of milk protein ingredients

2.1.1. Non-micellar caseins

Sodium caseinate (NaCas), a commercial milk protein ingredient, consisting of α_{s1}-, α_{s2}-, β- and κ-caseins, has been widely used as an emulsifier in food formulations [19,20]. During the production of NaCas, the colloidal calcium phosphate which is responsible for the integrity of native casein micelles is removed so the casein self-assemblies into small aggregates (~10 nm in radius) with a small weight fraction of large particles of ~65 nm hydrodynamic radius [21,22]. The adsorption behavior of NaCas is different from pure caseins as competitive adsorption between α_{s1}- and β-casein occurs in caseinate-stabilized emulsions. The adsorption behavior is dependent on the total protein concentration and/or the NaCas-to-oil ratio [23,24]. Srinivasan et al. found that β-casein gets more adsorbed at the oil/water interface than α_{s1}-casein at low protein-to-oil weight ratio (< 0.15), while the opposite is true, at high protein concentrations; this may be due to the fact that β-caseins are prone to self-assembly forming sub-micelles in concentrated solutions, therefore reducing their adsorption [23].

2.1.2. Casein micelles

The emulsifying ability and emulsion stability provided by casein micelles have been studied using commercial milk protein ingredients (i.e., skim milk powder, milk protein concentrate (MPC)/isolate (MPI), micellar casein) [15,25,26]. Casein micelles adsorb at oil/water interfaces during emulsification as they do in homogenized milk. However, much higher concentration of casein micelles are required to achieve similar droplet size comparing to individual casein at a constant homogenization conditions [15]. Casein micelles adsorb in thick dense layers that enhance the long term stability of emulsions [6,15]. The distribution of Ca and Na content in MPC changes the aggregation state of casein micelles. As Ca content decreases, the proportion of non-micellar caseins in serum phase increases [27]. During emulsification, non-micellar caseins competitively adsorb at the oil/water interface and form a thin surface layer when a low calcium MPC is used. Likewise, the surface loading and average layer thickness decreases accordingly, as illustrated in Fig. 1 [27].

2.1.3. Whey proteins

The commercial forms of whey proteins are whey protein isolate (WPI) and whey protein concentrate (WPC). The latter contains lactose, fat and variable amounts of calcium salts in addition to crude whey proteins. In general, the physical stability of WPI-stabilized emulsions are qualitatively similar to those stabilized by β-lg [28]. It is well known that all globular proteins will undergo unfolding, denaturation and subsequent aggregation when heated at above 70 °C [29••,30]. The final structure of whey protein-stabilized emulsions can be tuned between liquid-like and solid-like by changing the conditions of heat treatment, pH and ionic strength [31], the factors that control the degree of protein unfolding and aggregation.

2.1.4. Milk protein peptides

Milk protein ingredients can be modified by hydrolysis for specific functional and nutritional uses [32–36]. Casein protein hydrolyzate (CPH) and whey protein hydrolyzate (WPH) are products from the enzymatic hydrolysis of caseins and whey proteins which have been extensively used in hypoallergenic infant formulae and enteral formulations [36,37]. The functionality of WPH is affected by its degree of hydrolysis. Lower degrees of hydrolysis (1–10%) have been found to improve the emulsion stability and heat stability of WPH-stabilized oil-in-water emulsions [38,39] due to the lower susceptibility of the peptides to aggregate during heating [40]. Extensive hydrolysis (10–30%) of the whey proteins though, can cause rapid creaming and coalescence, which results in complete phase separation because of a decreased steric stability due to the reduced interfacial layer thickness and interfacial viscosity [32,38,39]. More extensive hydrolysis will cause a marked decrease in the gelling ability of the partially hydrolyzed protein because the increase in peptides leads to a lower hydrophobic attraction and a greater electrostatic repulsion.

2.1.5. Mixed milk proteins

Some competitive adsorption phenomena occur when mixed milk proteins are used for emulsification. Ye [41] reported that when 20% oil-in-water emulsions were formed by a combination of NaCas and WPC (1:1 by protein weight, at total concentrations <3%), whey proteins showed higher adsorption than caseins. Whereas at protein concentrations >3%, caseins absorbed at interfaces preferentially to whey proteins [41]. It is interesting to note that the addition of WPI to a NaCas-stabilized emulsions leads to a noticeable displacement of adsorbed caseins at temperature ≥40 °C. Increasing amounts of adsorbed β-lg and α-lac and desorbed α_{s1}- and β-caseins have been detected at the interface, with this phenomenon being accelerated at higher temperatures (e.g., 90 °C) [42•]. On the other hand, when oil droplets are coated with β-lg, the caseins (α_{s1}- or β-casein) did not

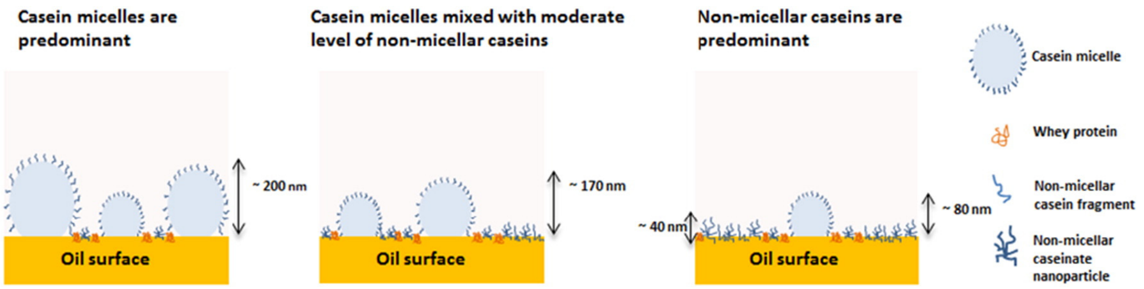

Fig. 1. Schematic illustration of the interfacial structure containing different portions of casein micelles, non-micellar casein fragments and caseinate nano-particles based on a study of oil-in-water emulsions prepared with MPCs [27].