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Review

Whey protein peptides as components of nanoemulsions: A review of emulsifying and biological functionalities

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ABSTRACT

Milk proteins are used to make emulsions, and may be used to make nanoemulsions. Nanoemulsions are a nanotechnology with food applications, and possess superior physicochemical and sensorial properties compared to macro- and microemulsions. They are also able to deliver bioactive compounds when consumed. In this review, three aspects of food nanoemulsions will be examined: (1) the production and properties of food nanoemulsions, (2) emulsifiers/surfactant (ionic, non-ionic, phospholipid, polysaccharide, and protein) used in nanoemulsions production. The suitability of proteins and protein hydrolysates as nanoemulsifiers is discussed, with a particular focus on whey protein, (3) the potential of whey protein derived peptides as both emulsifiers and bioactive compounds in nanoemulsion delivery systems. Lastly, the potential delivery of bioactive peptides and other bioactive compounds within nanoemulsion systems is also discussed.

Contents

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1. Introduction

Milk proteins, and whey proteins in particular, are valued as important food ingredients because of their functional and nutritional properties (Christiansen et al., 2004; Sarkar et al., 2009), and have been extensively used as emulsifiers in foods (Chu et al., 2007; Dissanayake and Vasiljevic, 2009; Lee and McClements, 2010). Recent studies have proven the potential of whey protein ingredients as emulsifiers in nanoemulsions that have been tailored for food applications (Lee and McClements, 2010; Relkin et al., 2011; Shah et al., 2012). Nanoemulsions are a specific type of colloidal dispersion characterised by very small droplet sizes, usually covering the size range of 10–200 nm (Chu et al., 2007; Lee and McClements, 2010; Wulff-Pérez et al., 2009). Nanoemulsions enhance the solubility, transport, dispersibility, bioavailability and bioaccessibility of active food and drug components (e.g. carotenoids, α-tocopherol, antioxidants, polyunsaturated fatty acids, hydrophobic vitamins, flavour and aroma compounds), and can act as excellent encapsulation systems compared to conventional emulsions (Bilbao-Sáinz et al., 2010; Qian et al., 2012a; Wulff-Pérez et al., 2009).

The advantages of nanoemulsions over other emulsions are derived from the smaller droplet sizes which impart distinct physicochemical properties in nanoemulsions (e.g. bulk viscosity, optical transparency, and physical stability) compared to those of other emulsion systems (Cortés-Muñoz et al., 2009; Donsì et al., 2012; Kentish et al., 2008; Peng et al., 2010; Sonneville-Aubrun et al., 2004). Most studies conducted so far have concentrated on the use of the synthetic and low molecular weight surfactants (e.g. the tweens and spans) due to their excellent interfacial diffusivity, compared to large biopolymers such as proteins and polysaccharides (Donsì et al., 2012; Ghosh et al., 2013; Lee and McClements, 2010; Qian and McClements, 2011). However, concerns about the safety, toxicity and metabolism of these synthetic emulsifiers in the human body limit their application to food systems.

The majority of the studies using proteins have reported on the native protein but not its hydrolysates. While hydrolysates may possess enhanced interfacial diffusivity and emulsifying capacity, they have shown poor stabilising ability in conventional emulsion systems, preventing long term storage (Agboola et al., 1998a; Scherze and Muschiolik, 2001). Moreover, studies on emulsion have often focused on the crude hydrolysate which consists of heterogeneous mixtures of amino acids, and small, medium to large chain peptides (Scherze and Muschiolik, 2001). The prospect of stepwise fractionation to enrich sufficiently large peptides may generate peptides with adequate surface activities that are capable of stabilising these nanodroplets, compared to the microdroplets (Gauthier and Pouliot, 2003).

Aside from enhancing the emulsifying properties of proteins, the products of enzymatic hydrolysis may also possess bioactivities (e.g. antioxidant activity, antihypertensive activity, mineral carrier, immuno-stimulant, anti-thrombotic, and anti-gastric, opioid, antimicrobial, and anti-cancer activities) which can be beneficial for promoting good health (Adjonu et al., 2013; Gauthier and Pouliot, 2003; Korhonen, 2009; Korhonen and Pihlanto, 2006). These bioactivities are usually absent or latent in the native unhydrolysed protein, but can be released or enhanced upon hydrolysis (Adjonu et al., 2013). Nanodispersions may serve as efficient delivery vehicles for incorporating these bioactive peptides into food, subsequently increasing their utilisation by the body as functional and nutraceutical agents (Chu et al., 2007; Qian et al., 2012a; Relkin et al., 2008) thus, allowing them to more effectively express their bioactivities *in vivo* (Prego et al., 2006).

This review will focus on: (a) the formation of nanoemulsions; (b) emulsifier (non-protein and protein emulsifiers) effects on nanoemulsion properties; (c) the emulsifying property of whey protein hydrolysates and the potential for whey protein peptides as both nanoemulsifiers and bioactive compounds in foods (i.e. dual-functionality) and (d) the potential applications for nanoemulsions for bioactive peptide delivery. The terminologies emulsifiers and surfactants are used interchangeably in the following discussion.

2. Nanoemulsions

2.1. Properties of nanoemulsions

Nanoemulsions are a technology that has food and pharmaceutical applications (Tarver, 2006), and their evolution has paralleled the development of efficient emulsification technologies (Cortés-Muñoz et al., 2009). An efficient emulsification process is able to form emulsions with small droplet sizes and narrow size distributions. These characteristics are, however, a function of the two opposing forces; droplet breakup and droplet–droplet coalescence (Jafari et al., 2006). These properties have been identified in several works (Donsì et al., 2012; Jafari et al., 2006; Qian and McClements, 2011) as being dependent upon several processes including:

- Homogenising mechanism.
- Type, concentration and interfacial properties of surfactant/emulsifier.
- Dispersed phase volume/mass fraction and viscosity.
- Timescale of surfactant adsorption onto the surfaces of newly created droplet.
- Frequency and timescale of inter droplet–droplet collision.

Nanoemulsions, like microemulsions are transparent/translucent systems and as a result, they can be incorporated as components of food beverages and gels, nutraceuticals and pharmaceutical preparations without a loss of clarity (Fig. 1) (Chu et al., 2007; Kentish et al., 2008; Wulff-Pérez et al., 2009). Increasing interest in nanoemulsions stems from the characteristic physicochemical properties that their small droplet sizes provide (Table 1). Their small droplet size allows for efficient delivery, accelerated release and rapid absorption of hydrophobic bioactive drug and food agents such as vitamin E, omega 3 fatty acids, flavonoids and various phyto-polyphenolic compounds (Balcão et al., 2013; Lee and McClements, 2010; Qian et al., 2012a; Tarver, 2006; Yang and McClements, 2013).

2.2. Formation of nanoemulsion

Nanoemulsion droplets are only kinetically stable, in that the free energy of the separated oil and aqueous phases is always lower than that of the formed emulsion and therefore, nanoemulsions do not form spontaneously (McClements and Rao, 2011). To break large emulsion droplets into nanodroplets, a large external force (homogenisation pressure, Pa; energy applied per volume of liquid) must be applied during homogenisation in order to overcome the Laplace pressure p (Pa; difference in pressure between the convex and concave sides of a curved interface) and to break up the interface between the oil and water phases (Eq. (1)) (Cortés-Muñoz et al., 2009; Walstra, 1993). The Laplace pressure characterises the interfacial force that acts on droplets to keep them from being disrupted (McClements, 2005).

$$P = \frac{2\gamma}{r} \tag{1}$$

where r (m) is the principal radius of curvature of the droplets (assuming droplets are spherical) and γ (N m^{-1}) is the interfacial tension between the two phases.