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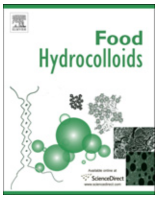

Formation of nanoemulsions stabilized by model food-grade emulsifiers using high-pressure homogenization: Factors affecting particle size

Cheng Qian, David Julian McClements*

Department of Food Science, University of Massachusetts Amherst, Amherst, MA 01003, USA

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ABSTRACT

Nanoemulsions are finding increasing utilization in the food and beverage industries for certain applications because of their unique physicochemical and functional properties: high encapsulation efficiency; low turbidity; high bioavailability; high physical stability. In this study, we examined the impact of system composition and homogenization conditions on the formation of nanoemulsions using a high-pressure homogenizer (microfluidizer). The mean particle diameter decreased with increasing homogenization pressure and number of passes, with a linear log–log relationship between mean particle diameter and homogenization pressure. The minimum droplet diameter that could be produced after 6 passes at 14 kbar depended strongly on emulsifier type and concentration: SDS < Tween 20 < β-lactoglobulin < sodium caseinate. Small-molecule surfactants formed smaller droplets than proteins, which was attributed to their ability to rapidly adsorb to the droplet surfaces during homogenization. The impact of phase viscosity was examined by using different octadecane-to-corn oil ratios in the oil phase and different glycerol-to-water ratios in the aqueous phase. The minimum droplet size achievable decreased as the ratio of disperse phase to continuous phase viscosities (η_D/η_C) decreased for SDS-stabilized emulsions, but was relatively independent of η_D/η_C for β-lactoglobulin-stabilized emulsions. At low viscosity ratios, much smaller mean droplet diameters could be achieved for SDS ($d \sim 60$ nm) than for β-lactoglobulin ($d \sim 150$ nm). The information reported in this study will facilitate the rational design of food-grade nanoemulsions using high-pressure homogenization methods.

1. Introduction

There is strong interest in the food and other industries in the use of nanoemulsions as delivery systems for non-polar functional components, such as lipophilic bioactive lipids, drugs, flavors, antioxidants, and antimicrobial agents (Hu, Johnston, & Williams, 2004; Kesisoglou, Panmai, & Wu, 2007; McClements, Decker, & Weiss, 2007; Sanguansri & Augustin, 2006; Weiss et al., 2008; Wissing, Kayser, & Muller, 2004). Oil-in-water nanoemulsions contain small oil droplets ($d < 100$ nm) dispersed within a watery continuous phase, with each oil droplet being surrounded by a protective coating of emulsifier molecules (Acosta, 2009; McClements et al., 2007; Tadros, Izquierdo, Esquena, & Solans, 2004). The stability, physicochemical properties and functional performance of nanoemulsion-based delivery systems can be controlled by altering their composition and preparation conditions so as to produce emulsions with different droplet concentrations, compositions, particle size distributions and/or interfacial properties (Lesmes & McClements, 2009; McClements, 2010).

A major potential advantage of nanoemulsions over conventional emulsions is that they can be made to be optically transparent by preparing droplets with dimensions much smaller than the wavelength of light ($d < \lambda$) so that scattering is relatively weak (McClements, 2002a, 2010; Wooster, Golding, & Sanguansri, 2008). Consequently, they can be used to incorporate non-polar functional components into transparent aqueous-based food and beverage products. Nevertheless, this type of emulsion may become turbid or even opaque if droplet growth occurs during storage, *e.g.*, due to flocculation, coalescence or Ostwald ripening. Hence, it is important to prevent these instability mechanisms from occurring in nanoemulsions after they have been formed. Nanoemulsions typically have much better stability to gravitational separation than conventional emulsions because the relatively small particle size means that Brownian motion effects dominate gravitational forces (McClements, 2005; Tadros et al., 2004). They also tend to have better stability against droplet flocculation and coalescence because the range of the attractive forces acting between the droplets decreases with decreasing particle size, while the range of

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* Corresponding author.
E-mail address: mcclements@foodsci.umass.edu (D.J. McClements).

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the steric repulsion is less dependent on particle size (McClements, 2005; Tadros et al., 2004). Recent studies suggest that the bioavailability of encapsulated non-polar components is higher in nanoemulsions than conventional emulsions because of the small particle size and high surface-to-volume ratio (Acosta, 2009; Huang, Yu, & Ru, 2010). Hence, food-grade nanoemulsions may be particularly useful for increasing the bioactivity of lipophilic components that are normally poorly absorbed.

A variety of preparation methods have been developed to prepare nanoemulsions, and these can conveniently be classified as either *high energy* or *low energy* approaches (Acosta, 2009; Leong et al., 2009; Tadros et al., 2004). High-energy approaches utilize mechanical devices capable of generating intense disruptive forces that breakup the oil and water phases and lead to the formation of tiny oil droplets, *e.g.*, high-pressure valve homogenizers, microfluidizers and sonication methods (Gutierrez et al., 2008; Leong et al., 2009; Velikov & Pelan, 2008; Wooster et al., 2008). On the other hand, low energy approaches rely on the spontaneous formation of tiny oil droplets within mixed oil–water-emulsifier systems when the solution or environmental conditions are altered (Anton, Benoit, & Saulnier, 2008; Bouchemal, Briancon, Perrier, & Fessi, 2004; Chu, Ichikawa, Kanafusa, & Nakajima, 2007; Freitas, Merkle, & Gander, 2005; Tadros et al., 2004; Yin, Chu, Kobayashi, & Nakajima, 2008). The minimum size of the droplets that can be produced using each approach depends on many different factors. Previous studies have shown that the minimum particle size achievable using the high-energy approach depends on homogenizer type, homogenizer operating conditions (*e.g.*, energy intensity, time, and temperature), sample composition (*e.g.*, oil type, emulsifier type, and relative concentrations), and the physicochemical properties of the component phases (*e.g.*, interfacial tension and viscosity).

The overall objective of the current research is to establish the major factors that determine the size of the droplets produced using a high-energy approach: microfluidization. Fine emulsions can be produced using microfluidization by passing a coarse emulsion through an interaction chamber using a high-pressure pumping device (Jafari, He, & Bhandari, 2007). The interaction chamber consists of two flow channels, which are designed so that they cause two streams of the coarse emulsion to impinge on each other at high velocity, thus creating a very high shearing action that provides an exceptionally fine emulsion (Jafari, He, & Bhandari, 2006). Studies have shown that the particle size distribution produced by microfluidizers tends to be narrower and smaller that those produced by other homogenization devices (Jafari et al., 2006, 2007; Perrier-Cornet, Marie, & Gervais, 2005; Wooster et al., 2008).

The final particle size achieved by a homogenizer is important because it determines the stability, appearance, texture, and bioavailability of the final product (Acosta, 2009; McClements et al., 2007). It is therefore important to establish the major factors that impact that particle size produced by different types of homogenizers. In this study, we systematically examined the influence of number of passes, homogenization pressure, emulsifier type, and disperse and continuous phase viscosities on the droplet size produced. Typically, the mean droplet diameter tends to decrease with increasing homogenization pressure and number of passes, but for certain emulsifiers (typically biopolymers) higher pressures and longer emulsification times may lead to “over-processing”, resulting in an increase in particle size (Jafari et al., 2007; Jafari, Assadpoor, He, & Bhandari 2008). Previous studies suggest that small-molecule surfactants adsorb to droplet surfaces more rapidly than biopolymers, which means they are more effective at producing the very small droplets in nanoemulsions (Azeem, Rizwan, Ahmad, Khar, et al., 2009a; Azeem, Rizwan, Ahmad, Iqbal, et al. 2009b; Jafari et al., 2007; Yuan, Gao, Zhao, & Mao, 2008). One of the aims of this paper was therefore to establish if biopolymers could be successfully used as emulsifiers to form food-grade nanoemulsions.

2. Materials and methods

2.1. Materials

Mazola Corn oil was supplied by ACH Food Company (Memphis, TN). Octadecane (approx 99%, EEC No 209-790-3, FW254.5) was purchased from Sigma Chemical Company (St Louis, MO). β-Lactoglobulin was a gift from Le Sueur Food Ingredient Company (Le Sueur, MN). Spray-dried sodium caseinate (ALANATE 180) with 1.2% sodium content and <0.1% calcium content was kindly provided by American Casein Company (Burlington, NJ). Tween 20 (P1379, CAS 9005-64-5), sodium dodecyl sulfate (SDS) (L-4509, EC No 205-788-1, FW 288.4), and sodium phosphate monobasic (S 0751, CAS 7558-80-7, FW 119.98) were purchased from the Sigma Chemical Company. Sodium phosphate dibasic anhydrous (S347-1, CAS 7558-79-4) was purchased from Fisher Scientific (Fair Lawn, NJ). Double distilled water was used for the preparation of all solutions.

2.2. Emulsion preparation

Oil-in-water emulsions were prepared by homogenizing 5 wt% lipid phase (corn oil and/or octadecane) with 95 wt% aqueous phase (1–10 wt% emulsifier, 0–50 wt% glycerol, 10 mM sodium phosphate buffer, pH 7.0). A coarse emulsion premix was prepared by blending the lipid and aqueous phases together using a high-speed mixer (Bamix, Biospec Products, Bartlesville, OK) for 2 min at room temperature. Fine emulsions were formed by passing the coarse emulsions through an air-driven microfluidizer (Microfluidics, Newton, MA, USA). The coarse emulsions were fed into the microfluidizer through a 100 ml glass reservoir, and were passed through the homogenization unit for different numbers of passes (1–14) at various homogenization pressures (4–14 kbar).

2.3. Particle size measurements

The particle size distribution and mean droplet diameter of diluted emulsions were measured by a commercial dynamic light scattering device (Nano-ZS, Malvern Instruments, Worcestershire, UK). Mean particle diameters were reported as “*Z*-average” diameters (the scattering intensity-weighted mean diameter), which were calculated from the signal intensity *versus* particle diameter data normalized to size increments using Mie Theory. Samples were diluted prior to making the particle size measurements to avoid multiple scattering effects with phosphate buffer (pH 7, no cosolvents) using a dilution factor of 1:100 sample-to-buffer.

2.4. Turbidity measurements

The turbidity of selected samples was measured using a UV–visible spectrophotometer (Agilent 7010 Particle Size Analyzer, Agilent Technologies. Inc, CA, USA). The samples were diluted in buffer solution to a range of different oil droplet concentrations, and the turbidity was determined at 600 nm.

2.5. Viscosity measurements

Viscosity measurements of selected samples were performed using a dynamic shear rheometer (Kinexus Rheometer, Malvern Instruments. Inc, MA, USA) using a shear rate profile from 0.1 to 1000 s^{-1}. All the measurements were performed at 40 °C.