Journal of Food Engineering 211 (2017) 60–68

Contents lists available at ScienceDirect

Journal of Food Engineering

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

Improvements in the formation and stability of fish oil-in-water nanoemulsions using carrier oils: MCT, thyme oil, & lemon oil

Rebecca M. Walker, Cansu E. Gumus, Eric A. Decker, David J. McClements*

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

ARTICLE INFO

Article history:
Received 13 March 2017
Received in revised form
1 May 2017
Accepted 7 May 2017
Available online 10 May 2017

Keywords:
Fish oil
Nanoemulsions
Oxidation
Lemon oil
Thyme oil
Essential oils

ABSTRACT

Nanoemulsion-based delivery systems are particularly effective tools for incorporating omega-3 polyunsaturated lipids into many foods and beverages. In this study, the impact of carrier oil type and concentration on the formation and stability of fish oil-in-water nanoemulsions was determined. Three carrier oils with different physicochemical and sensory properties were evaluated: medium chain triglycerides (MCT); lemon oil; and thyme oil. Nanoemulsions ($d < 200$ nm) were fabricated from oil phases containing lemon oil and MCT at all ratios with fish oil (0–100%), but only from thyme oil at high fish oil contents (75–100%). This effect was attributed to the high susceptibility of the nanoemulsions containing high levels of thyme oil to Ostwald ripening. Nanoemulsions fabricated from all carrier oils were physically stable (no increase in droplet size) during storage at 20 °C for 42 days when formulated from 75% fish oil and 25% carrier oil. However, carrier oil type did have an appreciable impact on the oxidative stability of these nanoemulsions, with the rate of lipid oxidation decreasing in the following order: MCT » lemon oil > thyme oil. This effect was attributed to the presence of high levels of natural antioxidants (phenolics) within the lemon and thyme oils. These results show that selection of an appropriate carrier oil type and concentration can lead to the formation of fish oil nanoemulsions with good physical and chemical stability.

1. Introduction

Consumption of sufficiently high levels of omega-3 fatty acids from fish oils has been linked to reduced mortality due to cardiovascular disease (Danaei et al., 2009; Maehre et al., 2015), as well as to other health benefits, including brain development and treatment of inflammatory diseases (Kris-Etherton et al., 2009; Papanikolaou et al., 2014). Currently, the populations of many developed countries are not consuming enough fish oil to obtain these health benefits (Kris-Etherton et al., 2009; Papanikolaou et al., 2014). Low levels of fish oil consumption have been attributed to numerous factors including the high cost of fish, a dislike of seafood by many consumers, concerns about the presence of methyl mercury in fish, and the low availability of fresh fish in many locations (Glanz et al., 1998; Kennedy et al., 2012; Racine and Deckelbaum, 2007). Consequently, fortification of foods and beverages with fish oil is being examined as a means of increasing omega-3 fatty acid consumption by the general population (Maki et al., 2014). Fish oils have low water-solubility and poor oxidative stability, and therefore appropriate delivery systems need to be designed to incorporate them into many types of functional food and beverage products (Jacobsen, 2015; McClements, 2012a; Taneja and Singh, 2012).

Oil-in-water nanoemulsions, which consist of small lipid droplets ($d < 200$ nm) dispersed in water, are particularly suitable for encapsulating hydrophobic bioactive agents (Anton and Vandamme, 2011; Mason et al., 2006; McClements, 2012b; Tadros et al., 2004). Indeed, they are gaining increasing popularity for this purpose because of their ease of preparation and handling, high physical stability, and good oral bioavailability (Walker et al., 2015a). The food, supplement, and pharmaceutical industries are actively developing nanoemulsion-based delivery systems to encapsulate, protect, and control the release of various types of hydrophobic bioactive agents (Acosta, 2009; Gleeson et al., 2016; McClements et al., 2007; Waraho et al., 2011).

Despite the many potential benefits of using nanoemulsions as delivery systems in the food industry, there are some obstacles that need to be overcome before they can be successfully used to fortify many functional foods with omega-3 fatty acids (Walker et al.,

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

http://dx.doi.org/10.1016/j.jfoodeng.2017.05.004
0260-8774/

2015a). In emulsions, lipid oxidation usually takes place at the oil-water interface due to interactions between hydrophilic pro-oxidants from the aqueous phase and hydrophobic lipid substrates from the oil phase (Arab-Tehrany et al., 2012; Berton-Carabin et al., 2014; McClements and Decker, 2000). Nanoemulsions have a relatively high oil-water interfacial area because of their small droplet dimensions (McClements, 2011), and therefore they are particularly susceptible to lipid oxidation (Walker et al., 2015a). In food products, lipid oxidation causes a variety of problems that adversely affect product shelf life, safety, nutritional value, and flavor profile (Arab-Tehrany et al., 2012; Dacaranhe and Terao, 2001). Therefore, nanoemulsion-based delivery systems must be carefully designed to inhibit lipid oxidation and therefore avoid these adverse effects.

Nanoemulsions are thermodynamically unstable systems, which means that they also have a tendency to undergo physical changes during storage (McClements, 2012b), which may cause undesirable alterations in the appearance, texture, and shelf life of food products. Compared to conventional emulsions, nanoemulsions are more stable to gravitational separation, coalescence, and flocculation because of their small droplet size, but they are more susceptible to Ostwald ripening (McClements and Rao, 2011). Ostwald ripening manifests itself as an increase in the mean droplet size during storage, which occurs as a result of the diffusion of oil molecules from smaller droplets to larger ones (Kabalnov, 2001; Tadros et al., 2004). Consequently, nanoemulsion-based delivery systems must also be carefully designed to ensure that they have good physical stability within food products.

Incorporation of carrier oils into the oil phase of nanoemulsions can be used to facilitate their formation, as well as to improve their oxidative and physical stability (Walker et al., 2015b; Wooster et al., 2008). Carrier oils are mixed with the lipophilic bioactive agent, in this case fish oil, during the preparation of the oil phase. The mechanism and degree of enhanced nanoemulsion formation and stability depends on the properties of the carrier oil. Mixing high viscosity bioactive oils with low viscosity carrier oils has been shown to decrease the size of the droplets produced during homogenization (Qian and McClements, 2011; Wooster et al., 2008). Mixing high water-solubility bioactive oils with low water-solubility carrier oils has been shown to improve physical stability by inhibiting Ostwald ripening (Li et al., 2009; McClements, 2011; McClements and Rao, 2011; Wooster et al., 2008). Mixing bioactive oils (such as fish oil) that are prone to lipid oxidation with carrier oils containing natural antioxidants may improve their oxidative stability (Walker et al., 2015b). In this study, we therefore examined the impact of three different types of carrier oil on the formation and stability of fish oil-in-water nanoemulsions: medium chain triglycerides (MCT); thyme oil; and lemon oil.

MCT oils typically consist of a mixture of triacylglycerols that are rich in saturated medium chain fatty acids ($C_{8:0}$ and $C_{10:0}$) (Clegg, 2010; Traul et al., 2000). As a result, they tend to be liquid at ambient temperature, have a relatively low water-solubility, and have little antioxidant/pro-oxidant activity. MCT oils have been successfully used to formulate nanoemulsions suitable as colloidal delivery systems in food products (Qian et al., 2012; Saberi et al., 2013). MCT oils have a neutral flavor profile, which means that they may be suitable for application in a wide range of products.

Lemon oil is a hydrophobic substance extracted from lemon peels that is widely used as a flavoring agent in food and beverage products, such as soft drinks, confectionaries, and baked goods (Nguyen et al., 2009). Lemon oil consists of a complex mixture of hydrophobic molecules, with the most prevalent being limonene, α-pinene, and γ-terpinene (Di Vaio et al., 2010; Misharina et al., 2011; Nguyen et al., 2009). Previous studies have shown that stable nanoemulsions with relatively small droplet sizes can be successfully formulated from lemon oils (Rao and McClements, 2011, 2012; Su and Zhong, 2016). A number of the constituents present in lemon oil have been shown to have good antioxidant activity (Di Vaio et al., 2010; Yang et al., 2010), which may be useful for inhibiting the oxidation of fish oils encapsulated in nanoemulsion-based delivery systems. Moreover, lemon oil has a desirable citrus flavor, which may mask any off-flavors associated with fish oil and facilitate its incorporation into certain types of food and beverage products.

Thyme oil is a hydrophobic substance isolated from the leaves of the thyme plant, whose main constituents are thymol, carvacrol and p-cymene (Teixeira et al., 2013). Studies have shown that nanoemulsions can be successfully formulated using thyme oil as part of the oil phase (Chang et al., 2012; Ziani et al., 2011). Other studies have shown that thyme oil can act as an effective antioxidant in oil-in-water emulsions (Abdalla and Roozen, 1999; Gallego et al., 2013; Turan, 2014). The antioxidant activity of thyme oil has mainly been attributed to the presence of thymol and carvacrol (Dogu-Baykut et al., 2014), and may be due to their radical scavenging capacity (Bozin et al., 2006). Like lemon oil, thyme oil has a characteristic flavor profile that may be useful for masking any off-flavors associated with fish oil, but which may restrict its application in certain products.

In this study, we hypothesized that the fabrication, physical stability, and oxidative stability of fish oil-in-water nanoemulsions would depend on the type and amount of carrier oil present in the oil phase. Consequently, we examined the impact of different levels (0–100%) of three food-grade carrier oils (MCT, thyme oil, and lemon oil) on the formation and stability of fish oil nanoemulsions. The information obtained from this study should provide valuable information for selecting appropriate carrier oils for different food and beverage applications.

2. Materials and methods

2.1. Materials

Fish oil (Omega 30 TG Food Grade Fish Oil (Non-GMO)) was kindly provided by DSM Nutritional Products Ltd. (Basal, Switzerland). The fish oil was composed of 157 mg of EPA/g of oil, 99 mg of DHA/g oil, and 326 mg of total omega-3 as triglycerides/g of oil. A fractionated (ten-fold) lemon oil (LO) was kindly donated by International Flavors & Fragrances Inc. (New York, NY, USA). The composition of this oil has been reported elsewhere (Rao and McClements, 2012). Thyme oil was purchased from Essential7 (Golden, CO, USA). The physicochemical properties of the oils are summarized in Table 1. Polysorbate 80 (Tween 80), polysorbate 20 (Tween 20), sodium benzoate, barium chloride, iron (II) sulfate heptahydrate, hydrochloric acid, cumene hydroperoxide, thiobarbituric acid (TBA), butylated hydroxytoluene (BHT), 1,1,3,3-tetraethoxypropane (TEP), sodium carbonate, Folin-Ciocalteu reagent, and gallic acid were purchased from Sigma-Aldrich Co. (St. Lois, MO, USA). Citric acid, 1,2-propanol, isooctane, butanol, and

Table 1
Summary of some physicochemical properties of the oils used in this study at room temperature. The properties of the oils were obtained from various sources: MCT (van Aken et al., 2011); lemon oil (Rao and McClements, 2012); thyme oil (Kim and Sharma, 2011; Ziani et al., 2011); fish oil (Cournarie et al., 2004). Here "NA" means not applicable (*i.e.,* data could not be found).

Properties	Fish oil	MCT	Lemon oil	Thyme oil
Density (g/cm^3)	0.923	0.945	0.910	0.923
Viscosity (mPa s)	46	30	5.3	14
Interfacial Tension (mN/m)	23	17	29	NA