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Influence of surfactant and processing conditions in the stability of oil-in-water nanoemulsions

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ABSTRACT

This work evaluates the influence of the type of surfactant (Tween 20, SDS and DTAB) and processing conditions on the stability of oil-in-water nanoemulsions, measured in terms of hydrodynamic diameter (H_d), polydispersity index (PdI) and zeta potential (Zp). Nanoemulsions were prepared using high-pressure homogenization based on a 2^4 level factorial design. Results show that processing parameters such as homogenization pressure, surfactant concentrations and oil:water ratio significantly affected the values of H_d and PdI of nanoemulsions. The value of H_d of anionic nanoemulsions decreased (from 177 to 128 nm) with the increase of the homogenization pressure. The increase in the surfactant concentration and the decrease of the oil:water ratio lead to a decrease of H_d for the cationic nanoemulsions (from 198 to 135 nm). The increase of the oil:water ratio lead to a decrease of H_d for the non-ionic nanoemulsions (from 341 to 171 nm); this is contrary to the usual assumption that higher content in oil results in higher values of H_d. Those nanoemulsions showed a good kinetic stability (evaluated after centrifugation, heating–cooling cycles and thermal stress) upon measuring the H_d during 28 and 35 days of storage, without visual evidence of creaming and phase separation. After one year of storage the nanoemulsions produced with the anionic surfactant remained kinetically stable, without visual evidence of creaming and/or phase separation.

1. Introduction

Driven by consumers' demands for new and healthier food products the food industry seeks for new methodologies able to encapsulate, protect and release functional compounds. Based on this, researchers are focusing their efforts in relevant issues to food and nutrition regarding the improvement of food quality, through nanotechnology (Cerqueira et al., 2013; Silva et al., 2012).

Nanoemulsions are interesting for the food industry due to their potential applications as delivery systems of bioactive compounds while preventing their degradation and improving their bioavailability (Donsì et al., 2011; Guttoff et al., 2015; Silva et al., 2012). Nanoemulsions generally consist of lipid droplets between 10 and 200 nm dispersed in an aqueous phase, where surfactant molecules surround each oil droplet (Acosta, 2009; Cerqueira et al., 2014). Nanoemulsions can be produced using either low-energy or high-energy methods. Low-energy methods mainly depend on the intrinsic physicochemical properties of surfactants and oily phase, forming nanoemulsions by simple mixing procedures or by changing the system conditions such as temperature or composition (Komaiko and McClements, 2015; Silva et al., 2012; Solans and Solé, 2012). High-energy methods make use of devices that apply high mechanical energy inputs to disrupt and combine the oil and water phases, forming small droplets (Abbas et al., 2013; Cerqueira et al., 2014; Komaiko and McClements, 2015; Silva et al., 2012). High-pressure homogenization is pointed as the most appropriate method for industrial applications, due to the facility of operation, scalability, reproducibility, and high throughput (Cerqueira et al., 2014; Donsì et al., 2011).

Preparing a nanoemulsion by a high-energy method implies using an oily and an aqueous phase, a surfactant and energy (Tadros et al., 2004; Walstra, 1993). The nano emulsification process by high-pressure homogenization comprises both the deformation and disruption of the droplets with the subsequent increase of the surface area and at the same time the droplet stabilization occurs by means of adsorption of the emulsifiers at the interface of the droplets (Donsì et al., 2011; Stang et al., 2001). The difference in the interfacial free energy between the initial and final state is by definition equal to the increase on the surface area between the oily and aqueous phases multiplied by the interfacial tension (McClements, 2005). The energy necessary to increase the interfacial area ($\gamma\Delta A$) is very high and positive (i.e. it increases after homogenization), while the small entropy of the

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dispersion, and the corresponding energy ($T\Delta S$) is also positive but cannot compensate the interfacial free energy (McClements, 2005; Schramm, 2006b; Tadros et al., 2004) and therefore Eq. (1) is always positive.

$$\Delta G_{\text{formation}} = \gamma \Delta A - T\Delta S \quad (1)$$

Thus nanoemulsion formation is always thermodynamically unfavorable, due to the increase of the interfacial area after emulsification and to the energy required to produce the droplets (McClements, 2005; Tadros et al., 2004; Walstra, 1993). In order to break up a droplet into smaller ones, it must be strongly deformed and this is opposed by the Laplace pressure, Δp, which is the difference in pressure between the inside and outside of the droplet, being the pressure greater on the inside of the droplet, given by:

$$\Delta p = \gamma(1/R_1 + 1/R_2) \quad (2)$$

where R_1 and R_2 are the principal radii of curvature of the droplet. For a nanoemulsion, a spherical droplet yields $R_1 = R_2 = R$ (Schramm, 2006b; Tadros et al., 2004; Walstra, 1993).

$$\Delta p = 2\gamma/R \quad (3)$$

Eq. (3) shows that the amount of energy needed to break the droplets increases when smaller droplets are produced; however, when lowering the interfacial tension Δp is reduced and therefore the amount of energy needed to break up a droplet is reduced. Lowering the interfacial tension is one of the roles of the surfactants; nevertheless, their most essential role is preventing the coalescence of the newly formed droplets (Schramm, 2006b; Tadros et al., 2004; Walstra, 1993).

Surfactants preferentially adsorbs to the interfaces, once their molecular structures have non-polar hydrocarbon tails that favor non-polar liquids. Lowering the interfacial tension they will minimize the interfacial area between the continuous and dispersed phases and keep the interfaces smooth (Mason et al., 2006). Low molecular weight surfactants are able to decrease the interfacial tension in a greater extension than high molecular weight surfactants. This is mainly due differences in the orientation and configuration of the surfactants at the interface (Sari et al., 2015). Low molecular weight surfactants entirely adsorb and instantaneously orient themselves and the partitioning of the entire molecule between the two phases facilitates a maximum reduction in the interfacial tension (Sari et al., 2015). Also, a significant excess of surfactant in the continuous phase is needed this enables the new surface area of droplets to be quickly coated during emulsification, inhibiting disruption induced coalescence. This generally forms surfactant micelles that dissociate into monomers that rapidly adsorbs to the surface of the droplets (Mason et al., 2006; Rao and McClements, 2012). After adsorption of the surfactant to the surface of a droplet, surfactants most provide repulsive forces strong enough to prevent droplets aggregation. Ionic surfactants provide a great stability due electrostatic repulsions between droplets. Non-ionic surfactants provide stability due short-range repulsive forces, such as steric overlap, hydration, thermal fluctuation interactions, that prevents droplets from getting to close. Briefly, a surfactant must have three characteristics to be effective, first, rapidly adsorption to the surface of the new droplets; second, drastically reduce the interfacial tension and third form a membrane that prevents droplets from aggregating (McClements, 2002).

Commercial applications of nanoemulsions are one of the emerging fields of nanotechnology applied to food industry; the appearance in the food market of nanoemulsion-based food products has been growing in the last years. The application of nanoemulsions in the food industry can be subdivided into five major categories: fortified beverages, with NutraLease, NovaSol and SunActive Iron beverages, from NutraLease, AquaNova and High Vive company's, respectively (AquaNova, 2013a; High Vive, 2013; NutraLease, 2011); food colorants, with NovaSol BCS and Color Emulsion from AquaNova and Wild Flavours Inc, respectively (AquaNova, 2013b; Wild Flavors Inc., 2013); food packaging with BioNutriCoat from Improveat (Improveat, 2014); food supplements, with NanoResveratrol from Life Enhancement (Life Enhancement, 2013), Spray for Life from NanoSinergy (NanoSinergy, 2013) and NutriNano CoQ-10 from Solgar (Solgar, 2013); and fortified oils with Canova Active Oil from Shemen Industries (Shemen Industries, 2013).

One of the aims of this work was to study the effects of different charge surfactants, an anionic surfactant, Sodium Dodecyl Sulphate (SDS); a cationic surfactant, dodecyltrimethylammonium bromide (DTAB) and a non-ionic surfactant, Tween 20 (Pinheiro et al., 2013). The effect of the process conditions i.e., pressure, number of cycles, surfactant concentrations and oil content in the mean hydrodynamic diameter (H_d), polydispersity index (PdI), zeta potential (Zp) and the stability of the nanoemulsion were also evaluated. Furthermore, the theoretical minimum mean droplet diameter, creaming, the specific surface area and the energy dispended to produce the nanoemulsions were evaluated.

The surfactants used in this study were applied as model surfactants based on their different charge. Despite, they are commonly used in biotechnology and cosmetics industry, for EFSA, SDS and DTAB cannot be applied in foods, while Tween 20 is consider a food additive (EFSA, 2010). Nevertheless, considering FDA regulation SDS can be applied in food products as surfactant in fruit juice drinks under 25 ppm and in coatings on fresh citrus fruit (FDA, 2014a, 2014b). Regarding DTAB, it can be used as an indirect food additives: adjuvants, production aids and sanitizers in contact with food products (FDA, 2014c).

2. Materials and methods

2.1. Materials

Neobee 1053 medium chain triglycerides (MCTs) is caprylic/-capric triglyceride oil with a fatty acid distribution of 55% of C8:0 and 44% of C10:0 was kindly provided by Stepan (The Netherlands) and was used without further purification. Tween 20 and sodium dodecyl sulphate (SDS) were purchased from Sigma–Aldrich (St. Louis, MO, USA) and dodecyltrimethylammonium bromide (DTAB) was acquired from Acros Organics (Geel, Belgium). Milli-Q water (Milli-Q apparatus, Millipore Corp., Bedford, MA, USA) was used to prepare all solutions.

2.2. Experimental procedures

2.2.1. Preparation of non-ionic, cationic and anionic nanoemulsions by high-pressure homogenization

Oil-in-water (O/W) emulsions were prepared according to (Pinheiro et al., 2013) with some modifications. Briefly, the nanoemulsions were pre-mixed during 2 min at 5000 rpm using an Ultra-Turrax homogenizer (T 25, Ika-Werke, Germany) followed by passage through a high-pressure homogenizer (Nano DeBEE, BEE International, USA) according to the fractional factorial design (Table 1). To assess the effect of operational conditions on emulsion stability at the nanoscale, samples were evaluated during a 28, 35 and 365 days of storage. The stability at day 365 was only performed for the nanoemulsions with the best stability results at day 35. The prepared emulsions were stored at 4 °C in the absence of light, during the evaluation period.

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