

Stability mechanisms of liquid water-in-oil emulsions



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ABSTRACT

Although the stability of emulsions is widely discussed in the literature, most of them dealt with oil-in-water emulsions or water-in-oil systems with solid and semi-solid structures, which are easier to stabilize. In this study, the stability mechanism of liquid water-in-oil emulsions was investigated in different systems. The combination of two different oils (soybean oil and hexadecane) and three emulsifiers (PGPR, Span 80 and lecithin) at two water:oil ratios was investigated. Emulsions with higher kinetic stability – water and soybean oil emulsion stabilized with PGPR and water and hexadecane with Span 80 – presented an interface with low initial interfacial tension and practically constant complex viscoelastic modulus with time. Therefore, small droplets were formed and their coalescence was hindered by a stable elastic interface. The molecular structure of both oil and emulsifier were important to define the emulsion stability. Better chemical affinity of the hydrophobic moieties of the emulsifier and the oil led to more stable interface. Steric stability was obtained in more viscous systems, such as those at higher water volume fraction content. However, the water incorporation capacity into the emulsion depended on the molecular structure of hydrophilic portion of the emulsifier. Moreover, the water – soybean oil systems with Span 80 or lecithin emulsifiers did not form a macroemulsion, but a gelled structure. This study discussed the many factors that affect the emulsion formation and stability, which can contribute to the development of new water-in-oil emulsion based products with higher stability.

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1. Introduction

There are many products in the pharmaceutical, cosmetic and food industry that contain water-in-oil (W/O) emulsions. The stability mechanism of those emulsions differs from the oil-in-water (O/W) emulsions, which can be stabilized by both steric and electrostatic repulsion. In the case of W/O emulsions, only steric forces are expected to stabilize the emulsion, because of the low electrical conductivity of the continuous phase (Claesson, Blomberg, & Poptoshev, 2004). In fact, most of the W/O emulsion based products are in the solid or semi-solid state, such as butter and margarine, and are stabilized by fat crystallization, which prevents the sedimentation of water droplets by the formation of a three-dimensional network (McClements, 2005; Rousseau, 2000).

However, fluid W/O emulsions generally present low stability because of the high mobility of water droplets, which can easily sediment, flocculate or coalesce. A number of studies about emulsions focuses on O/W systems, but there are few works about liquid W/O emulsions. A better understanding about the interactions

between water, oil and emulsifier at the interface and the factors that affect the emulsion stability would allow producing stable liquid W/O emulsions and, therefore, would encourage the development of new products and applications.

The emulsifiers used to prepare W/O emulsions have low hydrophile–lipophile balance (HLB). Among the hydrophobic food-grade emulsifiers, lecithin is the only natural one (Dickinson, 1993). It is an emulsifier with amphoteric character contained in different natural sources, such as soybean and egg, and is composed by a mixture of phospholipids. Its main component is the phosphatidylcholine (PC) (Fig. 1a), followed by phosphadylethanolamine (PE) (Fig. 1b), phosphatidylinositol (PI), phosphatidic acid (PA) and other minorities. The fatty acid composition of soybean lecithin is similar to that of the soybean oil (Bergentahl & Fontell, 1983). Lecithin is soluble in mineral oils, but practicable insoluble in non-heated vegetable oils. It is also insoluble but highly dispersible in water (Wendel, 2000). Moreover, a powerful hydrophobic emulsifier used in food industry is the polyglycerol polyricinoleate (PGPR), an oligomeric and non-ionic emulsifier (Fig. 2a) produced by the esterification of castor oil fatty acid (Fig. 2b) with polyglycerol. With lecithin, PGPR is widely used to reduce the viscosity in chocolate products (Weyland & Hartel, 2008). Other food-grade emulsifier

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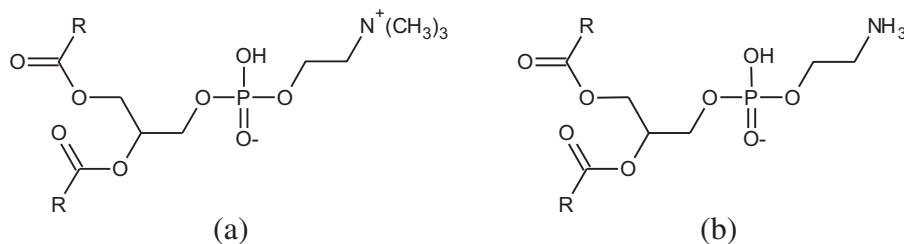


Fig. 1. Formula of (a) phosphatidylcholine and (b) phosphatidylethanolamine, in which RCOO⁻ are fatty acid residues.

with low HLB is sorbitan fatty acid esters, which are monomeric and non-ionic emulsifiers. Particularly, sorbitan monooleate (Span 80) is obtained from a reaction between sorbitol and fatty acids (Fig. 3). PGPR and Span 80 are soluble in mineral and vegetable oils, but insoluble in water. All those emulsifiers are commonly used in the food industry, such as in bakery, dairy, confectionary and oil processing (Bueschelberger, 2006; Cottrell & van Peij, 2006), in the cosmetic industry, such as skin care creams, lip balms, sunscreens, shampoos and soaps, and in pharmaceuticals (Tadros, 2008; Wendel, 2000).

Furthermore, the bulk physicochemical characteristics are also important for the formation and stability of the emulsion. For example, the density is decisive in the stability to sedimentation, the viscosity has influence in the droplets breakup and the mobility of droplets, and the oil polarity can affect the interfacial tension with the aqueous phase and the partitioning of the components at the interface. Besides, the chemical structure, such as fatty acids chain length, number of unsaturations, molecule configuration have also effect in the stability of the emulsion. Many studies use model systems with highly purified oils and with known chemical composition, but the behavior of those systems is different from the complex food-grade oils (McClements, 2005).

Thus, this study is aimed to evaluate the stability of W/O emulsions formulated with different types of oil and emulsifiers at two water:oil ratios. In order to understand the stability mechanisms, the interface of the systems was studied regarding the interfacial tension and the viscoelastic properties. Besides, the structure of the emulsions was analyzed microscopically through images and particle size distribution, and macroscopically, by the rheology of the emulsions.

2. Materials and methods

Oils with different characteristics were chosen to prepare the emulsions: n-hexadecane (C₁₆H₃₄) (Sigma Aldrich, USA), a linear chain hydrocarbon (molecular weight, MW = 226.4 g mol⁻¹), with very low polarity and viscosity (3 mPa s); and soybean oil (Soya, Bunge Alimentos S.A., Brazil), a triglyceride composed mainly by 43–56% linoleic (C_{18:2}), 15–33% oleic (C_{18:1}), 7–11% palmitic (C_{16:0}) and 5–11% α -linolenic (C_{18:3}) acids (Poth, 2001), (average MW = 278.2 g mol⁻¹) with higher polarity and viscosity (50 mPa s) than the former oil. Deionized water was used as aqueous phase.

The emulsifiers were sorbitan monooleate (Span 80), HLB 4.3, MW = 428.6 g mol⁻¹, kindly provided by Croda do Brasil

(Brazil); natural lipophilic lecithin (Solec SG), HLB 4, average MW \approx 750 g mol⁻¹, with phospholipid composition of 16% (w/w) phosphatidylcholine (PC), 14% phosphatidylethanolamine (PE), 9% phosphatidylinositol (PI) and 5% phosphatidic acid (PA), according to the supplier (Solae, Brazil) and polyglycerol polyricinoleate (GRINDSTED[®] PGPR), HLB 1.5–2.0, average MW \approx 3000 g mol⁻¹, donated by Danisco Brasil Ltda (Brazil).

2.1. Emulsion preparation

Emulsions were prepared at 30:70 and 60:40 ($w_{\text{water}}/w_{\text{oil}}$) ratios, aiming to evaluate the effect of the volume fraction of water in the W/O emulsion stability. In order to observe the interaction between the emulsifier and the oil, each emulsifier (Span 80, lecithin and PGPR) was used to stabilize water-in-oil (W/O) emulsions composed by water as aqueous phase and n-hexadecane or soybean oil as the oil phase.

For the emulsion preparation, the emulsifier was previously dissolved into the oil. Then, the aqueous phase was added dropwise to the oil phase while homogenizing in a rotor-stator system (Ultra Turrax T18, IKA, Germany) at 14,000 rpm. When the aqueous phase was completely incorporated into the emulsion (after 10 min at 30:70 water:oil ratio and after 20 min at 60:40), the rotational speed was decreased to 11,000 rpm and the system was homogenized for 4 min. The emulsions were prepared at room temperature (25 ± 1 °C).

2.2. Interfacial tension and dilational rheology

The interfacial tension was measured at ambient temperature (25 ± 1 °C) using the pendant drop method using a Tracker-S tensiometer (Teclis Sarl, France), in which the deionized water was injected with a syringe at a volume of 5 μ l and 1.5 μ l for soybean oil and hexadecane systems with emulsifiers, respectively, and 25 μ l for oil pure systems. For the calculation of the viscoelastic properties, an oscillation of 10% of the volume was set at a frequency of 0.2 Hz.

2.3. Evaluation of kinetic stability

The phase separation of the emulsions was observed in a 25 mL cylindrical tube (internal diameter = 17 mm), sealed with a plastic cap and stored for 14 days at 25 °C. The oil phase separation was expressed in sedimentation index (SI), which is calculated as the

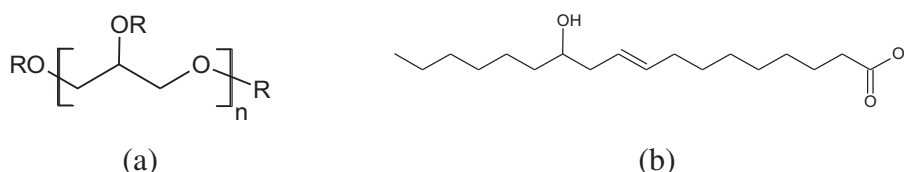


Fig. 2. (a) Formula of PGPR, in which R is a hydrogen, ricinoleic acid or polyricinoleic acid. (b) Formula of ricinoleic acid.

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