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Impact of oil type and WPI/Tween 80 ratio at the oil-water interface: Adsorption, interfacial rheology and emulsion features

Andresa Gomes, Ana Letícia Rodrigues Costa, Rosiane Lopes Cunha*

Department of Food Engineering (DEA), Faculty of Food Engineering (FEA), University of Campinas (UNICAMP), Rua Monteiro Lobato, 80, Campinas, SP, CEP: 13083-862, Brazil

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ABSTRACT

The relationship between the composition and structure of food emulsions was evaluated from the effect of a mixture of emulsifiers Whey protein (WPI) - Tween 80 (T80) and the oil phase features, such as chain length and unsaturation degree (sunflower oil, a long chain triacylglycerol - LCT or NEOBEE® 1053, a medium chain triacylglycerol - MCT). Emulsions with LCT showed higher droplet size than MCT as a consequence of its higher viscosity. All emulsions exhibited shear thinning behavior, but the viscosity was influenced by their interface composition. An occurrence of the destabilization mechanism by creaming was observed in turbidimetric measurements, but no visual phase separation could be observed, indicating a good kinetic stability after a 7-day storage. The initial interfacial tension of the water-LCT or water-MCT oil was about 25 mN/m, but the WPI addition (1% w/w) reduced the initial interfacial tension to approximately 20 mN/m. The increase of T80 concentration led to a decrease of the interfacial tension, reaching a value around 10 mN/m in systems with pure T80. The curves of interfacial tension of systems with LCT or MCT showed differences in the decay rate of tension over time. These differences were attributed to characteristics of the oil phase (hydrophobicity, unsaturation degree, presence of impurities) and the different proportions of each emulsifier within the mixture of emulsifiers. Finally, a higher viscoelastic interface was observed in LCT emulsions, which were mainly stabilized by WPI molecules. Such molecules presented a higher resistance to the displacement due to the competitive adsorption phenomenon, since the LCT is a more hydrophobic oil. On the other hand, the interface with MCT and a higher T80 concentration was less viscoelastic due to an easier displacement of WPI from the interface and the replacement by T80. The results indicate that T80 can be used in combination with WPI to produce emulsions with good stability and lower concentration of synthetic compounds. Lastly, the interfacial layer composition is not only dependent on the WPI-T80 ratio in the bulk phase, but also on the oily phase features. These results provide a potential strategy for designing emulsified foods based on the choice of ingredients and knowledge of the interaction between them.

1. Introduction

Many food, pharmaceutical and cosmetic formulations are based on emulsions. Oil in water emulsions are widely used to encapsulate, protect and vehiculate lipo-soluble components, allowing lipid absorption control and increasing bioaccessibility of bioactive compounds. However, emulsions are thermodynamically unstable systems that tend to destabilize with time due to different physicochemical mechanisms, such as gravitational separation, flocculation, coalescence and Ostwald ripening [1]. Therefore, the main challenge related to the application of emulsions in industrial processes is to understand the factors that influence their instability [2,3]. As a consequence, nowadays, there is a considerable interest to find out the relationship between the composition-structure of emulsions and their physicochemical stability, which means that an understanding about the interactions among the components is necessary [4–7]. The features of the interfacial layer surrounding the lipid droplets in oil-in-water emulsions, such as polarity, layer thickness, chemistry composition and the presence of charged molecules are governed by the nature of the emulsion composition [8]. Controlling the interfacial layer characteristics from engineering of the ingredients is one of the most powerful methods to create emulsified products with specific physical characteristics.

* Corresponding author.
E-mail address: rosiane@unicamp.br (R.L. Cunha).

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The characteristics of the emulsion droplets can be controlled by the selection of an oily phase and the type of the emulsifier or mixture of emulsifiers, such as protein-surfactant [1]. Proteins, like whey protein (WPI), are widely used to stabilize emulsions against flocculation and coalescence via electrostatic and/or steric repulsion, since these proteins contain ionic, polar and nonpolar regions in their structure. The structural properties of proteins adsorbed onto the oil–water interfaces are key factors in determining of the stability and other physicochemical properties such as the viscosity and texture of the emulsions [9]. The surface activity of proteins is fundamental for them to be used as emulsifiers, but when compared to surfactants, proteins show low efficiency in decreasing the interfacial tension, since slower diffusion and strong dependence on environmental conditions (such as temperature, pH and ionic strength) can restrict their application in colloidal systems [7]. On the other hand, Tween 80 (T80) which is often used in food products is a non-ionic and semi synthetic molecule derived from polyethoxylated sorbitan and oleic acid. This surfactant can quickly and effectively reduce interfacial tension, facilitating the process of emulsification and producing emulsions with greater resistance to destabilization by creaming. Thus, by working synergistically WPI and Tween 80 could complement each other, improving the short- and long-term kinetic stability of emulsions. The use of mixture of emulsifiers is a strategy to reduce the amount of chemical substances in food products formulations, specially if natural ingredients are used, meeting the demands of the consumer appeal for clean labelling [10].

Both the adsorption and the amount of rearrangements of protein-surfactant mixtures onto the O/W interface are influenced by the chemical structure of the organic phase, such as the chain length of fatty acids, unsaturation number, hydrophobicity, polarity and configuration of the molecule [11]. However, there are few published works on the interaction between the ingredients and how they may affect the structural characteristics of emulsions.

In the last years, some studies have been carried out concerning the interfacial and bulk properties of mixture of emulsifiers considering with a unique nonpolar phase [4,12,13]. In the same way, other works have been developed using different oily phases to evaluate the adsorption of only one type of emulsifier [6,9,14]. However, to the best of our knowledge, none of the manuscripts were dedicated to the evaluation of the effect of the hydrophobic phase on the behavior of the protein-surfactant mixture at the interface and most studies available used purified proteins and oils. The purification process can change the nature of the interface and, therefore, the use of commercial products without further purification is an interesting way of being close to the ingredients used in the food products [15,16].

In this study, the utilization of Whey protein (WPI)-Tween 80 (T80) mixtures and different oily phases, (sunflower oil, a long chain triacylglycerol (LCT) or NEOBEE® 1053, a medium chain triacylglycerol (MCT)) was proposed with the aim to understand how the nature of the ingredients can affect the interface behavior and, consequently, the emulsion characteristics. All the ingredients were used without further purification based on commercial products that are commonly used in industrial applications.

2. Material and methods

2.1. Material

The ingredients used to prepare the emulsions were polyoxyethylene sorbitan monooleate (Tween 80 - T80), obtained from Dinamica Quimica Contemporanea Ltda (Diadema, Brazil) and whey protein (WPI), kindly donated by Fonterra Co-operative Group Limited (Auckland, New Zealand).

Sunflower oil, a long chain triacylglycerol - LCT (Bunge Alimentos S.A., Brazil) was purchased in the local market. Its main fatty acid composition was 5.29% palmitic acid (16:0), 3.72% stearic acid (18:0), 41.48% oleic acid (18:1) and 47.64% linoleic acid (18:2). The medium-chain triacylglycerol - MCT (NEOBEE® 1053) was kindly donated by Stepan Lipid Nutrition (Northfield, USA). Its main fatty acid composition was 51.41% caprylic acid (8:0) and 47.30% capric acid (10:0).

2.2. Emulsion preparation

The oily phase was composed of sunflower (LCT) or MCT oil, while the aqueous phase was composed of solutions containing the mixture of emulsifiers composed of whey protein (WPI)-Tween 80 (T80) (1.0–0.0, 0.75–0.25, 0.5–0.5, 0.25–0.75 and 0–1.0% w/w). The total amount of emulsifier at the final emulsions was equal to 1% (w/w). Firstly, each emulsifier was separately dissolved in water for 2 h using a magnetic stirrer at 25 °C, before producing the mixture of emulsifiers.

Oil-in-water (O/W) emulsions were prepared using the same weight ratio (10:90) in oily to aqueous phases. Emulsions were produced by pre-mixing the oily and aqueous phase using an Ultra Turrax model T18 (IKA, Staufen, Germany) for 3 min at 14,000 rpm, followed by homogenization at 50 MPa/5 MPa using a Panda 2KNS1001L double-stage homogenizer (Niro Soavi, Parma, Italy) in two replicates. Fine emulsions were evaluated from kinetic stability (backscattering), optical microscopy, particle size distribution and rheological behavior.

2.3. Characterization of emulsions

2.3.1. Particle size distribution

The droplet size distribution was determined by a laser diffraction method using a Mastersizer 2000 (Malvern Instruments Ltd, Malvern, UK). The emulsions were dispersed in water at the rotational velocity of 1750 rpm. The droplet size was expressed as the volume-surface mean diameter (D_{32}) calculated according to Eq. (1). Measurements were performed immediately after the preparation of the emulsions and after a seven-day period of storage.

$$D_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

where n_i is the droplet number with diameter d_i.

2.3.2. Optical microscopy

The emulsion microstructure was observed in an optical microscope (Axio Scope.A1, Carl Zeiss, Germany) with 100x oil immersion objective lens. The images were captured with the software AxioVision Rel. 4.8 (Carl Zeiss, Germany). The optical microscopy was performed on the freshly prepared emulsions.

2.3.3. Rheological assays

Rheological measurements of emulsions were carried out using a stress-controlled rheometer (AR1500ex, TA Instruments, England) with double concentric cylinders geometry consisting of an inner cylinder (outer radius = 17.53 mm, inner radius = 16.02 mm) and an outside cup (outer radius = 18.45 mm, inner radius = 15.10 mm). The gap was fixed in 500 μm. The shear rate varied from 0.1 to 300 s^{-1} and the flow curves were obtained from a three-step sequential flow: up-down-up cycles. The third flow curve data were fitted to the model for power-law fluid (Eq. (2)). The emulsions were evaluated after their preparation at 25 °C.

$$\sigma = k \times (\dot{\gamma})^n \quad (2)$$