Synergistic performance of lecithin and glycerol monostearate in oil/water emulsions

María I. Moran-Valero, Víctor M. Pizones Ruiz-Henestrosa, Ana M.R. Pilosof*

Universidad de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas, Instituto de Tecnología de Alimentos y Procesos Químicos (ITAPROQ), Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Buenos Aires, Argentina

ARTICLE INFO

ABSTRACT

The effects of the combination of two low-molecular weight emulsifiers (lecithin and glycerol-monostearate (GMS)) on the stability, the dynamic interfacial properties and rheology of emulsions have been studied. Different lecithin/GMS ratios were tested in order to assess their impact in the formation and stabilization of oil in water emulsions. The combination of the two surfactants showed a synergistic behaviour, mainly when combined at the same ratio.

The dynamic film properties and ζ-potential showed that lecithin dominated the surface of oil droplets, providing stability to the emulsions against flocculation and coalescence, while allowing the formation of small oil droplets. At long times of adsorption, all of the mixtures showed similar interfacial activity. However, higher values of interfacial pressure at the initial times were reached when lecithin and GMS were at the same ratio. Interfacial viscoelasticity and viscosity of mixed films were also similar to that of lecithin alone. On the other hand, emulsions viscosity was dominated by GMS.

The synergistic performance of lecithin-GMS blends as stabilizers of oil/water emulsions is attributed to their interaction both in the bulk and at the interface.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The formation of stable colloidal dispersions (emulsions, foams, etc.) is important in the food industry. To this end, the use of specific surface-active substances (emulsifiers) is required for their formation and stabilization. The stability and mechanical properties of emulsions depend on the way in which the constituent emulsifiers, low-molecular weight emulsifiers (LMWE) and biopolymers adsorb and interact at fluid interfaces. The physico-chemical properties of the surface-active molecules are of great interest because they determine the colloidal stability of emulsions [1]. The optimum use of the emulsifiers depends on the knowledge of their physico-chemical characteristics (such as surface activity, structure, miscibility, interfacial viscosity, etc.) and the kinetics of the film formation at fluid interfaces [2,3]. The distribution of the emulsifiers in emulsions is determined by the competitive and cooperative adsorption between them at the fluid-fluid interfaces and also by the nature of their interactions, both at the interface and in the bulk phase [4].

Phospholipids (lecithin) and monoglycerides (MG) are the most common examples of LMWE used in the stabilization of different food products [5], as they are very surface active compounds [6,7] that can rapidly cover the interface, by the Gibss-Marangoni mechanism [8]. The understanding of these phenomena is a key factor in the development of strategies for controlling food dispersions, formation and stabilization [2,3].

Phospholipids are ionizable emulsifiers which are needed to increase colloidal stability and provide interfacial interactions between food components [4,9,10], that are important factors to further improve emulsion stability and shelf life in many foods. These applications include traditional food formulations (such a bakery, confectionery or meat products, ice-cream, dressings, etc.) or new formulations (low fats and instant foods, high- or low-alcohol food formulations, functional foods, etc.). The increasing demand for low-fat products, convenience, instant, and functional foods has placed a greater importance upon the use of phospholipids as emulsifiers in foods. Thus, the production of industrial foods requires a complete understanding of the behaviour of emulsifiers used as processing aids, both at interface and in the bulk phases, at equilibrium and under dynamic conditions [11]. Phospholipids at interfaces have been reviewed by Pichot et al. [7].

* Corresponding author.
E-mail addresses: inesmoran52@gmail.com (M.I. Moran-Valero), vicprh@gmail.com (V.M.P. Ruiz-Henestrosa), apilosof@di.fcen.uba.ar (A.M.R. Pilosof).

Phospholipid emulsifiers were proved to provide stability to emulsions by acting as both a mechanical and electrostatic barrier to coalescence [12]. Rydhag and Wilton investigated how the composition of PC affects the emulsion stability [13].

Due to its amphiphilic properties, MG are used to stabilize oil/water (O/W) emulsions. MG can develop different forms of liquid crystalline in these systems and structure the emulsions with modified properties (termed as structured emulsions) [14]. For this reason, MG are used in low-fat spreads, baked products (cakes and breads), creams and toppings (whipping and cream substitutes), and fat substitutes in low calories food, among others. Most of these food applications are related to the organoleptic and textural properties that MG confer to the final product [15].

Surfactants used in commercial applications typically consist of a mixture of surfactants because they can be produced at a lower cost than pure surfactants and because these mixtures can also exhibit better properties than each one alone [16]. Interactions between the adsorbed molecules of the emulsifiers could affect the structure, topography and dynamic characteristics (relaxation phenomena and viscoelasticity) of the mixed interfacial films [17,18]. The knowledge of the static (adsorption, structure, topography, etc.) and dynamic (dynamic surface tension and surface rheology) characteristics of surfactants mixtures adsorbed at the O/W interface is a key factor for the formation and stability of optimized food emulsions.

Emulsion structure, stability and rheology depend on the composition, thickness and viscoelasticity of the adsorbed stabilizing interfacial layer, as well as on the properties of the continuous phase. The interfacial rheology is a very sensitive technique to monitor the interfacial structure upon competitive adsorption and the magnitude of interactions between different emulsifiers at the interface [19,20]. Competitive adsorption can lead to different film compositions and structures, depending on the surface activity of each component and their concentration. When present at low subphase concentration, they can both adsorb at the interface as space is available. Nevertheless, at higher concentration, the most surface active component forming the most viscoelastic film would prevail in the film, at least initially [21].

The knowledge of the relationship between the interfacial properties of the surfactants and their emulsifying properties (emulsifying capacity and stability) is a very interesting challenge; nevertheless, the understanding of such relationship is not always simple.

The aim of the present work was to investigate the impact of the combination of lecithin and MG, specifically glycerol-monostearate (GMS), in the formation and stability of food emulsions. For both, pharmaceutical and food applications, attempts have been made to use mixtures of phospholipids and other emulsifiers to enhance emulsion stability. In this way, Klang et al. [22] evaluated submicron emulsions with mixtures of piroxicam and poloxamer to identify the optimal experimental conditions of its fabrication; Yu et al. [23] studied the formulation of intravenous emulsions with anti-tumor compounds in an O/W emulsion to achieve the administration of these compounds in anti-tumor therapy; Donsi et al. [24] evaluated the effect of the presence of two emulsifiers (lecithin and starch) with two different bioactive additives in order to design better nanoemulsion formulations and Pichot et al. [25] investigated the effect on the combination of different surfactant (Tween 60, lecithin and sodium caseinate) and their mixtures on the stability of emulsions. The observed improvements were attributed to the mixture of surfactants that, once adsorbed at the interface, resulted in a reduction of the dispersed phase droplet size.

The emulsifying characteristics of lecithin and GMS, as well as of lecithin/GMS mixed systems (evaluating different lecithin/GMS ratios), will be studied in the present work. To this end, parameters such as the formation and stability of the emulsions, as well as oil droplets size, ζ-potential and the viscosity of each emulsion will be determined. Finally, the relationship between these properties and the interfacial properties will be explored.

2. Materials and methods

2.1. Materials

Lecigran 1000P (de-oiled, powdered soy lecithin, a mixture of polar (phosphor- and glycol-) lipids and a small amount of carbohydrates, dispersible in water, soluble in fats/oils and partly soluble in ethanol. Corresponds with E-322 (EC regulation) for food additive: lecithin) was acquired from Cargill Texturizing Solution US, LLC (Decatur, United States) and a commercial GMS (glycerol ester of stearic acid, $C_{21}H_{42}O_4$) was purchased from Química Oeste S.A. (Buenos Aires, Argentina) [26]. A commercial chia oil (a valuable source of *ω-3 fatty acids*) without further purification was used as the oil phase in order to study the performance of lecithin and GMS in a real interface, because they are used without purification in the manufacturing of food products. Millipore water was used to prepare the different emulsions.

2.2. Emulsion preparation

The oil and lecigran/GMS solutions at total concentration of 1.8% (w/w) [27] were emulsified at a 10:90 O/W ratio. Lecigran and GMS were weighed, and the oil phase was added and stirred for 5 min with a vortex. Next, the water phase was added and the final solutions were pre-emulsified with an Ultra-Turrax for 3 min at 25000 rpm. Then, the samples were emulsified for 10 min using an ultrasonic processor Vibra Cell Sonics, model VCX 750 (Sonics & Materials Inc., Newtown, Connecticut, United States) at a frequency of 20 kHz and amplitude of 20%. A 13 mm tapered microtip was used to sonicate 10 mL of samples in a 15 mL glass tube reactor that was glycerine-jacketed at 60 °C with a thermostated bath (Polystat, Cole-Parmer) [28].

2.3. Droplet size determination

The particle size distribution of the emulsions was measured using a light scattering instrument. The droplet size of emulsions was measured using a Mastersizer 2000 with a Hydro 2000MU as dispersion unit, both from Malvern Instruments (Malvern Instruments, Worcestershire, United Kingdom). The emulsion was dispersed in recirculating water in the Hydro 2000MU with the pump speed set in 1800 rpm [29]. The refractive index (RI) of the dispersed phase (1.458) and its absorption parameter (0.001) were used in droplet size determination. The information about emulsion particle size was then obtained via a best fit between light scattering theory (Mie) and the measured light scattering pattern. The droplet size is reported as the volume-surface mean diameter or Sauter diameter ($D_{32} = \sum n_i d_i^3 / \sum n_i d_i^2$) and the equivalent volume-mean diameter or De Broucker diameter ($D_{43} = \sum n_i d_i^4 / \sum n_i d_i^3$), where n_i is the number of droplets of diameter d_i.

D_{32} was used to estimate the specific surface area of the emulsions and D_{43} was used to monitor the changes in the droplet size distribution. D_{43} is a surface diameter and is a parameter more sensitive than D_{32} to analyse the destabilization process (flocculation and coalescence) [30,31]. The interpretation of these two diameters will allow to analyse the stability of the different emulsions.

The droplet sizes were reported as the average and standard deviation of ten readings made on the sample. The measurements were carried out in duplicate of emulsion samples.