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Lipolysis of soy protein and HPMC mixed emulsion as modulated by interfacial
competence of emulsifiers

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1. Introduction

Obesity and cardiovascular diseases (and other long-term chronic diseases) are recognized as a serious public health problem with an increasing prevalence in the world where the diet is the principal factor that contributes strongly to this problem (especially high-fat content foods) (Reis, Watzke, Leser, Holmberg, & Miller, 2010). A recent study (Khan, et al., 2018) concluded that adults between ages 40 and 59 who are overweight or obese have a significantly increased risk of developing cardiovascular disease (increased risk of morbidity and mortality) as compared with their normal weight peers.

Approximately 50 % of all processed foods contain emulsified fats that promote their texture and flavor and also represent an important source of calories and energy (Torcello-Gómez & Foster, 2016). In order to reduce the health problems associated with the high consumption of fats, an important number of works in the last decades were focused in the development of different strategies to control the lipolysis process (Hu, et al., 2015; Lesmes & McClements, 2012; Li, Hu, Du, & McClements, 2011; Pilosof, 2017; Sandra, Decker, & McClements, 2008; Sarkar, et al., 2016). The capacity to control the lipids digestion could facilitate the development of functional foods to reduce the health problems associated with the high lipids absorption or to ensure the bioaccessibility of bioactive lipids (essential fatty acids, fats-soluble vitamins, etc.) maintaining their sensory properties.

Lipids exist in many different forms in food (Meynier & Genot, 2017) and may be surrounded by complex food matrices that impact their release, digestion, and absorption (McClements, David Julian, 2018). In oil/water emulsions, the lipids are embedded in form of droplets into an aqueous medium where the surface of these droplets is coated by adsorbed emulsifiers (McClements, David Julian, 2015).

The emulsifiers typically used in food emulsions consist of a mixture of proteins, polysaccharides and/or low molecular weight emulsifiers (lecithin, spans, etc.). These molecules tend to be adsorbed at fluid interfaces affecting the formation and stability of

emulsions. The composition and structure of the interfaces has been demonstrated to affect the behavior of the emulsified systems during gastrointestinal (GI) digestion (Bellesi, Martinez, Pizones Ruiz-Henestrosa, & Pilosof, 2016; Carrera Sanchez & Rodriguez Patino, 2005; Pilosof, 2017; Wang, et al., 2012).

Proteins are specifically known for their surface activity, playing a major role in the formation and stabilization of emulsions and foams by a combination of electrostatic and steric mechanisms (Dickinson, 1992; McClements, David Julian, 2015). Soy proteins (SP) are important food ingredients due to their good nutritional and functional properties as well as for their cholesterol-lowering effect (Dan Ramdath, Padhi, Sarfaraz, Renwick, & Duncan, 2017; Tang, C.-H., 2019; Tang, C. H., 2017). One of the potential mechanisms that have been proposed to explain how SP reduce blood cholesterol includes a decrease in the intestinal absorption of bile acids. Many authors have reported their *in vitro* capacity to bind bile salts under physiological conditions (Anderson, Johnstone, & Cook-Newell, 1995; Kahlon & Woodruff, 2002; Potter, 1998).

Most high molecular weight polysaccharides, being hydrophilic, are not prone to be adsorbed at the interface (Rodríguez Patino & Pilosof, 2011). However, hydroxypropylmethylcelluloses (HPMC), with technological applications in the food industry, exhibit interfacial activity due to their structure (methyl (hydrophobic) and hydroxypropyl (hydrophilic) groups added to the anhydride glucose backbone)(Bellesi, et al., 2016; Camino, Carrera Sánchez, Rodríguez Patino, & Pilosof, 2011; Pérez, Carrera Sánchez, Pilosof, & Rodríguez Patino, 2015).

Mixtures of proteins and polysaccharides are often used in many technological applications such as processed dispersions where the stability of these systems is generally achieved through the protective interfacial layer around the dispersed particles (Benichou, Aserin, Lutz, & Garti, 2007). However, protein-polysaccharide interactions may affect their interfacial behavior (Rodríguez Patino, et al., 2011) thus affecting the lipolysis process.

In humans, the lipids digestion process takes place firstly in the stomach but it is more important in the small intestine through the action of pancreatic lipase where 70–90% of the fat digestion occurs (Bauer, Jakob, & Mosenthin, 2005; Sarkar, Horne, & Singh, 2010b). The partially digested food in the stomach (chyme), is mixed in the duodenum with sodium bicarbonate, bile salts (BS), phospholipids and enzymes secreted by the liver, pancreas and gall bladder (Bauer, et al., 2005; McClements, D. J. & Yan Li, 2010a). During the duodenal lipolysis, the pancreatic lipase-colipase complex must adsorb to the oil droplet surface to hydrolyze each triglyceride into 2-monoacylglycerol and two free fatty acids (FFA) (Golding & Wooster, 2010). One of the key roles of BS is to prepare the surface of the fat to improve the access of lipolytic enzymes to the lipid substrates. The lipolytic products are then incorporated into BS micelles to be transported in the aqueous medium and absorbed to the mucosa of the small intestine (Maldonado-Valderrama, Wilde, Macierzanka, & Mackie, 2011). Therefore, according to Golding, et al. (2010), as the lipolysis is a fully interfacial process, one could expect that the nature of the interfacial layer surrounding the lipids droplets would impact in the extent and rate of the lipid hydrolysis. *In vitro* studies have shown that different emulsifiers can alter the lipase activity at o/w interfaces through different mechanical or sterical mechanisms: decreasing the interfacial area available for lipase/colipase adsorption or inhibiting the interfacial anchoring of lipase/colipase. Moreover, an increasing amount of works suggests the existence of indirect impact of adsorbed or unadsorbed emulsifiers which can interact with BS, affecting their activity and thus the rate and extent of lipolysis (Bellesi, et al., 2016; Bellesi, Ruiz-Henestrosa, Maldonado-Valderrama, Del Castillo Santaella, & Pilosof, 2018; Mun, Decker, & McClements, 2007; Singh, Ye, & Horne, 2009).

The aim of the present work was to study the performance of HPMC-SPI emulsions under *in vitro* physiological conditions in order to determine the impact of the interfacial composition in the lipolysis process. The prevalence at the interface of one of the

emulsifiers may affect the composition of the interfacial films and, hence the behavior of emulsion during the gastrointestinal tract affecting the lipolysis degree.

2. Materials and Methods

2.1 Materials

Methocell (food grade) HPMC from the Dow Chemical company was kindly supplied by Colorcon (Argentina) and used without purification. The characteristics of this HPMC (Table 1) were indicated previously by Pizones Ruiz-Henestrosa, Bellesi, Camino, and Pilosof (2017).

Commercial SPI was obtained from The Solae Company (Switzerland).

The aqueous solutions (pure emulsifiers and mixed systems) were prepared in deionized water at pH 7 (adjusted with NaOH) and in citrate buffer (0.1 M) at pH 3, that are typical values used in food systems. The final concentrations were 2 and 4% w/w.

Commercial sunflower oil was used as the oil phase to prepare the oil/water (O/W) emulsions. Furthermore, the oil was previously purified with Florisil 60-100 Mesh (Fluka) as described by Bellesi, Pizones Ruiz-Henestrosa, and Pilosof (2014) to eliminate the possible surface-active contaminants that could affect the interfacial characterization.

2.2 Methods

2.2.1 Interfacial properties

The interfacial pressure (π) and the interfacial dilatational rheology evolution with time were determined by using a Profile Analysis Tensiometer (PAT-1, SINTERFACE Technologies, Germany) with the pendant drop method (Bellesi, et al., 2014). The time-dependent interfacial pressure of the different emulsifier solutions at the O/W interface was analyzed forming a droplet (12 μ l) immersed in an optical glass cuvette containing the purified sunflower oil, thermostated at a 37 °C.

The dilatational modulus (E) of the interfacial films was obtained by applying a sinusoidal deformation (at an angular frequency of 0.05 Hz and an amplitude of the oscillation at 3% of the initial drop volume). The response of the interfacial tension to the deformation reflects the dilatational response of the interfacial film, obtained by applying the Fourier transform.

2.2.2 Emulsion preparation

O/W emulsions were prepared by mixing a commercial sunflower oil and emulsifiers solutions at a 10:90 ratio using an ultrasonic processor Vibra Cell, model VCX 750 (Sonics & Materials, Inc., Newton, CT, USA) at a frequency of 20 kHz and an amplitude of 20% for 15 min. The glass tube with the sample was introduced in a glycerine-jacketed at 0.5 °C to dissipate the heat produced during the sonication keeping the sample temperature below 25 °C (Bellesi, et al., 2016).

2.2.3 Particle size distribution

The oil droplet size distributions were determined by static light scattering using a Mastersizer 2000 with a Hydro 2000MU as dispersion unit (Malvern Instruments Ltd, UK). The pump speed was set at 1800 rpm. The refractive index and the absorption parameter were 1.47 and 0.001, respectively. Droplet size is reported as the volume-surface mean diameter or Sauter diameter ($D_{3,2}$) and the equivalent volume-mean diameter or De Broucker diameter ($D_{4,3}$). It is also reported the values corresponding to the specific surface area (SSA) that indicate the surface area per unit mass of the dispersed phase (Bellesi, et al., 2014).

2.2.4 *In vitro* digestion

The *in vitro* gastrointestinal digestion was carried out at 37 °C using a pH stat titration method (Metrhom). Fresh O/W emulsions (10 ml, previously incubated at 37 °C) were mixed with 10 ml of simulated gastric fluid (SGF: pH 2.5, 100 mM NaCl, 3 mM CaCl_2 , 5 mM NaH_2PO_4 and 22 mM KCl) in presence of pepsin from porcine gastric

mucosa (P700, powder ≥ 250 units/mg solid) and 1- α -phosphatidylcholine from egg yolk (type XVI-E, P3556) both purchased from Sigma-Aldrich (Bellesi, et al., 2014). After one hour of incubation, the gastric proteolysis was stopped by increasing the pH to 7 (NaOH 0.5 M). The *in vitro* digestion continued by incorporating of 10 ml of simulated intestinal fluid (SIF, pH 7.0, 39 mM K_2HPO_4 , 150 mM NaCl and 30 mM $CaCl_2$) (Sarkar, Horne, & Singh, 2010a; Sarkar, et al., 2010b) in the presence of bovine bile extract (B3883, 5 mg/ml), lipase from porcine pancreas (L3126, type II, 100–400 units/mg protein using olive oil – 30 min incubation) at a final concentration of 54 mg/ml, and the proteases: trypsin (type I, T8003) and 1- α -chymotrypsin (type II, C4129), both from bovine pancreas under physiological concentration (40 U/mg emulsifier and 0.45 U/mg emulsifier, respectively) (Martinez, Martos, Molina, & Pilosof, 2016). All biochemical agents were purchased from Sigma-Aldrich. During the duodenal stage (1 h), the pH was continuously controlled at 7.0 using NaOH (0.5 M) to neutralize the FFA released due to the lipase activity. The %FFA released during the duodenal stage was calculated from the number of moles of NaOH required to neutralized the fatty acid released using the expression reported by Zhang, Zhang, Zhang, Decker, and McClements (2015).

3. Results and Discussion

3.1 Soy Protein-HPMC adsorbed films

Competitive adsorption between SPI and HPMC at the O/W interface determines the composition of the stabilizing layer at the emulsion droplet surface. In order to better understand the impact of the presence of both emulsifiers, the interfacial parameters of the mixed systems were determined in relation to that of single emulsifiers.

The evolution of interfacial pressure (π) for SPI, HPMC and the mixed system (SPI-HPMC) at the O/W interface are shown in Fig. 1. The increase of π with time is

associated with emulsifiers adsorption at the O/W interface (Damodaran & Song, 1988). SPI presented a behavior similar to that observed for other proteins, such as whey protein isolate or β -lactoglobulin films (Bellesi, et al., 2014; Bellesi, et al., 2018; Niño, Sánchez, Fernández, & Patino, 2001; Pizones Ruíz-Henestrosa, et al., 2007). The results corresponding to HPMC are in accordance with those reported by (Camino, Carrera Sánchez, et al., 2011) using different types of modified celluloses.

An almost constant saturation value (π at around 15 – 18 mN/m) was reached very quickly as reported in the literature (Bellesi, et al., 2014; Camino, Carrera Sánchez, et al., 2011; Torcello-Gómez & Foster, 2014). In spite of changing the concentration of the emulsifiers as well as the pH of the aqueous medium, small differences of π values were observed, that could be associated to the O/W interface saturation (Baeza, Carrera Sanchez, Pilosof, & Rodríguez Patino, 2004) (the lower concentration (2 % w/w) was high enough to saturate the O/W interface).

The dynamics of co-adsorption of the mixed systems was measured (Fig. 1 (full symbols)) in all conditions. However the time evolution of π for each mixture did not show changes in relation with the behavior of pure emulsifiers, probably because single components performed similarly. On the other hand, an effect of the concentration or the pH of each formulation was not observed.

The existence of competitive or cooperative adsorption between SPI and HPMC at the O/W interface could be deduced from the analysis of the interfacial dilatational modulus (E) in Fig. 2. The time dependent behavior of E is consistent with the existence of interactions between the adsorbed emulsifiers. The closer packing of SPI at higher adsorption time is a consequence of the existence of a molecular rearrangement of the previously adsorbed soy protein molecules that is reflected by the increment of E . SPI formed more elastic films than HPMC because of a higher degree of interaction between the adsorbed molecules. The most elastic films (E around 13 mN/m) was observed at the lower protein bulk concentration (2% w/w, both pH),

suggesting that a better protein interaction could be established at the lower concentration (Martínez, Carrera Sánchez, Rodríguez Patino, & Pilosof, 2009).

HPMC films showed very low E values (between 2 and 6 mN/m) (Fig. 2), reflecting the formation of a weak interfacial layer, that presents a poor response to the small area deformations of the films. The rheological performance of HPMC interfacial films at O/W and air/water interfaces has been previously reported by Camino, Carrera Sánchez, et al. (2011) that demonstrated the low ability of HPMC to form elastic films (consistent with the results in the present work) which could be related to the low tendency to associate in the bulk phase, as demonstrated by dynamic light scattering.

The behavior of E values for the mixed systems (Fig. 2, full symbols), showed that HPMC dominated the interface at low adsorption times. The higher impact of HPMC activity in the elastic modulus should be related to its molecular structure. The predominance of HPMC at low adsorption times in all the experimental conditions could be associated with their smaller size than SPI since no cluster formation at both pH (being predominant the monomeric form) has been previously reported by Pizones Ruiz-Henestrosa, et al. (2017) and Camino, Carrera Sánchez, et al. (2011). This behavior is closely related to the fact that small aggregates can diffuse quickly from the bulk phase to the interface. Moreover, the predominance of HPMC could be related to its higher number of potential adsorbing groups along the backbone molecule (Camino, Carrera Sánchez, et al., 2011).

However, the interface corresponding to the system at 2% and pH 3 (Fig. 2C) was always dominated by HPMC. This result can be associated to the results observed in the inset figure (Figure 1C), where HPMC molecules diffused faster than SPI.

Once after this initial period, an increase in E was observed, as a general trend, for the other mixed systems, which could be attributed to SPI adsorption at the O/W interface. Although the complex molecular structure of SPI retards not only their diffusion to the interface but also the subsequent adsorption and reorganization at the

interface, once it is adsorbed it could be dominating the rheological interfacial properties.

These results prove the presence of both emulsifiers at the O/W interface

3.2 Droplet size distribution of O/W emulsions

Figure 3 shows the oil droplet size distributions for O/W (10/90) emulsions prepared with HPMC, SPI and HPMC-SPI at pH 7 and 3 (Fig. 3A and Fig. 3B, respectively) at a concentration of 2 and 4% w/w. SPI emulsions showed a monomodal but broad distribution with a predominant population at around 0.3 and 0.4 μm . A smaller oil droplet diameter ($D_{3,2}$) was obtained at 4% w/w in comparison to the emulsions prepared at 2% w/w at both pH values (Table 2). The emulsions formed by HPMC at 4% w/w concentration also revealed a monomodal distribution (with a mean peak at 1 μm). However, emulsions prepared at 2% w/w showed a distribution characterized by a population with a shoulder between 0.15 and 0.5 μm and a mean peak at 1 μm . As expected, in all the cases, an increase in the specific surface area (SSA) (lower $D_{3,2}$ values) was observed when increasing the emulsifier concentration from 2% to 4% w/w, while $D_{4,3}$ values (related with the destabilization processes) were higher at 2% w/w (Table 2) associated with the highest lowering of the interfacial free energy (Pinnamaneni, Das, & Das, 2003).

Overall, the oil droplets size was always smaller for SPI emulsions (Table 2), indicating that SPI was more effective than HPMC at producing small droplets during the emulsification and to prevent their subsequent aggregation (Malaki Nik, Wright, & Corredig, 2011). This behavior can be due to the best interfacial properties of SPI in comparison with HPMC (Fig. 2) as has also been reported previously (Bellesi, et al., 2016; Camino & Pilosof, 2011).

The size distribution corresponding to the mixed emulsions was closer to that of single HPMC emulsion (Fig. 3 and Table 2). Moreover, the presence of both emulsifiers affected negatively the emulsion droplet size, as even higher sizes than for single

HPMC were obtained. The predominance of HPMC at the interface (Fig. 2) of the mixed systems is in a close relation with the behavior of emulsions. Similar results were reported by Camino, Sanchez, Rodríguez Patino, and Pilosof (2012) on studying O/W emulsions stabilized by HPMC- β lactoglobulin mixtures. Also in that mixture the interfacial pressure and the elastic film character were influenced by HPMC, thus presenting the resulted emulsion higher average diameters than emulsions formed by single emulsifiers.

3.3 Impact of interfacial composition on lipolysis

In order to better understand the impact of the interfacial composition of emulsions on lipolysis, the amount of free fatty acid (FFA) released during the *in vitro* digestion of emulsions was determined (Fig. 4).

No lag phase was observed independently of the interfacial composition, showing a rapid increase in the amount of FFA during the first minutes of the reaction. This fact suggests that the lipase could adsorb at the interface in order to hydrolyze the lipids. In accordance with other works, an almost constant value was reached after this period, indicating the accumulation of the resulting lipolysis products (FFA and monoglycerides) at the droplets surface, as they tend to form a liquid crystalline phase that reduce the accessibility of lipase to the interface and thus, avoiding the lipase to continue exerting its activity (Bellesi, et al., 2016; Malaki Nik, et al., 2011; McClements, D. J. & Y. Li, 2010b).

Independently of the pH or emulsifiers concentration, the emulsions stabilized by HPMC showed a lower degree of lipolysis (% FFA_{max}) than SPI emulsions (Table 2). The lowest % FFA_{max} of HPMC emulsions could be due to two factors reported in the literature to affect the lipolysis degree: (1) HPMC is not affected by pepsin during the gastric phase and, thus HPMC interfacial films (and their emulsions) present a more intact structure once they are exposed to the duodenal conditions. In fact a lower degree of destabilization under gastric condition was reported for HPMC emulsions

(Bellesi, et al., 2018) in comparison with proteins (β -lactoglobulin and SPI) stabilized emulsions. (2) The capacity of the adsorbed as well as the non adsorbed HPMC molecules to interact with BS may reduce their availability, favoring then the accumulation of inhibitory lipolysis products (FFA, monoacylglycerols) at the interface or hindering the access of lipase to the interface (Pilosof, 2017). The binding of BS onto cellulose has been assessed by Torcello-Gómez, et al. (2014) and Torcello-Gómez, et al. (2016) who postulated the existence of hydrophobic interactions between these components. More recently, Pizones Ruiz-Henestrosa, et al. (2017) also demonstrated the binding between BS and two HPMCs with different molecular structures, both in the aqueous phase and o/w interface.

The digestion of mixed emulsions (SPI-HPMC emulsions) was almost identical to that of HPMC emulsions, thus reflecting the predominance of HPMC at the interface of the emulsions as revealed by the rheological parameters at a short initial timescale for the mixed interfacial films (Fig. 2).

The lipolysis is an interfacial reaction where the pancreatic lipase has to bind to the O/W interface via complexation with BS and/or colipase (Jódar-Reyes, Torcello-Gómez, Wulff-Pérez, Gálvez-Ruiz, & Martín-Rodríguez, 2010; McClements, D. J., et al., 2010a). The size of the oil droplets should impact in the degree of lipolysis, being higher in the presence of smaller oil droplets (higher surface area) (Armand, et al., 1992; Mantovani, Pinheiro, Vicente, & Cunha, 2017; Singh & Ye, 2013). A linear relationship (r^2 : 0.97) was found between the initial interfacial area of each emulsion and the % FFA_{max}, where the highest % FFA_{max} was obtained for emulsions with the highest interfacial area (lowest droplet diameter) (Fig. 5). This reflects the impact of interfacial composition on the degree of lipolysis as that influences the droplet size and therefore the available interfacial area for lipolysis.

4. Conclusion

The results of the present work highlight the importance of the interfacial composition as it may affect the oil droplet size and hence their functionality, thus affecting the behavior of emulsions during the gastrointestinal tract, as well as the lipolysis degree. The interfacial rheology was a valuable tool to analyze the behavior of emulsifiers adsorbed at the interface and to explain the characteristics of the mixed emulsions.

In the mixed SPI-HPMC systems, regardless of the emulsifier concentration or pH conditions, the interfacial films were dominated during the first minutes of adsorption time by HPMC, although the presence of SPI was evidenced at long adsorption times. Therefore, upon emulsion formation conditions HPMC predominated at the surface of oil, controlling the emulsion droplet size distributions and surface area and hence the degree of lipolysis.

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Figure 1. Interfacial pressure (π) of films formed at 2% pH 7 (A), 4% pH 7 (B), 2% pH 3 (C) and 4% pH 3 (D) with time. SPI ($\square$), HPMC (o) and mixed system ($\blacksquare$). The final concentrations of the mixed systems were 2% or 4% of total polymer.

Figure 2. Interfacial dilatational modulus (E) of films formed at 2% pH 7 (A), 4% pH 7 (B), 2% pH 3 (C) and 4% pH 3 (D) with time. SPI ($\square$), HPMC (o) and mixed system ($\blacksquare$). The final concentrations of the mixed systems were 2% or 4% of total polymer.

Figure 3. Volume particle size distribution of oil in water emulsions stabilized by SPI ($\square$), HPMC (o) and the mixed systems ($\blacksquare$) at pH 7 (A) and pH 3 (B). The final concentrations of the mixed systems were 2% or 4% of total polymer.

Figure 4. Free fatty acids release (FFA) during the duodenal stage from emulsions stabilized by SPI ($\square$), HPMC (o) and mixed system ($\blacksquare$) at 2% pH 7 (A), 4% pH 7 (B), 2% pH 3 (C) and 4% pH 3 (D). The final concentrations of the mixed systems were 2% or 4% of total polymer.

Figure 5. Correlation between free fatty acids released (FFAmax (%)), and specific surface area of fresh emulsions (SSA). SPI ($\blacksquare$), HPMC (o) and the mixed systems ($\blacktriangle$)

Properties	HPMC
% methyl	29.5
% hydroxypropyl	9.7
Methyl/hydroxypropyl ratio	3.0
Methyl substitution (DS)	1.90
Hydroxypropyl substitution (MS)	0.23
Total substitution (DS + MS)	2.13
Viscosity (cp), 2% wt solution (20 °C)	5.4
Molecular weight (kDa)	2

Table 1: Hydroxypropylmethylcellulose (HPMC) properties.

			$D_{3,2}$ (μm)	$D_{4,3}$ (μm)	SSA (m^2/g)	FFA _{max} (%)
pH 7	2%	HPMC	0.78 ± 0.08	1.18 ± 0.05	7.7 ± 0.9	48.5 ± 0.8
		SPI	0.359 ± 0.001	0.5265 ± 0.0007	16.65 ± 0.07	68.3 ± 0.4
		MIX	0.86 ± 0.06	1.07 ± 0.01	7.0 ± 0.5	52 ± 4
	4%	HPMC	0.528 ± 0.007	0.717 ± 0.007	11.40 ± 0.09	60 ± 1
		SPI	0.2960 ± 0.0007	0.4115 ± 0.0007	20.25 ± 0.07	80.8 ± 0.1
		MIX	0.65 ± 0.03	0.91 ± 0.03	9.3 ± 0.4	61 ± 2
pH 3	2%	HPMC	0.84 ± 0.06	1.08 ± 0.09	7.1 ± 0.5	49.7 ± 0.6
		SPI	0.41 ± 0.02	0.59 ± 0.02	14.7 ± 0.6	68 ± 3
		MIX	0.72 ± 0.01	1.12 ± 0.01	8.3 ± 0.1	53 ± 2
	4%	HPMC	0.55 ± 0.01	0.73 ± 0.03	10.9 ± 0.3	56 ± 4
		SPI	0.35 ± 0.02	0.52 ± 0.05	17.4 ± 0.8	81 ± 4
		MIX	0.64 ± 0.01	0.83 ± 0.04	9.4 ± 0.6	53 ± 3

Table 2. Mean droplet sizes ($D_{3,2}$ and $D_{4,3}$), specific surface area (SSA) and free fatty acids released (FFA_{max}) for emulsions stabilized by HPMC, SPI and the mixed system (MIX).

- Competitive adsorption controls the degree of lipolysis.
- The interfacial rheology was a valuable tool to analyze the competitive adsorption.
- HPMC dominated the interface, controlling the emulsions size and lipolysis degree.