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Demystifying Emulsifiers as Additives through Molecular Gastronomy: A Contribution to Rise Consumer's Sovereignty

Lígia Rebelo Gomes, Cláudia Silva and Catarina D. Simões

Abstract

According to the Food and Agriculture Organisation of the United Nations, one third of food produced annually for human consumption results in food losses or wastage, which is environmentally degrading, economically unviable, ethically incorrect, and does not contribute to sustainable development. The use of additives can help prevent the waste of food that is still fit for consumption in a world where about 16% of the world's population goes hungry. Food additives may overcome the problem of limited supply of natural ingredients, increase the shelf life of foods and simplify the complex cooking procedures. To raise the consumer's knowledge about food additives, this work presents and explain in a simple manner some physical/chemical properties of emulsifiers, namely fatty acids esters and sucrose esters of fatty acids. Moreover, this work reviews and illustrates, recurring to recipes of molecular gastronomy, how these additives are used in food preparation to achieve and maintain certain desirable characteristics, how they contribute to obtain a better result in final preparation, and how they can be used in modern cuisine. Preparations coming from the discipline of molecular gastronomy have been chosen since they are based on laboratory related procedures and only use few ingredients, including an additive.

Keywords: food additives, emulsifiers, sucrose esters, mono- and diglycerides of fatty acids, molecular gastronomy

1. Introduction

Despite all the literature available concerning the food additives, the availability of easy reading yet scientifically sounding information about the nature, chemical composition, role, and safety of the additives is scarce. It appears that, in a world where fake information is quickly spread in social media and food additives start to be perceived as harmful, the development of tools that permit the demystification of their use and therefore their acceptance, is essential as they, at least, contribute to the expansion of food's the shelf life and fight waste.

Following the work that our group has undertaken, to raise the consumer's knowledge about additives, we desire to present and explain in a simple manner some physical/chemical properties of emulsifiers, EU codes, in the 400–499 range,

namely fatty acids esters and sucrose esters of fatty acids. How those additives are used in food preparation in order to achieve and maintain certain desirable characteristics, how they contribute to obtain a better result in final preparation and how they can be used in modern cuisine will be illustrated and reviewed recurring to recipes of molecular gastronomy. Preparations coming from the discipline of molecular gastronomy have been chosen since they are based on laboratory related procedures and they use only a few ingredients, including an additive.

This review chapter is a means to attain a final objective which is to develop tools for the demystification of food additives targeted to wider target people audience than researchers as, for example, undergraduate students of chemical, biological and nutrition sciences, students of gastronomy, chefs and high school teachers, in the hope of encouraging them to spread genuine scientific information based, as far as possible, on the current state-of-art. This will contribute to the raising of the level of knowledge of those additives thus allowing the consumer to make informed decisions.

Emulsifying agents are discussed first, the chapter begins with a simple review of emulsification and interfacial tension. Then the E471 and E473 class of additives will be presented (chemical constitution and relevant physical properties). For each class the most common uses in food processing will be discussed as well as their role in a particular recipe. Finally, a brief summary concerning their safety will be made.

2. Interfacial tension and emulsions

A mixture is formed when it is thermodynamically more stable than the states given by its separate components. That occurs when the interaction energies between molecules of the mixture are higher than the sum of the interaction energies of the primary constituents [1]. This condition is usually satisfied when the molecular constituents that are to be mixed have cohesive forces of similar magnitude. Otherwise, they do not tend to mix, even when shaken and whipped, and phase separation occurs spontaneously [2]. Anyhow, components must contact in the interfaces and interfaces are particular: surface phenomena such as surface tension (or interfacial tension) applies. The term interfacial tension usually relates to the liquid/liquid and liquid/solid phase boundaries; the term surface tension applies to the liquid/gaseous interface and the term surface free energy applies for the solid/gaseous. The surface free energy affects wettability [3].

Interfacial tension and surface tension are defined as the work that must be done to maintain the unit of interface or free surface, respectively [1]. By way of an example, consider the interface of two immiscible liquids (oil and water), see **Figure 1**. The molecules placed in the boundary surface are interacting with molecules of both liquids, as such, the sum of interactive forces that act in the boundary molecule is unbalanced. That means that there is a net force that tends to push those molecules into their respective bulk. Thus, in order to keep the surface or the interface, a network of molecules is formed against the pull, as so, work must be done in order to maintain or increase the size of the interface. As consequence, when a water solution is vigorously stirred with an oil solution, the droplets formed after stirring tend to aggregate and phase separation occur. This happens because the system will minimise its energy when it reaches the smaller surface of contact [3].

The additives that will be here presented can act as surfactants that is, they have the capability of modify the surface tension/interfacial tension/surface free energy of the heterogeneous systems. As so, they can act as emulsifiers and/or humectants. This ability comes from their chemical constitution: they are amphipathic molecules, *e.g.*, they are unbalanced in their charge distribution, which means that one
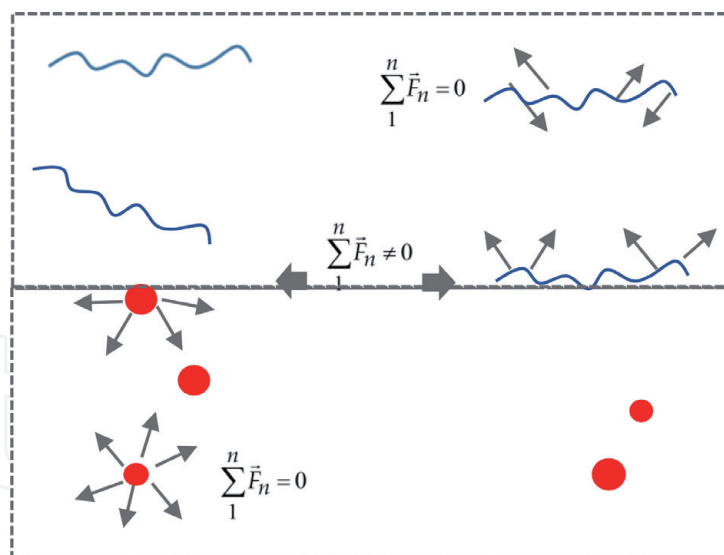
Figure 1.
Schematic representation of the differences on the net forces in two liquid that are not mixable, e.g., polar water molecules (in red circles) and non-polar oil molecules (blue curved lines): in the bulk of each liquid the net forces between molecules are balanced while on the interface the net forces acting on the molecules are not, as consequence of the differences on the mutual interaction energies. Such molecules tend to undergo a displacement to the respective bulk solution and new molecules are displaced to the inner solution to replace them. This dynamic is kept in order to maintain the interface and the energy required to do it, per surface unit, is called the interfacial tension.

can recognise a part of the molecule that is polar (hydrophilic) and another that is non-polar (hydrophobic), see **Figure 2(a)** for an example (a sucrose ester). Those kinds of molecules are named as surfactants agents due to their ability to modify the interface/surface tension value. If this value is lowered by action of the surfactant agent, then they stabilise the interface. The mechanism by which this is possible is related to the amphiphilic nature of the molecule: the polar part of the molecule will interact preferentially with the polar liquid (water) and the non-polar preferentially with the oil, see **Figure 2(c)** and **(d)**.

Two common two-phase systems in food products are emulsions and foams. Emulsions are composed of two immiscible liquids that may be stabilised by a type of surfactant named emulsifier [3]. Foams are dispersions of gas bubbles in a liquid continuous phase containing foaming agents, i.e., surface-active substances that ensure the stability of the system [2].

An emulsion is characterised by the existence of small droplets that constitute the dispersed phase imbibed in an immiscible liquid, which forms the continuous phase, see **Figure 2(d)**. Foams are a state where air (gas) is confined as bubbles into a continuous phase that could be a water solution, fat, or a hydrocolloid. When the emulsion is called oil–water (O/W), the oil is the dispersed phase and water is the continuous phase and the reverse happens for a water–oil emulsion (W/O). An emulsifier agent is a tension-active molecule (or mixture of molecules) that has the ability to be adsorbed at the O/W/W/O interface, lowering the tension and preventing the dispersed-phase droplets from aggregating [4]. The type of emulsion formed when an aqueous solution is mixed with an oil and with an emulsifying agent depends on the solubility of that agent: "The phase where the emulsifier is most soluble will be the continuous phase", hence, even if a preparation has 60% of constituents of oily origin an O/W emulsion will be obtained if the emulsifier chosen is soluble in water [1].

The mechanisms by which the emulsifiers stabilise emulsions and dispersions are based in electrostatic or/and steric phenomena. Non-ionic emulsifiers, as sucrose esters of fatty acids and mono and di-glycerides of fatty acids are good
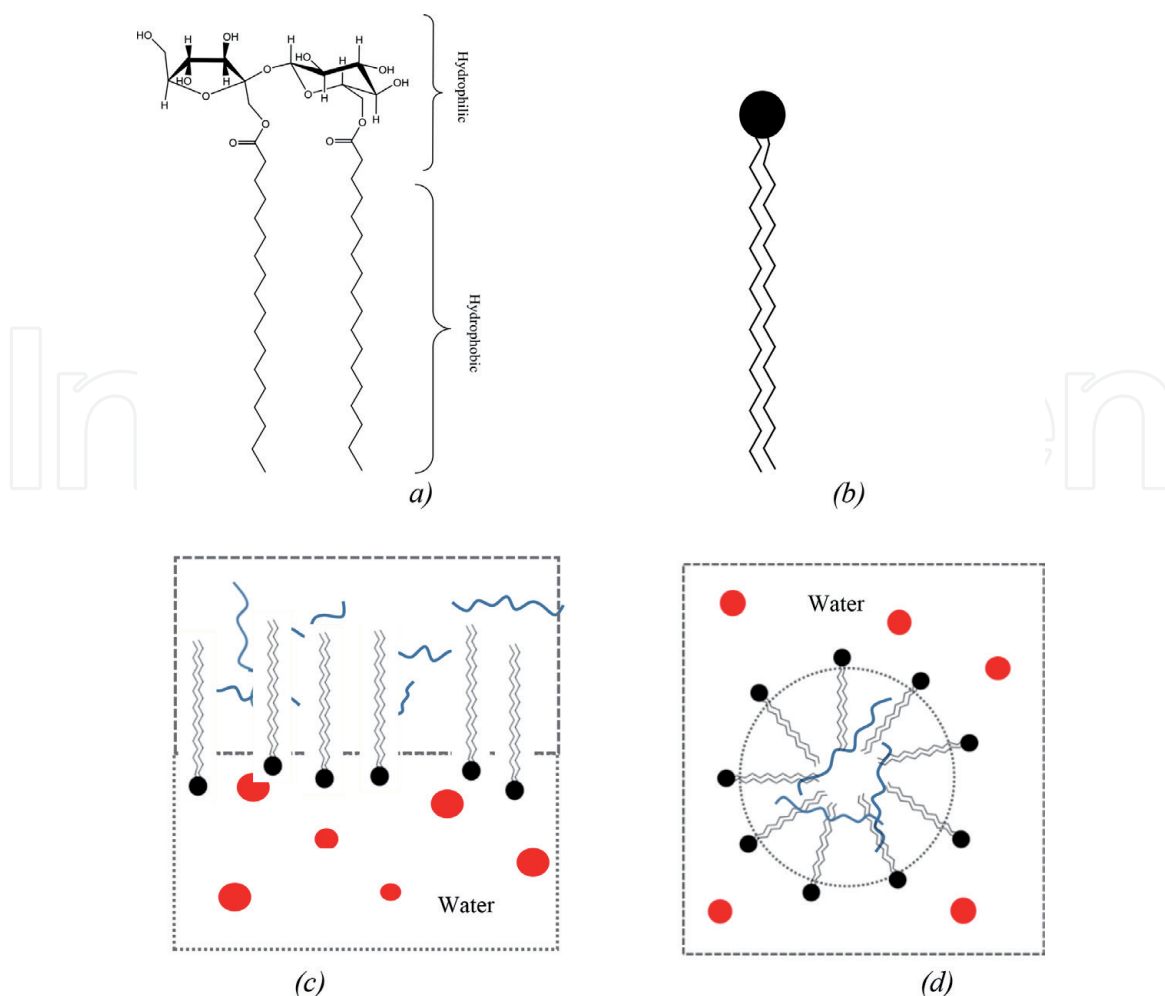
Figure 2.
(a) Structure of a sucrose di-ester (derived from stearic acid). The polar part of the molecule is identified as hydrophilic and the non-polar as hydrophobic (or lipophilic), (b) usual scheme representation of the molecule, (c) the surface-active agent has the ability to stabilise the interface: The polar part of the molecule interacts preferentially with the polar liquid (water) and the non-polar preferentially with the oil; (d) when the mixture is shaken, droplets of oil disperse into the water phase (continuous phase).

steric stabilisers. In most cases, they cope with presence of any ions in solution and do not react with them, allowing for a wide application in various systems, especially in water of unknown hardness [1, 5].

Thus, in order to stabilise an emulsion, the appropriate emulsifier must be selected. One of the challenges is to select an emulsifier with an adequate hydrophilic/lipophilic balance (HLB) suitable for the system. The HLB is a measure of the hydrophilicity of an emulsifier: higher HLB values indicate a higher hydrophilicity. Emulsifiers with HLB values of 3.5–6 tend to be the most suitable for W/O emulsions, and those with HLB values from 8–18 are best suited for O/W emulsions. Surfactants with values ranging from 7–9 are good wetting agents [1, 5].

Most commercial emulsifiers, especially glycerides of fatty acids and sucrose esters, are mixtures of mono-, di- and tri-esters. Emulsifier HLB values are largely dependent on the monoester content; a greater monoester content leads to a higher HLB value [5]. The HLB value also depends on the chain length(s) of the fatty acids attached to the emulsifier; short fatty acid chains lead to higher HLB values [6].

Another factor to take into account is the molecular weight of the surfactant: emulsifiers with low molecular weight are usually more rapidly adsorbed onto the phase interface and prevent droplet coalescence during homogenisation, they are a preferable choice for making micro-emulsions, as those used in food processing [7, 8].
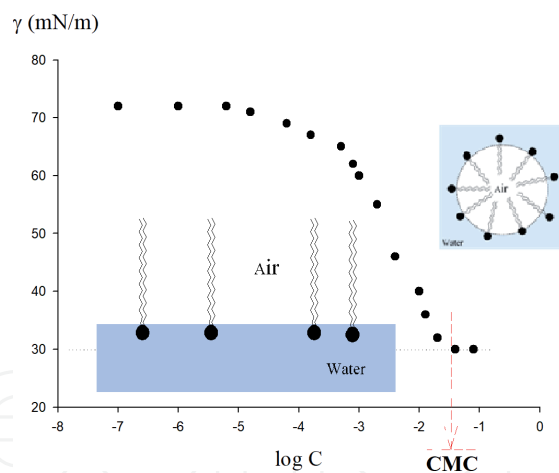
Figure 3.
A graphical representation of the surface tension (γ) of water solutions of a fatty acid ester of a glucopyranoside at various concentrations. The arrow indicates the value of the critical micelle concentration (CMC): before the CMC there is a strong change of the surface tension; after the CMC that value is minimum and stays constant and the air micelle in water is stabilised. Adapted from [9, 10].

2.1 The critical micelle concentration

A micelle is considered a supramolecular aggregate shape of molecules with spherical that is formed by surfactant molecules. Micelles in water are aggregates with the hydrophilic part of the molecule contacting with surrounding solvent and the hydrophobic tail regions in the micelle centre. The micelle content can be air (see **Figure 3**) or a fat. In colloidal and surface chemistry, the critical micelle concentration (CMC) is defined as "the concentration of surfactants above which micelles form and all additional surfactants added to the system will form micelles".

Figure 3 depicts a graphical representation of the surface tension (γ) of water solutions of a fatty acid di-ester of a glucopyranoside at various concentrations. When the concentration of the surfactant is low, the whipping of the solution will not give "stable bubbles", but this will occur after the surfactant concentration reaches the CMC (value indicated by the arrow). As seen, before the CMC there is a strong change of the surface tension and after the CMC that value reaches a minimum and stays independent of the concentration, giving stability to the air droplets. For the mono and di-glycerides of fatty acids and as well for sucrose esters the stability of the micelles is given by the strong hydrogen bonds that the sugar moiety can make with water [9, 10].

The CMC depends on the temperature, the pressure and it also changes with the composition of the water solution, namely with the presence of other surface-active compounds.

3. E473 and E471 classes of additives

This revision will concern about two classes of food additives, the sucrose esters of fatty acids (E473) and the mono- and diglycerides of fatty acids (E471). Both are widely used nowadays in food industry and thus present in the preparations available in supermarket shelves. The sucrose esters of fatty acids are used to obtain mostly O/W emulsion (but not only) and mono- and diglycerides of fatty acids are used to obtain W/O emulsions. Both are good agents for form stable foams.

3.1 Sucrose esters of fatty acids (sucrose esters), E473

Sucrose esters of fatty acids class of compounds (E473) are tensioactive agents that have fatty acids esterified in sucrose. They synthesised by the esterification of the available hydroxyl groups of sucrose (O-α-D-glucopyranosyl-(1 → 2)-β-D-fructofuranoside) and fatty acids. In **Figure 4** the structure of sucrose is depicted: this is a disaccharide formed from condensation of glucose and fructose to produce α-D-glucopyranosyl-(1 → 2)-β-D-fructofuranoside. The free hydroxyl groups are numbered as red labels; the primary hydroxyl groups are more reactive since they are not so steric hindered, as such, their reaction with fatty acids is most probable giving the sucrose mono-, di-, or tri-esters. They can be obtained with a very wide range of variation in the molecular structure due to the different combinations between the length of the fatty acid chain, the degree of saturation of the fatty acid and the degree of esterification. The length of the fatty acid chain generally varies between 4 and 18 carbon atoms, but the most used fatty acids for esterification are i) the saturated lauric, myristic, palmitic and stearic acids, see **Figure 5(a)**, and ii) the unsaturated oleic and erucic acids, **Figure 5(b)**.

Sucrose esters can be synthesised either chemically or enzymatically. In industrial scale they are obtained by trans-esterification (see **Figure 6**): the reactants are sucrose, a triglyceride (TG), potassium carbonate as catalyst in *N,N*-dimethyformamide (DMF, **CAS:** 68–12-2) or dimethylsulfoxide (DMSO, **CAS:** 67–68-5) as solvents. This reaction gives a product that is a mixture of the sucrose monoester (> 50%), sucrose di-esters (~10%) higher esters, sucrose and TAG [11]. This processing method has issues connected with the removal of the solvents that have high boiling points [426.2 ± 0.7 K (~153°C) for DMF and 463 ± 1 K (~189°C) for DMSO] and the separation of the monoester from the other by-products. Sucrose monoesters may be also produced in large scale by the reversible trans-esterification process, see **Figure 6**, using sucrose and a fatty acid methyl ester as reagents and sucrose esters and methanol will be obtained as products. This this a reversible process, so, the methanol should be removed during the reaction. Under the optimal conditions this protocol can provide material containing upwards of 70% of the monoester [11].

Chemical synthesis uses solvents such as DMSO and/or DMF that display toxicity [12–14]. In alternative, enzymatic based reaction procedures have been developed more recently [15, 16], and present some advantages over the chemical reactions: i) they can take place under lower temperatures ii) they use less toxic solvents and iii) they allow better control over the reaction final products. However, the main obstacle to commercial sucrose ester production by the enzymatic means is the fact that the reaction has to be run in batch rather than flow mode [17]. The most promising enzymes are a group of esterases that catalyse the hydrolysis of lipids. In the present context, important lipases are the
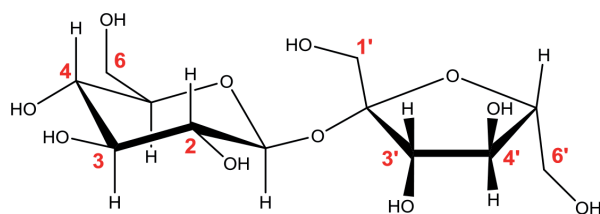

Figure 4.
The structure of produce α-D-glucopyranosyl-(1 → 2)-β-D-fructofuranoside (sucrose). The labelled atoms are carbons atoms containing hydroxyl groups available for sterifications. The primary C1', C6' and C6 are the most reactive.
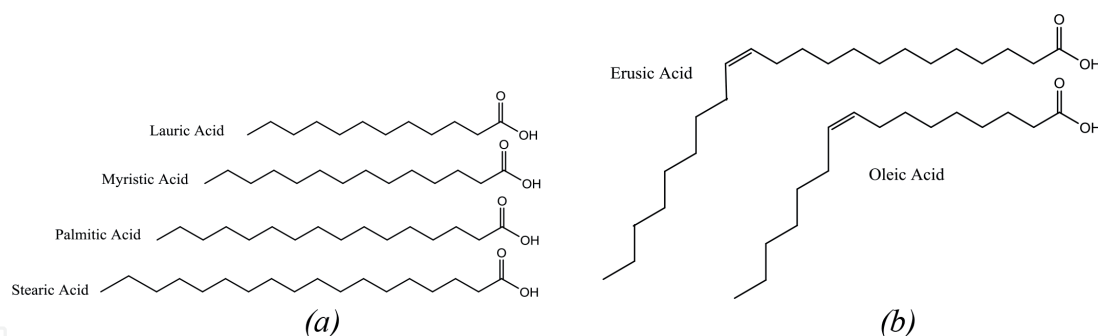
Figure 5.
The most used fatty acids for esterification into sucrose (a) saturated fatty acids (b) unsaturated fatty acids.
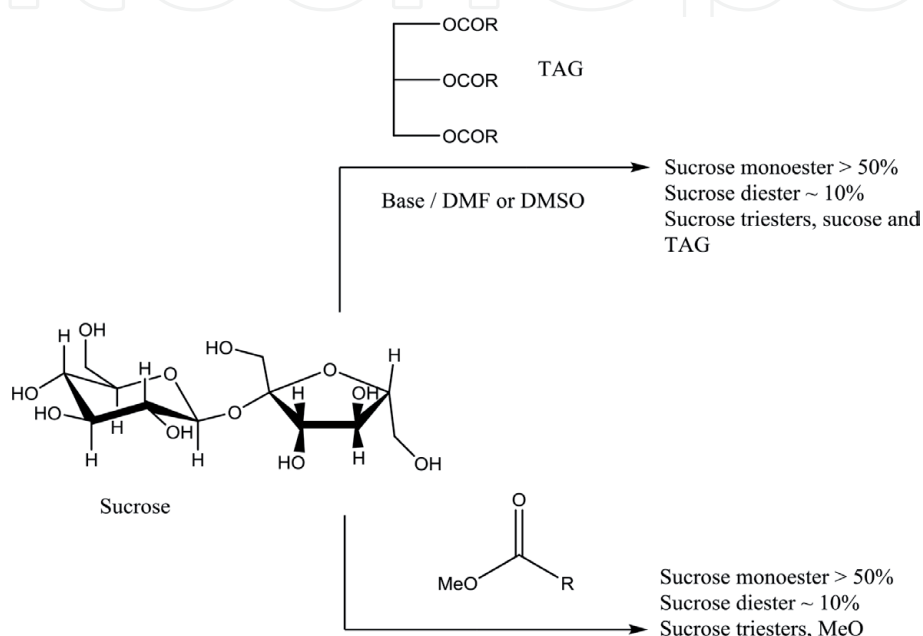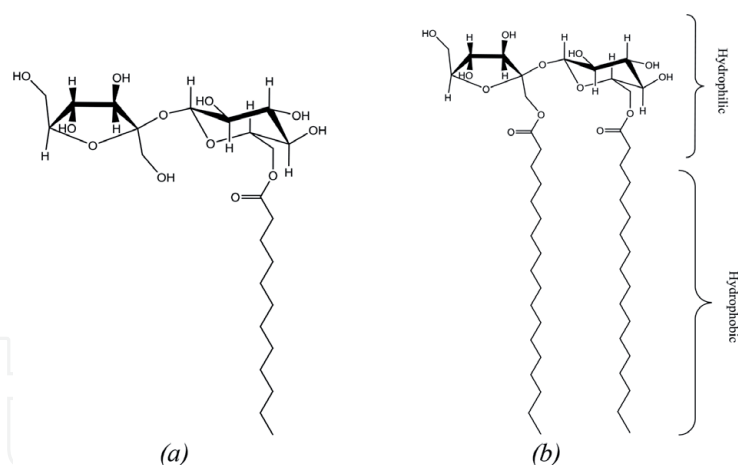

Figure 6.
Reaction pathways to obtain the sucrose esters.

triacylglycerol lipases that selectively hydrolyse insoluble triacylglycerol's at the substrate-water interface [18, 19].

Most of the physical–chemical characteristics of a determined sucrose ester are related to the kind of fatty acids used for esterification. In **Figure 7** the chemical formula of a di-ester of sucrose is show, where the esterification occurred in the 1 and 6' position and the fatty acid used was the stearic acid.

Sugar esters are considered as typical low molecular weight surfactants, they decrease the surface tension on interfaces and form micelle sub-structures of oil and air in water after reaching the CMC. The CMC depends on the structure of the sugar ester. Having low molecular weight, sucrose esters are soluble in water and they will make the stabilisation of O/W emulsions. The HLB value depends on the type of fatty acids used in esterification [20]. The relationship between HLB water-solubility and composition in the sucrose esters is dependent on three factors: (a) the degree of emulsition; (b) the alkyl chain length in the ester group; and (c) the presence of dienoic or trienoic acyl groups. Providing the right blend of mono- and di- sucrose esters linear values of HLB range from 10–16. If mixtures are made with glycerides and sucrose esters the HLB range from 4–16 can be covered [21]. The HLB scale of sucrose esters is usually defined by suppliers and it should be merely considered as an index of ranking: from the most hydrophilic (high HLB) to the most lipophilic (low HLB) within the sucrose ester family.

Figure 7.
The chemical formula of (a) a mono-acyl-sucrose ester and of a (b) di-acyl sucrose ester.

Some authors [22] worked on the clarification of the real HLB for the sucrose esters. They concluded that the experimental HLB of sucrose monoesters, would be around 11–12 for short fatty chains (6 to 12 carbons) and around 10–11 for long fatty chains (14 to 18 carbons). Those values are slightly different than the values presented by the producers that range from 2–16. Sucrose esters powders may come with residual amounts of fatty acids and those, by their turn, may appear in the neutral form or in the protonated form. Fatty acids in neutral state are also able to act as surfactants and they are good to stabilise the O/W emulsions.

The easiest parameter to evaluate the thermal stability of sucrose esters is the melting point, it can vary within the 40–60°C range depending on the type of fatty acids that have been esterified. Nevertheless, the emulsions can be heated to about 180°C (they decompose above 220°C) without compromise their emulsification properties of the surfactants (however a colour change may be observed in high temperatures if sugars are present due to caramelisation). The thermal properties of sucrose esters depend on the various HLB values: high or medium HLB values tend to be vitrified by melting. Since sucrose esters are usually a mixture, apart from crystallisation, they also present amorphous structures which slowly crystallise in time [23].

Sucrose esters are stable in the pH range of 4 to 8, so they can be used as an additive in most foods. At pH higher than 8, saponification (hydrolysis of the ester bond to release the original sucrose and the salt of fatty acids) might occur. Hydrolysis could also occur at pH lower than 4.

3.1.1 Common uses for sucrose esters

Monoesters of sucrose esters are most commonly studied, although applications of di-esters or higher esters have also a wide range of applications. The sugar esters can be used in white sauces, dairy products that are alternative to milk, aerated dairy desserts, like ice cream, mousses, bakery, confectionery, preparation of cereal based products [18].

Thus, no wonder that the use of sucrose esters as surfactants in the food industry has been increasing exponentially. Apart from the emulsification power that will be discussed next, they also present advantages concerning about their biodegradability: after ingestion, the sucrose esters are hydrolysed by digestive enzymes into sucrose and their component fatty acids that are further metabolised in the usual way [5].

In a general approach the use of sucrose esters as additive in food preparations will allow the formation of O/W emulsions. The presence of the sucrose ester will replace the oil (fat) continuous phase by smaller globules/oil droplets imbied into a water

phase. The encapsulation of the oil will protect it against oxidation, which occurs in the presence of oxygen and light. This will improve the stability of the prepared food and will increase the shelf life. They can also act as humectants as they can make the stabilisation of the water/air interface, as so, they are popular in preparations of foams. In addition of acting as emulsifiers and texturizers, they present several other advantages such as the protection of proteins from flocculation, the prevention of sugar crystallisation and they form stable structures resulting from interaction with starch.

3.1.1.1 Preparations based in oil/water emulsions

Typical O/W emulsions are mayonnaise and dressings. Sucrose esters are used in their preparation as an alternative to egg yolk. Sucrose esters with a high HLB value are soluble in cold water so the preparation can be made at room temperature. They also do permit the formation of stable emulsions with very small droplets; this is only possible due to their ability of significantly lowering the tension in the oil–water interface. Another important feature is that emulsions can be made with homogeneous droplet radius; this will avoid coalescence of the small droplets into to bigger, ones once the former have higher Laplace pressure.

Visually the emulsions made with sucrose esters appear like a white sauce and they impart a creamy sensation. A large number of small oil droplets give the impression of a higher fat content, thus, the creamy mouth feel and flavour perception of the preparations and will mimic the sensation of taste provided by fats. In addition, the small droplets will scatter the light into various directions increasing the brightness of the preparation and giving a whiter appearance. In the preparation of mayonnaise, the emulsion must be made before adding the acidic components in order to prevent the hydrolysis of the ester that can occur at values below pH 4.

Sucrose esters can replace milk proteins in the preparation of white sauces and improve the stability of the emulsion. There are sucrose esters (or mixture of sucrose esters) in the market that have higher O/W emulsification power than proteins. The small size of the oil droplets obtained and their homogeneity, provide high stability against flocculation and the emulsions may not require a high viscous continuous phase. The viscosity of the continuous phase is, generally, obtained by adding starch (in this case it will work as a stabiliser). The advantage in gastronomic terms is to have sauces that are less sticky, more satiny and with good power to release flavours. Furthermore, the preparation does not decompose by Maillard reaction[1] during pasteurisation or sterilisation. Drinks based on soy, almond, rice and coconut are popular alternative products to milk. The addition of sucrose esters in their processing allows the stabilisation of the oil emulsion in a continuous hydrophilic phase that usually displays low viscosity. Again, "the milk alternative product" will appear whiter. Usually the mono-esterified esters are chosen since they interact better with proteins that are pH sensitive due to their isoelectric point. The tension-active agent will interact with these proteins, stabilising preparations against flocculation [28].

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[1] Reaction between amino acids and reducing sugars that initiate a complex cascade of reactions during heating, resulting in the final formation of substances brown called melanoidins. It begins with the nucleophilic attack of the α-carbonyl group of a reducing sugar, for example, to the amino group of proteins. The occurrence of the reaction in food depends on several factors: high temperatures (above 40°C), water activity in the range of 0.4 to 0.7, pH in the range of 6 to 8 (preferably alkaline), relative humidity of 30% at 70%, the presence of transition metal ions such as $Cu2+$ and $Fe2+$, which can catalyse the reaction [24–27].

Pre-preparations of fat-soluble substances for further water dilution: fat soluble substances such as omega-3 and some natural dyes may be previously mixed with sucrose esters and kept as a concentrated emulsion for further incorporation into water-dispersed form in beverages, dairy products, and confectionery.

3.1.1.2 Preparations based in oil/water emulsions with significant sugar content

In preparations with sugar like chewy soft candy and ices, sucrose esters are also widely used nowadays. The reason for that is related to the capacity of sugar esters to control sugar crystallisation. Sucrose esters promote the formation of secondary grains during crystal growth process and prevent the agglomeration by making a homogenisation of the crystal size. The delay on sucrose crystallisation may be due to the decrease of the molecular mobility [29] or to the disrupting the crystal lattice due to molecular interactions between sucrose and the additive [30]. The polar group of the sucrose ester interferes with crystallisation after cooling precluding the crystal growth: during cooling the non-polar fatty acid of the sucrose ester will move from the polar sugar solution to the less polar sugar crystal. As a result, the sugar crystals will be surrounded by a layer of fatty acids that will prevent further crystal growth see **Figure 8**. The re-solubilisation and re-crystallisation of the sugar will be inhibited. The sugar ester layer around the micro-crystalline nuclei stabilises the outer shell of water and prevents water evaporation from the sugar mixture (in fondants). This will result in a gritty mouth feel.

Bakery products with sucrose esters as additives are very usual. The esters form a flexible network with gluten making the preparations more resistant to mechanical stress during processing. In addition, they contribute to maximise gas retention due to their properties of stabilisation of the air/solid interface (see 3.2.1.3). Sucrose esters are also able to interact with starch: they have the ability to complex with the linear and helical amylose and the branched amylopectin. In consequence the temperature and enthalpy of gelatinization will change [31]. The capacity of interaction with starch varies with the length of the monoester and the degree of saturation. The sucrose fatty acids interact preferentially with amylose and form a helical complex during gelatinization. This reaction prevents retrogradation of the starch and increases the long-life term [32].

3.1.1.3 Aerated oil/water emulsions preparations

Sucrose esters are good humectant agents since they significantly decrease the surface tension value of water solutions or hydrocolloids. They help into aeration and promote foam stabilisation.

Foams correspond to the macroscopic manifestation of an air/liquid or air/solid interface, air appearing as bubbles. The dispersive phase can be a water
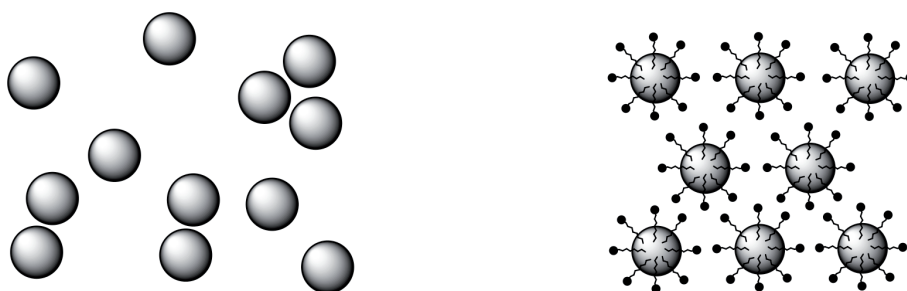

Figure 8.
Effect of sucrose ester into the crystal growth of sugar (a) without the surfactant; (b) with surfactant: the crystals are surrounded by the fatty acid chain that protect the micro-crystals from further growth.

	% of monoester	HLB value	Surface tension 10^{-3} (N/m)
Sucrose laurate	70	15	28.5
Sucrose palmitate	75	16	34.0
Sucrose stearate	70	15	34.5
Sucrose stearate	50	11	36.7
Sucrose stearate	30	6	46.8
water			72.8

Table 1.
Values for hydrophilic/lipophilic balance (HLB) and surface tension (Du Noüy method) for several sucrose esters surfactants and for water at T = 20°C [33]. Concentration above the critical micelle concentration.

solution, fat, protein or hydrocolloids. Water has a high surface tension thus, without a surfactant, it is difficult to retain air inside. The addition of a sugar ester to the preparation reduces the surface tension in the interphase and makes the foam stable. **Table 1** gives the values for surface tension of several sucrose surfactants [33, 34].

The lower the surface tension the easier to prepare the foam and to keep it over time. The value for the surface tension of air/water interfaces that is obtained at concentrations higher than the CMC tends to be in the range of 24–44 mN/m. One of the most effective surfactants is the sucrose laurate with HLB of 15 and surface tension of 28.5 mN/m.

The presence of three phases (water/oil/air) puts additional challenges to the stabilisation of the preparation. First, the presence of fatty materials destabilises the aqueous foams because the water film around the air bubble will be squeezed by the presence of the fat: this will decrease its thickness leading to the collapse of the air bubble. If an emulsion is made previously to aeration the surfactant must be used to stabilise the fat droplets first in order to preclude the interference of the fat with the water layer around the bubble. For this purpose, the use of a surfactant with medium HLB value (6–11) is the better choice since they can make stable oil-in-water emulsions. However, to ensure a longer shelf life without syneresis and retraction, preparations must contain stabilising and gelling agents.

The second challenge deals with the presence of proteins. Proteins are surface active agents and compete with the sucrose esters in the surface of air/water and in the interface of oil/water droplets and, as seen, generally the formation of the oil/water emulsion precedes the aeration process. In preparations of creams those proteins are egg and milk proteins. It seems that egg proteins are more effectively absorbed in the oil/water interface than milk proteins [35], but low weight surfactants are able to displace the proteins from the fat layer drops, lowering the steric stabilisation made by the macromolecules, especially if they are daily proteins [36]. This will increase the probability of the coalescence of the emulsion during whipping. Those effects have been studied at least one decade ago and it seems that the content of sucrose ester is a key to obtain a good stability for the foam: in concentrations lower than 0.1% the amount of sucrose ester that is absorbed into the surface oil films is insignificant while in concentrations higher than 0.1125% most of the proteins are displaced by the surfactant in the oil/water interface [37], that is, little protein is left around the oil droplets of the emulsion due to the preferential adsorption of sucrose ester over milk proteins (**Figure 9**).

Additionally, the shear stress given by whipping promotes a higher desorption of milk proteins on the oil/water interface, that is, the egg proteins are better for
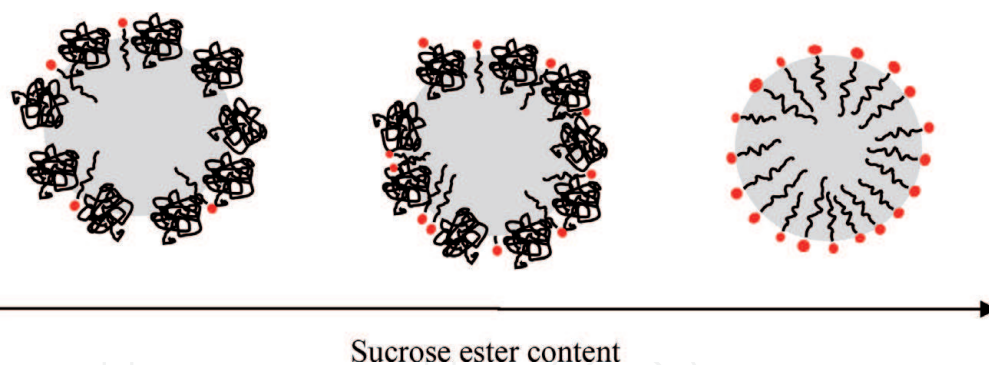
Figure 9.
There is a competitive absorption in the oil–water interface between milk proteins: in consequence a mixed surfactant protein film is formed around oil droplets. This last film is weaker than that obtained when only protein is present and will contribute to the destabilisation of the emulsion. The higher the content of sucrose ester in the preparation, the higher the degree of substitution.

preparation of stable foams, but in order to get a stable foam, partially coalescence of fat droplets should occur [38, 39].

3.1.2 Examples for the use of sucrose esters in molecular gastronomy

3.1.2.1 Preparation of a butter cream

The ingredients for the preparation of a butter cream are: egg whites (4 units); sugar (267 g) and water (60 g); unsalted butter (454 g); salt (1.5 g) and sucrose esters (5.4 g) (**Figure 10**).
Preparation consists in:

1. Mixing the surface-active agents: whisk the whites and sucrose esters and beat in an electric mixer initially at low speed (1) and then at medium speed (3).

2. Preparing the sugar syrup (aqueous phase): heat the sugar with the water to $T = 115°C$.

3. Incorporating of surfactants in the aqueous phase: slowly mix the glucose syrup into the egg whites until incorporated, increase the speed to medium-high and beat for 10 minutes. Allow to cool.

(a)   *(b)*

Figure 10.
Butter cream (a) and cream bubbles (b) preparations using sucrose esters, suggestion of presentation.

4. Preparing the O/W emulsion: add the butter slowly at room temperature (2 tablespoons at a time), until a homogeneous mixture is obtained.

5. Preparing the foam: add the salt and beat the mixture until it is well ventilated.

This is a typical O/W emulsion even if it looks like the opposite; although the amount of fat is higher than that of the water, the nature of the surface-active agent (its HLB) dictates the type of the obtained emulsion. On first step, protein egg whites (including globulins as albumins and mucoproteins) that can act also as tensioactive agents are mixed with the sucrose esters. After the preparation of the sugar syrup the tensioactive agents are to be mix with the aqueous phase. Sucrose esters interact in stabilisation of sugar crystallisation process but here the sugar syrup is kept always warm, as so, sugar esters will play a role into the solid/liquid interface only after aeration. Careful must be taken with temperature: not too low to avoid sugar crystallisation; not too high to avoid proteins denaturation (sugar esters protect protein against from flocculation). The oil phase is added slowly at room temperature in order to form the emulsion. In step 5 the whipping allows the air to be retain in the pre-obtained emulsion, that will be stabilised by the sucrose esters in the air/(O/W) emulsion.

3.1.2.2 Cream bubbles

Ingredients: Cream (250 g); milk (125 g); water (87.5 g); water for sugar syrup (37.5 g); sugar (37.5 g); sucrose ester (5 g) and spices (seeds of 1 piece cardamom, seeds of 1 piece of vanilla, ginger flower).
Preparation consists in:

1. Preparing the sugar syrup (aqueous phase): heat the sugar with the water to $T = 115°C$.

2. Incorporation of the sucrose esters with cream and milk (plus spices).

3. Incorporation of the sugar syrup into the of the oil/water emulsion: using a hand blender make a mixture of the syrup with the remaining boiled ingredients.

4. Filtration of the solids (spices): make a filtration with fine mesh sieves and keep warm.

5. Formation of the foam: mix with a hand blender right before serving.

Foams and whipped emulsions are stabilised by dairy proteins. The illustrated preparation has fats, proteins, hydrocolloids, and colloidal components. The presence of the sucrose ester contributes, together with the proteins, to stabilising the interacting components of the preparation as an emulsion when they are first boiled and mix (homogenisation). Then, at last minute, the aeration process to make the foam should be implemented (aeration).

Proteins (namely dairy proteins) and the sucrose ester present in the bulk preparation compete at interfaces air/water and oil/water. At high concentrations, the water-soluble sucrose ester is more effectively adsorbed at those interfaces and displace the proteins. This mechanism occurs depending on the ratio protein/surfactant. As so, proteins they are to be apportioned between the bulk phase (water) and interfaces (oil/water).

The mix of the sucrose ester with proteins in the interfacial layers makes the surface film to be weaker when compared only with proteins, contributing to the destabilisation of the emulsion. This is important to the aeration process: when a cream is whipped, shear forces are acting into an aqueous dispersive system with a high interface area that encloses, oil and gaseous phases brought together. The destabilisation of the emulsion will make the incorporating of air easier during the foam manufacture and at same time the aqueous phase behaves like a reservoir of active material surface, say, protein and surfactant. This is beneficial for building a network of partially coalesced fat globules around the air bubbles and for stabilising new formed air-water interfaces.

3.1.3 Safety and maximum daily intake

Sucrose esters were approved and registered by European Food Safety Authority or EFSA under the E number of 473. The authorization for the use of sucrose esters of fatty acids (E 473) was made in 1995 in various preparations but not for colour stabilisation and sweetening preparations but, having a wide range of applications, sucrose esters are used in many industrial preparations and the European Food Safety Authority (EFSA) requested to the food industries extra data about the use of the sucrose esters in baked goods and flavoured drinks (chocolate milk, cocoa, eggnog, drinking yogurt and whey based drinks) in 2004 [40].

The and the panel responsible for the evaluation concluded that the daily the exposure to the additive exceeded the acceptable daily intake of 40 mg/kg/bw/day.

Meanwhile health concerns on high consumption of the sugar esters of fatty acids raised since it is used in several categories of food of preparations where data was not provided from producers. As so, the current exposes could be higher than that advised by the panel.

In 2010, the panel recommend the collection of reported used form industry for fine bakery and flavoured drinks and in the light of new data, ANS Panel indeed concluded that the use of sucrose esters of fatty acids (E 473) may lead to an exposure higher than the 40 mg/kg/bw/day [41].

The uncertainty regarding the amount of E473 that could be ingested by the population, due to the wide use of these additives, led the commission to launch of a public call for data aiming at collecting reported use levels from industry or analytical data and a motorization of the presence of the surfactant on the label of foods in 2014. A refined analysis was made based on the preference of the population for consuming certain food categories and brands (flavoured drinks, fine bakery, only dairy-based and almond drinks). The panel concluded that the refined exposure in the brand-loyal scenario could be estimated as 54 mg/kg/bw/per day for babies (12–35 months) and as 124 mg/kg/bw/per day for children (3–9 years), but as not all categories were included this value may be overestimated [42].

The panel in 2018 recommended a higher detail in data collection in order to provide the scientific experts with data for a more realistic estimation. Thus, the actual studies point that there is an over cumulative intake of this additive by the European population due to quantity of preparations available in marked that use sucrose esters of fatty acids [42].

3.2 Mono- and diglycerides of fatty acids (E471)

Monoglycerides and diglycerides are lipid molecules composed of a single fatty acid or two fatty acids, respectively, esterified with hydroxyl groups of the glycerol [43, 44]. The food additive itself, consists of a mixture of glycerol mono-, di- and

tri-esters of fatty acids derived from edible oils and fats [45, 46]. The amount of mono- and di-esters should be at least 70% according to the European Regulation (2012), and may also contain a small quantity of free glycerol (maximum 7%) and fatty acids [45]. Therefore, it is a mixture of substances which may contain different mono- and diglycerides of fatty acids, depending on the fatty acid sources. The fatty acids in mono- and diglycerides may be saturated or unsaturated, being the lauric, linoleic, myristic, oleic, palmitic, and stearic fatty acids the most prevalent. [46].

A revision concerning the synthesis of monoglycerides was published some years ago [46]. Their synthesis can be made according to schematic reactions presented in **Figure 11**. As seen, mono- and diglycerides of fatty acids may be produced by chemical methods, such as inter-esterification (glycerolysis) of fatty acid esters with glycerol and direct esterification of glycerol with fatty acids [47–49]. Some methyl esters of the fatty acids used are depicted in **Figure 12**. Both reactions occur under alkaline conditions at a high temperature (200–250°C), and yield a mixture of mono-, di- and triglycerides in addition to a reduced fraction of free glycerol [46, 50]. Alternatively, mono- and diglycerides of fatty acids may be produced by enzymatic hydrolysis of triglycerides [51, 52]. The advantages of enzymatic synthesis are higher yields and mild reaction conditions, resulting in products of higher quality and lower energy consumption [53].

Regardless of the chosen method, it is usually necessary to separate and to concentrate these glycerides [48]. Monoglycerides may be separated from the
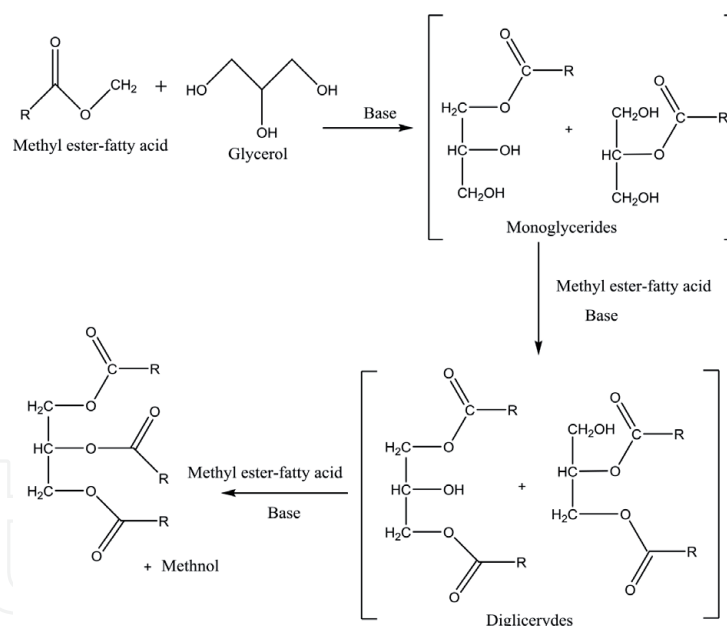

Figure 11.
Synthesis of monoglycerides, diglycerides and triglycerides via trans-esterification (glycerolysis) using methyl-fatty acids and glycerol in a basic reaction medium (adapted from [46]).
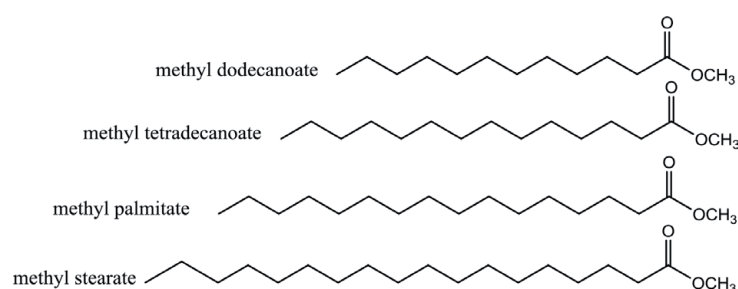

Figure 12.
Examples of methyl esters fatty acids used in the esterification of glycerol.

diglycerides, triglycerides, and glycerol by molecular distillation. This a method to separate and purify thermally unstable compounds and substances with low vapour pressure and higher molecular weight, without significant thermal decomposition [48]. Molecular distilled monoglycerides contain an equilibrium of 1-monoglycerides and 2-monoglycerides dependent on the temperature used during the process. The monoester content is usually 90–95% in commercially distilled monoglycerides [50]. Distilled monoglycerides have a better dispersibility in water than the mono- and diglycerides of fatty acids because they present high purity and well-defined molecular structure, forming a liquid crystalline mesomorphic phase with ordered bilayers of the fatty acid chains, separated by water layers associated with the polar groups [50]. This feature is useful in food products where interactions with water-soluble ingredients (e.g., starch components) or the aerating properties of fat-free products are of importance [54]. When distilled monoglycerides are heated to their melting point with water, a gel is formed in which the water layers alternate with lipid bilayers [55]. The melting point depends on the chain length of the fatty acid and on the purity of the monoglyceride [50].

Mono- and diglycerides of fatty acids are amphipathic molecules, which can be represented as depicted in synthetic pathways of **Figure 11**. They can be absorbed in the water/oil surfaces once the hydrophilic head has a high affinity for water, and a lipophilic tail to the oil [49]. The structure of mono- and di-glycerides of fatty acids classifies them as surfactants, i.e., surface-active agents or molecules that migrate to the interface between two phases (solid, liquid, or gas).

The functional properties of mono- and diglycerides of fatty acids are determined by the HLB of the mixture that will depend on i) the type of fat used as the base ingredient, i.e., if the original fat is saturated or unsaturated, ii) the length of the hydrocarbon chain fatty acids and iii) the percentage of monoglycerides. The mono- and di-glycerides of fatty acids are non-ionic oil soluble surfactants, predominantly lipophilic and only sparingly soluble in water, having a low HLB. Therefore, they stabilise W/O emulsions such as margarines and spreads, by forming reversed micelles in oil [50, 56]. They are also used to inhibit fat crystallisation in some O/W emulsions because this improves the stability of the food product to refrigeration conditions, for example, in dressings. Moreover, oil-soluble emulsifiers can be used in combination with water-soluble emulsifiers to facilitate protein displacement from fat droplets during the manufacturing of ice creams, whipped creams, and toppings.

3.2.1 Common uses for mono- and diglycerides of fatty acids

The food additive mono- and diglycerides of fatty acids offers the food industry many solutions for optimal product formulation and processing. When used as additive in food products such as bread and baked products and ice cream, mono- and diglycerides of fatty acids require a high concentration of monoglycerides [57, 58]. The high interest of the food industry in the utilisation of mono- and diglycerides of fatty acid additives is due to the fact they are safe for consumption and have useful properties that improve the production of food products [59].

Food-grade mono- and diglycerides of fatty acids have been studied as surface-active substances or foaming agents. Diglycerol monomyristate influences the foamability and stability of olive oil foams, depending on the surfactant concentration, and the size of its solid particles [60]. Moreover, the addition of a mixture of distilled mono- and diglycerides of edible saturated fatty acids from vegetable origin with a total content in monoglycerides larger than 90% result in high stable foams of rapeseed oil, in which a dense layer of surfactant crystals at the oil-air interface protects the air bubbles, thus preventing the dissolution and coalescence

of the system [61]. In addition, there is reported evidence of Pickering stabilisation of gas bubbles by monoglyceride crystals at the air–oil interface. Gunes *et al*. observed that the air bubbles produced in sunflower oil with a monoglyceride (98% saturated) were covered by a layer of monoglyceride crystals preventing rapid dissolution and coalescence of the oil foam [62]. In addition, whipping is an important mechanical process for the effective coverage of the bubble surface with the stabilising layer of fat crystals as compared to foams obtained by depressurization [62].

3.2.2 Examples for the use of mono- and diglycerides of fatty acids in molecular gastronomy

3.2.2.1 Mono- and diglycerides of fatty acids to prepare "olive oil foam"

To prepare "olive oil foam", two ingredients are necessary: extra virgin olive oil (200 g) and mono- and diglycerides flakes (200 g) **Figure 13**.
Preparation consists in:

1. Heat the olive oil with the mono- and diglycerides of fatty acids flakes until the mixture reaches the temperature of 60°C. Stir until the flakes dissolve.

2. Pour the mixture into a heat resistant whipping siphon and charge as instructed by the manufacturer.

3. Serve warm. To use it later, keep the whipping siphon at room temperature.

3.2.3 Safety and maximum daily intake

According to the European Regulation the presentation of the food additive E-471 varies from a pale yellow to pale brown oily liquid to a white or slightly off-white hard waxy solid. The solids may be in the form of flakes, powders, or small beads [63].
Mono- and diglycerides of fatty acids are the most widely used food emulsifiers, accounting for around 70% of the world production of food emulsifiers [3, 56]. Commercial mono- and diglycerides of fatty acids usually contain 45–55% mono-glycerides, 38–45% diglycerides, 8–12% triglyceride and 1–7% free glycerol [50]. Mono- and diglycerides of fatty acids are also produced in the gastrointestinal tract during the hydrolysis of the food derived triglycerides by gastric and pancreatic lipases [64]. Mono- and diglycerides of fatty acids have been evaluated by the Joint

Figure 13.
A olive oil foam prepared with diglycerides flakes.

FAO/WHO Expert Committee on Food Additives in 1974. The commission recommended a specific risk assessment for its use in food products for infants under the age of 12 weeks [65]. In 2017, the safety of mono- and diglycerides of fatty acids when used as a food additive was re-evaluated by the EFSA Panel on Food Additives and Nutrient Sources added to Food for ages above 12 weeks of age [66]. Since the hydrolysis of mono- and diglycerides of fatty acids is likely to occur in the gastrointestinal tract with production of free glycerol and free fatty acids. For this reason, the Panel also evaluated the safety of the food additives glycerol (E 422) and fatty acids (E 570). No evidence for adverse effects was reported in toxicity studies that assessed these additives. Neither genotoxic nor carcinogenic effects have been observed [67]. On the other hand, exposure to mono- and diglycerides of fatty acids may be compared with the fat consumed, due to the similarity in their metabolic breakdown. US dietary guidelines recommend an overall fat consumption of 30% of total energy intake and saturated fat consumption of 10% of total energy intake [68]. High saturated fat intake has been associated with higher risk of coronary heart disease and mortality [69]. Although not all saturated fats have the same biological activity, the saturated fatty acids palmitic acid and myristic acid, often used in E-471 additives, may have the most negative impact on serum lipidic levels [70]. However, EFSA Panel reports a small contribution of mono- and diglycerides of fatty acids to the daily fat intake, representing around 0.8–3.5% of the recommendation [67]. EFSA Panel concluded that there was no safety concern regarding the use of these food additives for the general population and that there was no need for a numerical acceptable daily intake [66]. In addition, since the dietary exposure to emulsifiers has not increased over the 10-year period there is no reason to suspect that the dietary exposure may cause a safety concern [47].

As mentioned before, the additives here discussed act as surfactant food additives. Independently of the assessment and evaluation, it is worthy to be mention that there are studies concerning their possible effects on intestinal barriers and microbiota that probably will keep the experts watchful. Recent studies suggest that high doses of emulsifier consumption may contribute to the rising incidence of several diseases involving the gastro-intestinal tract [71–73]. The rise of scientific reports and population studies will help risk assessors make adequate re-evaluations concerning the authorised food emulsifiers.

4. Conclusions

The utilisation of sucrose esters of fatty acids and mono- and diacylglycerides of fatty acids as food additives has been increasing exponentially. Those molecules act as surfactants and, depending of their mixtures and nature of the esterified fatty acids, they can present a wide range of HLB values. As so, they are useful for promoting the stabilisation of oil–water; water–oil and water/oil-gas emulsions. They are a common ingredient in industrial bakery, white sauces, alternative dairy to milk, aerated dairy desserts, ice creams, mousses, confectionery and preparation of cereals based products. They are obtained by chemical or enzymatic synthesises from natural reagents as fatty acids, sucrose and glycerol by esterification present advantages concerning about their biodegradability: after ingestion, they are hydrolysed by digestive enzymes into sucrose/glycerol and their component fatty acids that are further metabolised in the usual way. Despite this, concerns about their safety are rising since the daily intake doses may become higher than the maximum safe daily intake doses. Evaluation panels made studies about refined exposure in the brand-loyal scenario concluding that the daily intake doses could be overestimated specially in babies and children.

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