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Lipids. Colloidal components with functionality in food systems

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Abstract

The multitude of natural and / or partially or fully processed food products, regardless of the technology accessed, can be found at some point in the form of emulsions, or in a colloidal physical state. These emulsions contain a variety of ingredients, such as water, lipids, proteins, carbohydrates, minerals, sugars, and surfactants. By the combined action of covalent and physical binding forces, the constituent components give personality to the structural individuals that imprint on the product the final physical-chemical properties. Food lipids are generators and supports for many substances that give the taste and aroma of each food product. The quality and specificity of the flavor depend on the composition, the heat treatment applied and the processing. The major role of agri-food processing is to detect the complex relationship between the structural properties of the network and the molecular ones in order to finally obtain functional foods with beneficial characteristics on the body.

Keywords: lipids, emulsions, emulsifiers, lipids in food

1. Definitions

The etymology of the word "lipids" comes from the Greek "lipos", meaning "fat", "grease", this being the most widespread and representative combination in the group of lipids. Generally, lipids are considered natural mixtures of animal or vegetable origin, whose characteristic components are triglycerides [2].

Being insoluble in water, they are found naturally in living organisms, in the form of emulsions and they have a lipophilic character [2,3].

By restricting the area of definition, in specialized terms, lipids refer to higher organic acids and their derivatives (mono-, di-, triglycerides and phospholipids), sterols and metabolic compounds (cholesterol) [2,14,16,20].

Figure 1 shows some examples of lipid structures.

2. Structural characterization of vegetable or animal origin lipids

Lipids are a heterogeneous group of natural organic compounds present in all plant and animal tissues, performing biological functions of the utmost importance. Thus, some lipids are the structural element of the cell membrane that isolates the cell with its subcellular components from the organic environment, and others constitute the energy reserve of the living organism. Due to the presence of lipids in agri-food raw materials, they appear in different proportions also in the products resulting from their processing [23,28,29].

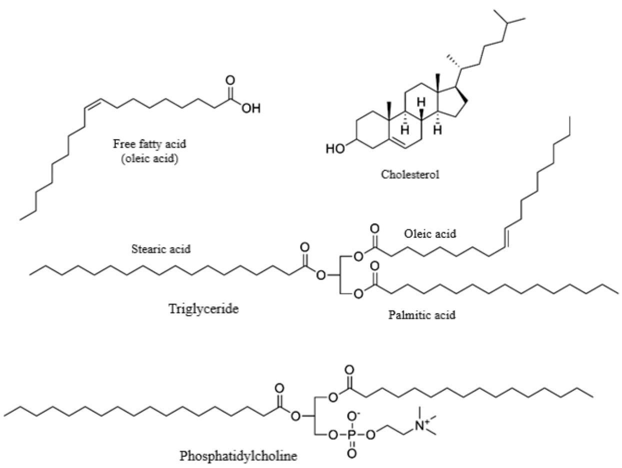

Figure 1. Lipid structures (examples)

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In a mixture, the lipid content does not exceed 2% of the biomass, but in certain plant and animal tissues they are concentrated (15%÷60%). This offers the possibility of their economic separation in the form of animal fats and vegetable oils, waxes, phospholipids, etc. [1,2].

Lipids have great biological value as component parts of foods, which, through their physical-chemical properties (reactivity, structure and energy equivalent of approximately 39 kJ / g fat), gives them *nutritional*, *organoleptic* and *textural qualities*, which particularizes many foods [28].

In most cases, lipids, in addition to the role of transmembrane transporters in the biological functions of the cell, they also have a technological role for all organic and inorganic components. Thus, lipophilic substances can be transported due to hydrophobic residues (fats and non-polar substances), and with the help of hydrophilic groups can be transported polar components or water. This structural property confers the *amphiphilic* character of polar lipids. Their structure is linear or ring-shaped, some being flexible or rigid, having a non-polar part that does not interact with water, and another polar part (figure 2) [23].

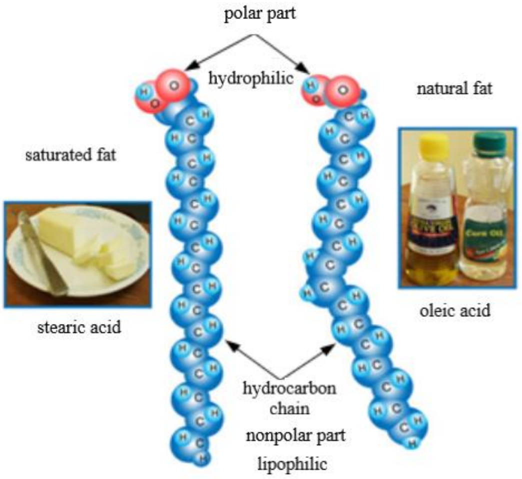


Figure 2. Molecular structure of some lipids (triglycerides) with the two characters: polar (hydrophilic) and (nonpolar) lipophilic

From the point of view of the *biological role* that they play in the body, lipids are classified into:

- ✓ *reserve lipids*, stored in cells and tissues as the body's primary energy and functional source.
- ✓ *constitution lipids*, these are constant elements present between the cellular components, without changing the composition in relation to the nutritional intake, because the basic function is physiological in nature and not energetic [2,3].

3. Lipids - functional basis of food emulsions

Emulsions have been known for a long time, first in practice, and then they were studied theoretically. As early as 1845, F. Selmi studied the nature of emulsions, but the scientific basis for their study was laid by F.G. Donnan in 1923, by establishing a link between the emulsification process and the variation of the surface tension at the limit of the droplets of the two phases. W. Harkins, A. Clark (1917) and others studied the emulsions in terms of surface phenomena. Also, W.C.M. Lewis (1932) and W. Clayton (1943) obtained a whole series of emulsions and studied their properties [6,12,17,24,34].

An emulsion is a dispersion of the drops of one liquid into another liquid, the two liquids being immiscible with each other (lyophobic in relation to each other) [8,31].

Dispersion can be done either by directly fractionating large droplets of liquid into smaller droplets, either by pre-forming a film of liquid and then breaking it into small drops. The means for performing the emulsification can be: mechanical, electrical or ultrasonic. The emulsification process eventually leads to the formation of a colloidal dispersion - **the emulsion** [5].

In food, the major immiscible liquid components are **water** and **oil**. The diameter of the droplets in the emulsions varies between 0,1÷50 µm. A system made up of oil droplets in water is called an *oil-in-water emulsion* (O/W). A system of water droplets dispersed in an oil-saturated phase is called a *water-in-oil emulsion* (W/O). The causal component of the appearance of drops in an emulsion is called the *disperser* or *internal phase*, and the component that creates the surrounding fluid is called the *continuous phase* or the *external phase* [8,31].

Technological possibilities have led to the obtaining of **multiple emulsions** useful in providing a protective environment or films for certain bio- or chemo-constituents, for speed control and conditioning flow of ingredients, or for obtaining products with low energy value [35].

Emulsions are thermodynamically unstable systems caused by the positive energy needed to increase the surface between phases (oil-water).

The antagonistic interaction between oil and water originates from the binding energies; for water molecules these binding energies are strong hydrogen bonds, which do not form bonds with oil molecules.

The role of the emulsion is to reduce the surface area between the two immiscible liquids, liquids that tend to separate into two phases - a layer of oil (low density) at the top of the emulsion and a layer of water (higher density) at the bottom.

This can be exemplified by homogenizing the oil and pure water: initially an emulsion is formed, but after a few minutes the separation phase takes place (figure 3) [8,33].

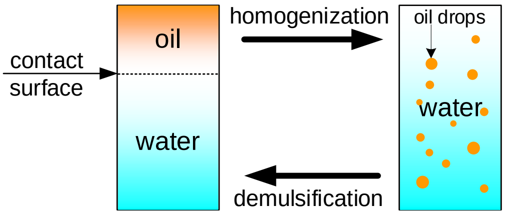


Figure 3. Example of mechanical formation of an O/W type emulsion. The emulsions are thermodynamically unstable systems, which tend to return over time to individual components (oil and aqueous phase). To obtain an emulsion, a certain energy consumption is required.

The instability of emulsions can be manifested by a variety of physical-chemical mechanisms, including mixing, flocculation, coalescence and phase reversal, statements made since the 6th century. For the formation of emulsions that have stability over a longer period of time (even years), chemicals known as emulsifying agents are important in the homogenization phase. Emulsifying agents (emulsifiers) shows superficial activity by adsorption to the surface of freshly formed drop molecules during homogenization, forming a protective membrane by maintaining a distance between the drops so that they cannot aggregate. Most emulsifiers are **amphiphilic molecules** in which the polar and non-polar regions coexist. The most common types of emulsifiers useful in the food industry are lipid-based emulsifiers (small chain surfactant molecules and phospholipids) and ***amphiphilic biopolymer molecules*** (proteins and polysaccharides) [10,11,22].

Most food emulsions are a complex multivariate compositional system. The aqueous phase may contain water-soluble ingredients of various types (sugars, salts, acids, bases, surfactants, proteins and polysaccharides). The oily phase may contain a variety of lipid soluble components, such as: tri-, di-mono-glycerides, higher organic acids, fat-soluble vitamins and cholesterol. The separation membrane may contain a wide variety of surface-active components (small surfactant molecules, phospholipids, polysaccharides and proteins).

Some components of food emulsions do not have localization exclusively in a single phase, these being distributed between the aqueous phase, oily phase and the interfacial space, depending on their partition coefficient. Many of the minor components present in an emulsion (even in low concentrations) can have a pronounced character on the physical-chemical properties of the whole food system.

Food emulsions may consist of oil droplets dispersed in the aqueous phase (ex.: milk, mayonnaise, creams, soups, etc.), or water droplets dispersed in the oily phase (ex.: margarine, butter). The droplets and / or the continuous phase can be fluid, gel, crystalline or glassy, and the size of the droplets can vary from units smaller than 1 μm to units of several hundred μm and can be more or less polydisperse [18,22,26,30].

Furthermore, things can be complicated, because the properties of food emulsions constantly undergo, over time, a series of transformations under the combined action of the technological path of physical, chemical, microbiological or enzymatic processing. In addition, during processing, storage, transport, handling, food emulsions are subjected to thermal "shocks" (ex.: sterilization, pasteurization, fractional crystallization, frying, refrigeration, freezing) and also to various mechanical forces (ex.: mixing, homogenization, centrifugation at high pressures, flow through pipes), which ultimately contributes to the modification of physical-chemical parameters. Although the compositional, structural, dynamic complexity of food emulsions is very varied, so far, a number of progresses have been made in understanding the mechanism of the major influencing factors determining the physicochemical properties for the entire food colloidal system [10,19,22].

The criteria for classifying emulsions are multiple:

- by their nature or provenance;
- by the type of the two liquid phases;
- by the concentration of the constituent phases;
- by particle size.

a) *according to the nature* of the emulsions, we distinguish: natural and artificial emulsions. Natural emulsions can be of vegetable origin (ex.: the latex of some plants (natural rubber)) and of animal origin (ex.: milk, fats in digestive juices, lipids in the blood, etc.). Artificial emulsions are particularly varied (ex.: mercury in water, oil in water, liquid polymers in water, etc.);

b) *according to the type of liquid phases - their polarity* - the emulsions are divided into: oil-in-water emulsions (symbolized ***O/W***) or first (**I**) order, wherein the dispersed phase is a non-polar (or weakly polar) liquid and the external phase is a polar liquid; water-in-oil emulsions (symbolized ***W/O***) or the second order (**II**), wherein the dispersed phase is a polar liquid and the external phase is a non-polar liquid (or weakly polar);

c) *according to the concentration*, emulsions can be: diluted, in which the internal phase represents a maximum of 2% of the emulsion volume; concentrated, in which the internal phase can reach 74% by volume (emulsions appear as relatively fluid) and gelled (or highly concentrated) in which the concentration of the internal phase exceeds 74% by volume (emulsions appear as gels);

d) *according to particle size,* we distinguish:

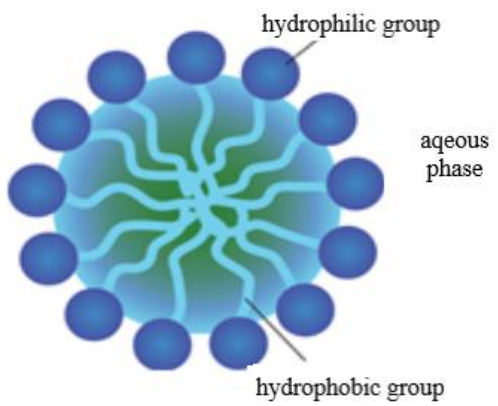
- ✓ macroemulsions or emulsoids - with particle size of 10^{-5} m;
- ✓ nanoemulsions - with particle sizes of the order $10^{-6} \div 10^{-7}$ m;
- ✓ microemulsions - with particle sizes of the order 10^{-8} m [4,31].

4.Molecular characterization of colloidal lipid systems

The most important types of emulsions based on a lipid complex useful in the food industry are small molecule surfactants (ex.: Tweens and Spans products, salts of higher organic acids) and phospholipids (ex.: lecithin).

The main role of lipid-based emulsifiers for food emulsions is to generate shape and stability of the food matrix, although they can induce changes in physicochemical properties by interacting with other participating elements (proteins, minerals, polysaccharides), or by changing the size of the crystal lattice. Emulsions in this class are *amphiphilic*, consisting of a hydrophilic "*head*", with high affinity for water and a lipophilic "*body*" with affinity for lipid mass. This class can be represented by the form RX, where X represents the hydrophilic "head" and R the lipophilic "body". The "head" may be an anionic, cationic, amphiphilic or nonionic group. The most common emulsifiers, based on a lipid complex, used in the food industry, are those of a non-ionic nature (ex.: monoglycerides, sucrose esters, Tweens and Spans products), anionic nature (ex.: higher organic acids) or amphiphilic (ex.: lecithin). Generally, the "body" consists of one or more hydrocarbon chains having between 10 and 20 carbon atoms / chain. The hydrocarbon chain may be saturated / unsaturated, linear or branched, aliphatic and / or aromatic. Of these, the largest share in food is represented by single or paired hydrocarbon chains, linear aliphatic, saturated / unsaturated. Each representative of this class of emulsifiers has unique *functional properties*, dependent on the chemical structure [7,9,13,15,27].

Micellar lyophilic soils contain as a dispersed phase a soluble micromolecular substance, which, depending on some conditions, has a certain particularity - **the association**. They can form spontaneously aggregates in solution thus giving thermodynamic stability to the system. These structures are known as ***association colloids*** (ex.: micelles, double membrane layer, vesicles, inverted micelles) (figure 4) [8].



spherical micelle

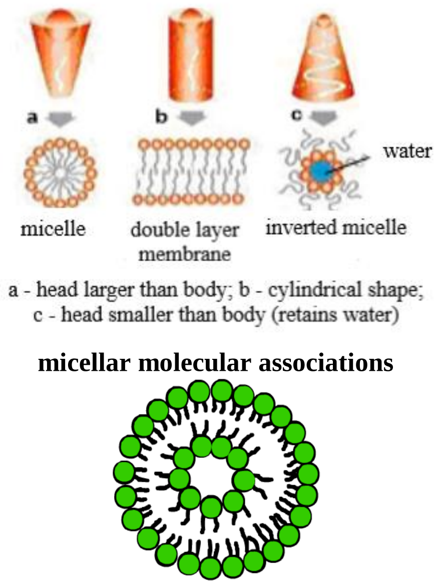


Figure 4. Presentation of common structures adopted by amphiphilic lipids in aqueous environment

These structural types are often adopted in processing for their role in reducing the contact surface between the nonpolar "body" of the molecules from the colloidal system and water.

The colloidal typology (figure 4) is mainly dependent on the polarity and molecular geometry adopted, characterized in turn by a number of factors (lipid class, crystallization temperature, polymorphism, operating parameters, etc.). The forces that allow the maintenance of grouped colloids are relatively *weak*, which gives *dynamics* and *flexibility* to the structure. Their size and shape are constantly changing, and molecular individuals allow rapid exchanges between the micelle and the environment. Relatively weak bonding forces that keep the association colloids grouped, causes some structural sensitivity to the intervention of external environmental factors (temperature, pH, ionic strength, type of ions). Micellar surfactants are the most important in the class of association colloids that are formed in most food emulsions, which requires the knowledge and detection of their characteristics [8,32].

Considering the amphiphilic character of lipid molecules, they aggregate having a strongly hydrophobic character to the aqueous environment. Hydrophobic hydrocarbon chains will avoid water, facing the inside of the unit and the hydrophilic part to the aqueous medium (in contact with water molecules). Hydrophilic groups will repel each other, which requires a certain balance between the forces of attraction and / or repulsion at the separation interface hydrophilic group → water molecules, in order to achieve a convenient stability. Thus, a wide range of micellar networks / structures can be formed depending on the molecular organization, the nature of the hydrophilic group and the concentration of the reactants in the mixture (figure 4).

The formation of these structures, well defined, are the simplest examples of modeling to which is added the characteristic of most natural biopolymer systems of self-formulation (self-modeling). This feature does not require the intervention of external forces, being the direct consequence of the molecular "design" and of the electrostatic forces of attraction and / or repulsion between molecules, generated by the Brownian motion.

Some authors describe this behavior of lipids as molecular self-organization, similar to proteins, widely used as surfactants (substances that reduce the surface tension of a liquid) and emulsifiers (substances that give stability to a colloidal system). This property also gives the micelle a detoxifying character, by the ability to incorporate (retain) the potentially toxic lipophilic element for the body (figure 5), but also with applicability in other industries that require wastewater treatment and not only [16,23,25,36].

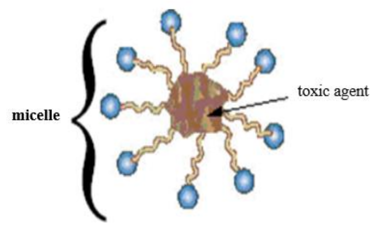


Figure 5. Schematic representation of how to "catch" the toxic agent

Figure 5 shows that the orientation of the hydrophilic groups to the outside determines the appearance of repulsive forces between the micelles with the formation of aggregates, effectively encapsulating the toxic agent. At high concentrations or the existence of structurally different lipids, inverted micelles appear, in which case the hydrophilic groups, oriented inwards, encapsulate the potentially toxic component in a lipid matrix.

The structure of the lipids double layer (figure 6), illustrates the arrangement / orientation of phospholipids in the cell membrane. The cell membrane formed by the lipid bilayer, represents a barrier for the passage (diffusion) of ions and large molecules, being traversed by certain proteins from one end to the other, which allow their selective passage (integral membrane proteins, phospholipid translocators or flipases that potentiate a rapid flip-flop movement from the cytosolic to the lumen monolayer). Molecular and ion transport, associated with membrane structures, has a role in cell signaling, recognition, binding and transmission of molecules, signal that stores information as well as immunity [21,23,37].

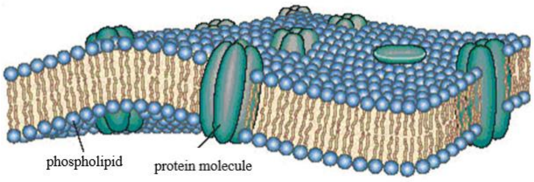


Figure 6. Illustrated representation of a cell membrane: average thickness of ≈10 nm. Green structures are protein structures, some crossing the membrane and others on the surface of the membrane

Spherical structures formed by lipid binary structures, which have a compartment inside, are structures known as vesicles or liposomes, depending on the context. The term liposome is used with predilection for lipid binary structures obtained by synthesis. The formed compartment can be used as a transporter of substances and information or it can be used as a "bank" for storing information and various items. Thus, liposomes can be used to encapsulate water-soluble substances (vaccines, drugs, vitamins, enzymes, biologically active elements) and transport them targeted to the cell of interest. This represents a considerable potential in the personalization of diet and drug treatments on a clear casuistry [16,38,39].

5. Conclusions

- From the literature study it can be stated that: the approached field is one of interest and perspective, with a real impact on the development of new foods with health benefits, by integrating colloidal lipid systems with other functions than the base material. This requires a careful "structural" (microstructural) physical-chemical approach, for a better understanding of colloidal phenomena and characters, conditioned by the structural elements of the food matrix. The data must be correlated with the action of the processing parameters specific to the technological, sequential operations, which forms the process as a whole.
- New trends in the *diet* that require a reciprocal response from food technologies have had a common ground: excessive urbanization and the new stressors generated by it, for which the human body cannot emit an effective immune response. The cause that generated the common goal: introduction of new minimally invasive processing technologies and "humanized" raw materials, bio-functional ones, with target effect at the cellular level.
- It is important to correlate experimental physical-chemical data with the evolution of rheological character and solubility properties, which can generate information on flow behavior (ex.: dough), an important technological parameter (in the manufacturing process) but also a digestive parameter (absorption of the constituent elements of the ingested product (in this case bread) and the form in which they are circulated at the cellular level)).
- Understanding these characteristics, directly related to the colloidal and micellar behavior of lipids, requires a thorough laborious study, which can generate new ideas for food processing and integration of different food groups as functional, closer to the needs of the body.

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human or animal subjects (if exist) respect the specific regulation and standards.

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