



**Review Article** 

# Surfactants: Basics and Versatility in Food Industries

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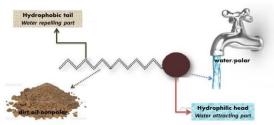
# ABSTRACT

Surfactant, as an abbreviation of "surface active agent", is an organic compound that is amphiphilic comprising both hydrophilic groups (commonly referred to as "polar heads") and hydrophobic groups ("nonpolar tails"). Based on the electron charges of the polar head parts, surfactants are classified as anionic, cationic, nonionic, zwitterionic. Many other pecular class of compounds also categorized in the types of gemini, cyclodextrin based, polymeric surfactants etc. Due to their some interesting properties such as nontoxicity, higher rate of biodegradability, high foaming capacity and optimal activity at extreme conditions like temperatures, pH and salinity, surfactants have been increasingly attracting the attention of the scientific and industrial community. Biocompatible, biodegradable, and/or nontoxic emulsion-based formulations of surfactants have great potential for applications in the food preparation and processing. Basics of surfactants and mainly there way of utility as food emulsifiers in food industries is thoroughly discussed.

Key words: Surfactants, Fatty Acids, Monoglycerides, Emulsifiers, Food Industries

## INTRODUCTION

"A Surface Active Agent, Surfactant, is a substance, when present in system has the characteristics of adsorbing on to the surface/interface of the system and of altering to a mark degree of the surface/interfacial free energy of the system". In general, many solutes even when present in very low concentration alter the surface energy of their solvents in their solutions to an extreme degree are considered as the Surfactants.





Surfactants are amphiphiles containing both hydrophobic (nonpolar) and hydrophilic (polar) moieties that confer ability to accumulate between fluid phases such as oil/water or air/water, reducing the surface and interfacial tensions and forming micelles/emulsions. This is uniqueness and versatility of these а compounds. In English the term surfactant designates a substance which exhibits some superficial or interfacial activity. It is worth remarking that all amhiphiles do not display such activity; in effect, only the amphiphiles with more or less equilibrated hydrophilic and lipophilic tendencies are likely to migrate to the surface or interface. It does not happen if the amphiphilic molecule is too hydrophilic or too hydrophobic, in which case it stays. In other languages such as French, German or Spanish the word "surfactant" does not exist, and the

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actual term used to describe these substances is based on their properties to lower the surface or interface tension, e.g. *tensioactif*(French), *tenside*(German), *tensioactivo*(Spanish). This would imply that surface activity is strictly equivalent to tension lowering, which is not absolutely general, although it is true in many cases.

Good starting points to get information and understanding about the surfactants are found in classic books like those of Rosen<sup>[1]</sup>, Myers<sup>[2]</sup>, Mittal <sup>[3,4]</sup> and Shinoda <sup>[5]</sup>. Other books on surfactants including Karsa's, Industrial Applications of Surfactants Series [7,8] and the Marcel Dekker Inc. (www.dekker.com/) was publishing more than 100 volumes in Surfactant Science Series <sup>[9]</sup> since 1966. There are also glossaries and dictionaries available which one covering terminology in surfactant science and technology <sup>[10]</sup>. The most comprehensive source for surfactant information on the internet is probably Huibers' The Surfactants Virtual Library, which contains over 1000 links to surfactant and detergent related web sites <sup>[11]</sup>.

Conventional surfactants are amphipathic molecules with polar head groups, which may be anionic, cationic, non-ionic and zwitterionic, hydrophobic tails, and that may be hydrogenated fluorinated, or linear or branched. Recently, some interest has been devoted to the new class of so-called Gemini surfactants. They are composed of two polar heads flanked by a spacer to which hydrophobic tails are linked; the spacer can be rigid or flexible, polar or apolar. Attention has been also addressed to polymeric surfactants which are copolymers with two or more blocks having variable monomeric compositions. A peculiar class of surfactants is represented by the cyclodextrins which possesses the properties of inclusion of self-organization and simultaneously, resulting very promising materials for an enhanced encapsulation of variety of solutes sparingly soluble in water <sup>[12]</sup>.

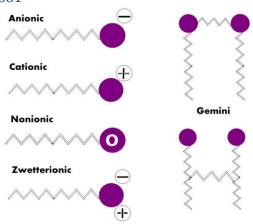


Fig.2 : Classification of Surfactants

The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soaps. Most of the anionic surfactants are carboxylate, sulfate and sulfonate ions <sup>[13]</sup>. The straight chain is a saturated/unsaturated C<sub>12</sub>-C<sub>18</sub> aliphatic group. The water solubility potential of the surfactant is determined by the presence of double bonds in it <sup>[14]</sup>. Cationic surfactants are mainly cetrimide which has tetradecyltrimethyl ammonium bromide with minimum amount of dodecyl and hexadecyl compounds. Other cationics are benzalkonium chloride, cetylpyridinium chloride etc are effective compounds. Non-ionic surfactants contribute to making the surfactant system less hardness sensitive.

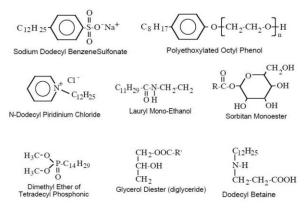


Fig.3 : Few examples of Surfactants



The nonionic surfactant can be of polyol esters, polyoxyethylene esters, and poloxamers or pluronics which are poly(oxyethylene)poly(oxypropylene)-poly(oxyethylene) tri-block copolymers. The polyol esters include glycol and glycerol esters and sorbitan derivatives. Polyoxyethylene esters majorly include polyethylene glycol (PEGs). The most commonly used nonionic surfactants are ethers of fatty Alcohol<sup>15</sup>. Amphoteric surfactants are very mild, making them particularly suited for use in personal care preparations over sensitive skins. They can be anionic, cationic or non-ionic in solution, depending on the acidity or pH of the water. Those surfactants may contain two charged groups of different sign. The frequently used compound is alkyl betaines <sup>[15]</sup>. The chemical structures of few commonly used surfactants are shown in Fig.3

# APPLICABILITY OF SURFACTANTS

In recent years, surfactants have been widely applied, such as wetting agents, enhance oil recovery (EOR), emulsifiers and/or manufacturing textiles and leather finishing agents to reduce surface tension or speed the drying process <sup>[7]</sup>. Due to their interesting properties such as lower toxicity, higher degree of biodegradability, higher foaming capacity and optimal activity at extreme conditions of

temperatures, pH levels and salinity, these have been increasingly attracting the attention of the scientific and industrial community. The world production of soaps, detergents and other surfactants was about 18 Mt (million tons) in 1970, 25 Mt in 1990 and 40 Mt in 2000 (not counting polymeric surfactants) <sup>[7,8]</sup>. Fig.4 represents the advancement in utilization of surfactants in various industries like personal care, pharmaceutical, food, paint, agriculture, paper, mineral processing, electrical, etc. Versatile surfactants applied in industries in general as follows;

- Foods emulsions, foams, dispersions, fouling etc.
- Pharmaceuticals emulsions, dispersions, fouling, etc.
- Household products dirt removal, foam control etc.
- Paints & coatings cleanliness, wetting, adhesion, wicking, dispersion stability
- Mineral Processing froth flotation
- Semi-conductors cleanliness, adhesion of thin layers, characterization of surface treatments
- Heavy industry lubrication/wear, degreasing
- Crude oil oil recovery
- Paper printing, adhesion in packaging etc.
- Biomaterials fouling, tissue adhesion



Fig.4: Important surfactant-based products in the current market.



The widespread importance of surfactants in practical applications, and scientific interest in their nature and properties, have precipitated a wealth of published literature on the subject and many ways these materials are exploited by research community through quality papers in various journals(Fig.5).



Fig.5 : Reputed core research journals of Surfactant Science

# SURFACTANT IN FOOD INDUSTRIES

Due to their unique chemical structure, surfactants strongly affect the stability of colloid systems and can interact with all the main components of flour (starch, gluten and lipids). Surfactants act as lubricants, emulsify oil or fat in butters, build structure, aerate, improve certain qualities of the final product, extend shelf life, modify crystallization, prevent sticking, and retain moisture <sup>[16]</sup>.

Naturally occurring surfactants such a lecithin from egg yolk and various proteins from milk are used for the preparation of many food products such as mayonnaise, salad creams, dressings, deserts, etc. Alanine, phenylalanine, leucine and isoleucine contain nonpolar aliphatic and aromatic side chains. Amino acids, such as arginine, lysine and tryptophane, contain amino groups, which promote cationic character to the protein. Aspartic and glutamic acids possess side chains with carboxyl groups, which contribute to anionic character. The nature, number and location of the polar amino acids determine the isoelectric point of a protein; e.g., the pH at which the protein is uncharged. In food systems where the pH is above the isoelectric point, the protein will behave as the anionic emulsifiers, while at pH values below their isoelectric point, it will become cationic. One complicating factor in using emulsifiers is that their charge makes them vulnerable to interactions with other charged species, such as calcium ions and some gums16. Later, polar lipids as monoglycerides were introduced as food emulsifiers. More recently, synthetic surfactants such sorbitan esters (Tweens) and their ethoxylates and sucrose esters have been widely applied in food emulsions.

In commercial food emulsifiers, in general, the hydrophilic part can consist of glycerol, sorbitol, sucrose, propylene glycol or polyglycerol. The lipophilic part is formed by fatty acids derived from fats and oils such as soybean oil, rapeseed oil, coconut oil and palm kernel oils.

## **Emulsions in Foods**

The understanding of the formation, structures, and properties of emulsions is essential to the creation and stabilization of various structures in foods. Three main type of emulsions (shown in Fig.6) organized in foods are as follows;



i) Oil-*in*-Water (O/W) emulsions: Droplets of oil are suspended in an aqueous continuous phase. Such emulsions exist in many forms of food like creamers, cream liqueur, whippable toppings, ice creams mixes, mayonnaises. The properties of such emulsions are controlled through the surfactants utilized and the other components present in water phase.

ii) Water-in-Oil (W/O) emulsions: Droplets of water are suspended in an oily continuous

phase. Mainly these emulsions exist in butter, margarines, and fat-based spreads. The stability of these emulsions depends more mainly on the properties of fat or oil, dispersed phase and also surfactant used in water phase.

iii) Water-*in*-Oil-*in*-Water (W/O/W) emulsions: In effect, an o/w emulsions whose droplets themselves contain water droplets. This type of emulsion often found in variety of baked products.

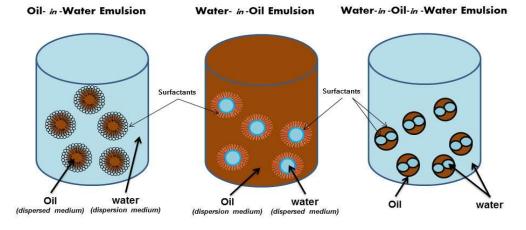


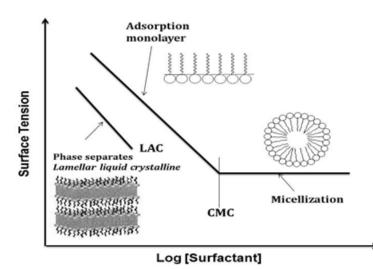
Fig.6 : Type of emulsions in Foods

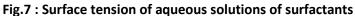
A large number of surfactants traditionally used in foods which are water soluble as well as water insoluble. Surfactants, which have a Krafft point beneath room temperature, are classified as water insoluble as a contrast to ionic surfactants like SDS, which are classified as water soluble, because they form transparent aqueous solutions with large concentrations. Due to Micellization of Surfactant, aqueous solutions with high surfactant concentrations are transparent low viscosity liquids, which would indicate very significant solubility in water. However, in order to understand emulsion stability it is essential to realize that the surfactant molecules are not at all soluble to this extent. Generally surfactants/emulsifiers can be characterized by the Hydrophilic Lipophilic Balance. The balance is measured on molecular weight and is an indication of the

solubility of the emulsifier. The HLB scale varies between 0 and 20. An emulsifier with a low HLB value is more soluble in oil and promotes waterin-oil emulsions. An emulsifier with a high HLB value is more soluble in water and promotes oilin-water emulsions. The HLB value is a somewhat theoretical value, it only considers water and oil, and food systems are more complicated. But the HLB value of an emulsifier can be used as an indication about its possible use. The second group of surfactants, the "insoluble" ones, differs from the first group only by the structure of the association. This difference is in reality important to comprehend the stability of food emulsion <sup>[17]</sup>. The emulsion stabilization is in the phenomena at the critical surfactant concentration, when the selfaggregation in water is started (Fig.7). For the water soluble surfactant the association is



limited to spherical aggregates, micelles, which form a thermodynamically stable dispersion in water, the system remains a one phase transparent liquid. In case of water insoluble surfactant the association structure is a lamellar liquid crystal (shown in Fig.7) which does not have size limitation like the micelle, the association continues infinitely and distinct a separate phase appears. For the water soluble surfactants the adsorption of the surfactant to the interface increases with concentration in the aqueous solution until the CMC is reached, at which the surfactant has formed a monolayer at the interface. After that point the additional surfactant forms micelles, in the bulk.





The water insoluble surfactants behave in a completely different manner. It forms a separate phase and the adsorption to the oil/water interface is now not a question of individual molecules; the adsorption is mainly adjudged by the three interfacial free energies with four possible dispersed structures(Fig.8).

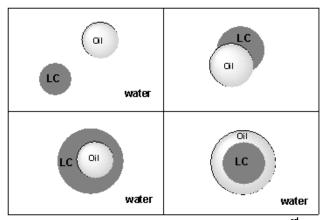


Fig.8 : Arrangements for an emulsion with LC as 3<sup>rd</sup> phase

In the Fig.8, the repulsion between the liquid crystal particles and the oil drops are sufficient to prevent aggregation (provide colloidal

stability) and they exist as separate entities. If flocculation occurs, three arrangements are possible depending on the magnitude of the



interfacial free energies, which are  $\gamma(O/W)$ ,  $\gamma(O/LC)$  and  $\gamma(LC/W)$  emulsions. The emulsion now has increased the number of phases from two to three, and the presence of the third phase has three vital consequences. It radically changes the volume ratios in the emulsion, it gives rise to another structure during emulsification and the temperature variation during and after the emulsification has decisive effect on the properties.

The most complex colloids and emulsions are those of food and food products, which are difficult to stabilize, because a large number of microstructures of combinations of proteins, carbohydrates, fats and lipids etc. are present. This almost infinite number of combinations are organized and arranged in very complex internal microstructures with various types of assemblies such as dispersions, emulsions, foams, gels, etc. In addition, Mother Nature has provided us with many small molecular weight molecules with surfactants that are known, as food additives (vitamins. antioxidants. acidulants, enzymes, flavors, etc.). The additives have many functional properties and play significant role in food quality and long-term stability <sup>[17]</sup>.

# **Common Food emulsifiers/surfactants**

Surfactant molecules, which are part of these emulsions, play a major role in determining the microstructure of the product and in affecting its structural and textural stability in the food. Commercially utilized common surfactants or food emulsifiers are listed in Table-1. Here in the table, an E-number is a reference number given to food additives that have passed safety test and have been approved for use throughout the European Union and Switzerland (the "E" stands for "Europe"). They are commonly found on food labels throughout the European Union<sup>[18]</sup>. Safety assessment and approval are the responsibility of the European Food Safety Authority. Today the worldwide food surfactant production has reached approximately 500,000 tons from 20 different types with a 3% annual growth<sup>[19]</sup>. Surprisely about 50% of surfactants are used in bakery products.

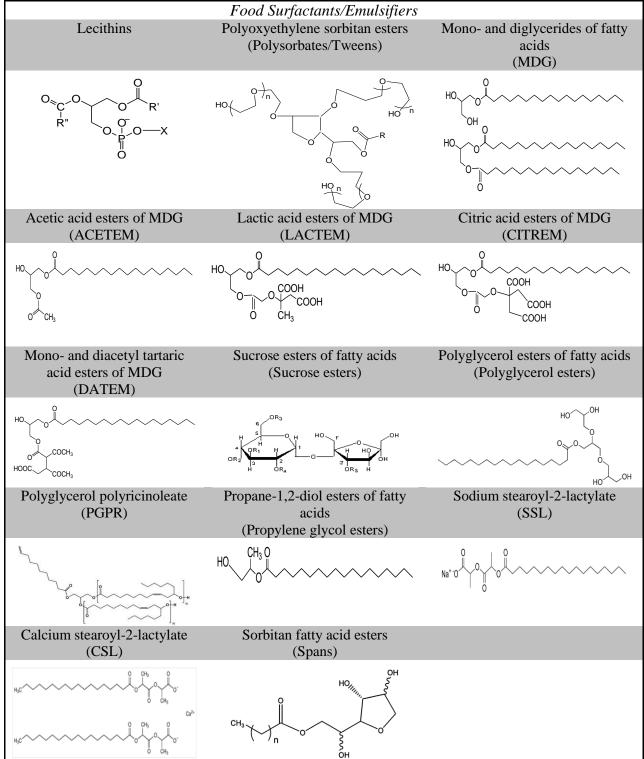
Name of Food surfactant/Emulsifier	Code name	E-Number
Lecithins	Lecithins	E 322
Polyoxyethylene sorbitan esters	Polysorbates/Tweens	E 432 – 436
Mono- and diglycerides of fatty acids	MDG/ Monoglycerides	E 471
Acetic acid esters of MDG	ACETEM	E 472 a
Lactic acid esters of MDG	LACTEM	E 472 b
Citric acid esters of MDG	CITREM	Е 472 с
Mono- and diacetyl tartaric acid esters of MDG	DATEM	E 472 e
Sucrose esters of fatty acids	Sucrose esters	E 473
Polyglycerol esters of fatty acids	Polyglycerol esters	E 475
Polyglycerol polyricinoleate	PGPR	E 476
Propane-1,2-diol esters of fatty acids	Propylene glycol esters	E 477
Sodium stearoyl-2-lactylate	SSL	E 481
Calcium stearoyl-2-lactylate	CSL	E 482
Sorbitan fatty acid esters	Spans	E 491 – 495

Table-1 : Most common food surfactants/emulsifiers used in the food industries.

The chemical structure of commercial food emulsifiers is represented in Table-2. In most cases, the hydrophilic part is of glycerol, sorbitol, sucrose, propylene glycol or polyglycerol and lipophilic, hydrophobic part is formed by fatty acids derived from fats and oils.



Table-2 : Chemical structure of MOST common food Surfactants/emulsifiers used in the food industries.





## Manufacture of Food emulsifiers/surfactants

Lecithin (E322) is a mixture of phospholipids, it consists of a glycerol backbone with phosphatidyl groups. The phosphatidyl groups are phosphate esters of diglyceride. Lecithin is a natural emulsifier, obtained mainly from vegetable oilseeds and egg yolk.

Basic source for manufacture of food emulsifiers is actually come out from fats or oils or fatty acids. Main food emulsifiers, monoglycerides are produced with the reaction of fats or oils or fatty acids with glycerol. Such monoglycerides can be further processed by esterification with organic acids like acetic acid, lactic acid, citric acid and tartaric acid, produces ACETAM, LACTEM, CITREM as well as DATEM, respectively. Even some important hydrophilic alcohols can be used for the manufacturing of food emulsifiers (shown in Fig.9).

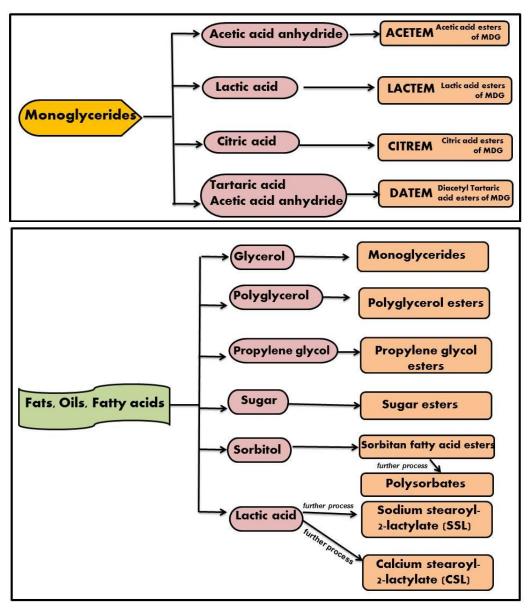


Fig.9 : Source and manufacturing of Food emulsifiers/surfactants



# FEW APPLICATIONS OF FOOD EMULSIFIERS / SURFACTANTS IN FOOD INDUSTRIES

Surfactants are involved in the production of many common food items and can be found in the extraction of cholesterol, solubiliztion of oils, liquor emulsification, prevention of component separation, and solubiliztion of essential nutrients.

The nontoxicity of lecithin leads to its variety of uses in food, as an additive or emulsifier. In confectionery, lecithin reduces viscosity, replaces more expensive ingredients, controls sugar solidification and the flowness properties of chocolate, helps in the homogeneous mixing and it can be used as a coating. In emulsions and fat spreads, it stabilizes emulsions, reduces spattering during frying, and improves texture of spreads and flavour release. In dough's and bakery, it reduces fat and egg requirements, helps even distribution of ingredients in dough, stabilizes fermentation. increases volume. protects yeast cells in dough when frozen, and acts as a releasing agent to prevent sticking and simplify cleaning. It improves wetting properties of hydrophilic powders (e.g., low-fat proteins) and lipophilic powders (e.g., cocoa powder), controls dust, and helps complete dispersion in water to adsorb at interfaces. Lecithin keeps cocoa and cocoa butter in a candy bar from separating. In margarines, especially those containing high levels of fat (>75%), lecithin is added as an 'antispattering' agent for shallow frying. Margarine is an example of a W/O emulsion which consisting of 80% fat, the hot homogenized mixture of fat crystals, oil and water. It does not have to be a stabile emulsion since the emulsion is quickly set by rapid chilling. Lecithin, a typical ingredient in margarine, enhances the solubility of monoglycerides in the oil blend, and monoglycerides reduce the interfacial tension between the oil and water phases.

If we discuss about an ice cream, partially frozen foam that is 40–50% air (by volume). The first step in formulating ice cream is to create

an emulsion. The homogenization step forces the hot ingredients (milk fats, milk solids-no-fat, sweeteners, corn-syrup solids, stabilizers/ emulsifiers, other dry solids) through small stirring under moderate pressure. Diameter of fat droplet decreases to 0.4 to 2.0 µm approximately, allowing a large surface area for adsorption of proteins (which in responsible for stabilization of emulsion), and the uniformity of drop sizes result in greater stability of fat droplets during ageing process and made more uniform final food product. The adsorption of emulsifiers (such as Lecithins, Tweens, MDG) decreases the interfacial tension between fat globules and the surrounding liquid phase, even more than does just mere adsorption of proteins (to about 2.2 dyne/cm). The stabilizers (such as guar, carboxymethyl cellulose, xanthan, etc.) are used to produce smoothness in body and texture, reduce the ice content and lactose crystal growth during storage, provide the product uniformity and resist against easy melting <sup>[20]</sup>. The second stage in ice cream production is foaming and emulsion destabilization. This is analogous to the foaming step in whipped cream <sup>[21,22]</sup>. Air is incorporated by whipping or by air injection. The added shear causes controlled partial coalescence (enhanced by the adsorbed surfactants), causing air to be trapped in clumped fat globules, and also ice formation. When whipping and freezing occur simultaneously, good fat destabilization is achieved and a complex internal structure is achieved <sup>[20]</sup>.

Surfactants are a key component in the manufacture of edible coatings. A finish coat or polish may be added to chocolate- and sugarpanned confectionery products to produce an aesthetically pleasing gloss. These are commonly alcohol-based shellac and corn zein coatings, but may also include water-based whey proteins <sup>[23]</sup>. Surfactants are added to create a dispersion of the coating particles, which then allows for proper wetting and adhesion over the candy surface. The problem



with chocolate blend coating is happened when the fat crystalizes and the cocoa butter separates. MDG, LACTEM, polysorbates are added as crystal modifiers/emulifiers to stabilize the coating. The latter may also be used to increase the palatability of the confection by forming an emulsion between the fat and mouth saliva, which minimizes the waxy mouthfeel<sup>[24]</sup>.

As monoglycerides, MDGs increase the fermentation stability of dough, bread and fermented bakery goods. The general dosage is 0.2% of the flour weight. Other major uses of MDGs are sponge cakes and cakes margarines, [19] chewing ice creams and gums Diacetyltartaric acid esters, DATEM, are commonly used as dough conditioners for all baked products, particularly yeast-leavened products, white bread and in flour mixes for quality foods. Their approximate dosage is between 0.2% and 0.5% of the flour weight. They are also used in dairy products and approved for use in special infant formulae based on crystalline amino acids <sup>[16]</sup>. Sodium stearoyl-2-lactylate (SSL) and calcium stearoyl-2-lactylate (CSL), commonly applied anionic surfactants in breadmaking processes to improve dough gas retention and stability to yield a finer structure in the final product. SSL is used in yeast-leavened products usually in a dosage of about 0.4%. They are also used in breakfast cereals, cookies, crackers, cereal and potato based snacks and quick cook rices <sup>[16,25]</sup>.

In the USA sucrose esters are used in breads but oppsitely the use of sucrose esters is not permitted in breads at Europe. As sucrose esters have excellent ability to stabilize emulsions these are utilized to dressing sauces, mayonnaise-like products, and ice creams. The use of sucrose ester in infant foods is very vital. During the production of infant formulas (given instead of milk) the proteins which are already in the product are usually enough to ensure colloid stability of the emulsion. However, in the case of hypoallergenic products containing

hydrolyzed proteins, peptides or free amino acids, the use of emulsifiers is necessary to stabilize the emulsion. That is the reason why sucrose esters are used in special baby formula [19,25] products made for allergic infants Polyglycerol esters of fatty acids are applied in the formulation of low fat margarines, spreads, butter creams and breakfast cereals. Special types of polyglycerol esters are used as crystallization inhibitors in the oil and fat industry to prevent the formation of turbidity of sunflower oils during storage. Sorbitan esters of fatty acids (Span series) and their ethoxylated derivatives Polysorbates (Tween series) are excellent emulsifiers, aerating agents and lubricants in cakes, toppings, cookies and crackers. Polysorbate 60 is used as dough strengthener co-emulsifier in bakery products. The usual dosage is 0.2% of flour weight. Polysorbate 80 is often used in dairy products, ice creams, and whipped cream and non-dairy cream alternatives <sup>[26]</sup>. Surfactant mixtures are usually much more effective than using a single surfactant alone. Therefore, surfactants are usually used in combinations. For example a common bread surfactant combination contains mono- and diglycerides of fatty acids. A fluid cake shortening (semisolid fats used in food preparation, especially for baked goods) can contain a combination of Polysorbate 60, glyceryl monostearate and propylene glycol monostearate. Other popular example in food was shown in beer manufacturing <sup>[26]</sup>. The quality of beer is mainly judged by the foam creation of the dispensed beer. Desirable visual qualities include stability, lacing (adhesion), whiteness, creaminess and strength. Foam stability is the perceived best indicator of a good beer. Foam stabilization comes from amphipathic polypeptides from malt and bitter compounds, particularly iso- $\alpha$ -acids, and from the absence of lipophilic materials. Unlike champagne, where foam film lifetimes are short (hydrodynamic control), beer foam has a slower drainage rate due to the effect of disjoining



pressure of two interfaces in close proximity. A beer that has smaller bubbles of uniform size tends to have more stable foam. Several reviews have been written on this aspect of beer (and champagne) foams <sup>[27,28]</sup>.

## CONCLUSIONS

Surfactants are amphiphilic compounds containing both hydrophobic (nonpolar) and hydrophilic (polar) moieties that confer ability to accumulate between fluid phases such as oil/water or air/water, reducing the surface and interfacial tensions and forming emulsions and micelles. The surface activity properties make surfactants one of the most important and versatile class of chemical products, used on a variety of applications in household, food, paint, paper, and agriculture industries.

Surfactant molecules, which are an important part of the food emulsions, play a key role in determining the microstructure of the product and in affecting its structural and textural stability in the food. Naturally occurring surfactants like lecithins, MDGs, various saturated, unsaturated and trans fatty acids and functionalized proteins as well as synthetic surfactants Tweens, SSL, CSL and sucrose esters etc. are often used in the preparation of food products such as mayonnaise, salad creams, dressings, deserts, coffee, icecreams etc. Also the biocompatible, biodegradable, and/or nontoxic emulsion-based formulations of surfactants like ACETAM, LACTEM, CITREM as well as DATEM have great potential for food applications and which are discussed.

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