

## Some aspects of the formation of emulsions and foams in food industry

**Olga Rybak**

*Ternopil Ivan Pul'uj National Technical University, Ternopil, Ukraine*

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**ABSTRACT**

Emulsions and foams are dispersed systems which are often presented in foodstuffs. A good knowledge of the structure and the mechanical properties of the external and internal phases as well as the interfacial films are essential for controlling the behaviour of such systems. Foods' macromolecules, such as proteins and polysaccharides, are widely used as functional ingredients of the formation and stabilisation of these systems. These molecules contain simultaneously polar and non-polar regions, which give them surface-active properties. During the emulsification or foaming processes, they rapidly adsorb and form the film at the surface of the oil droplets or gas bubbles. The objective of this article is a substantiation of the functionalities of surface-active agents and their usage in food industry.

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Recent experimental investigations of the stability of foam and emulsion have shown that milk proteins have excellent surface-active properties such as emulsification, gelling, foaming, water binding. However, milk proteins do not show the same behaviour: whey proteins are less surface-active than caseins, mainly because of their globular structure. Application of enzymatic hydrolysis is found to improve surface properties of whey proteins. Moreover, the surface-active properties of milk proteins increase when protein-polysaccharide complexes form in the interfacial region of emulsion and foam. The conditions and treatments of formation of multicomponent dispersed systems, which are stabilized by these protein-polysaccharide complexes, should be more investigated.

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**Corresponding author:**

Olga Rybak  
E-mail:  
cmakota@ukr.net

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### Introduction

Emulsions and foams form the basis of a wide variety of natural and manufactured materials used in the food [1-7]. One of the major concerns for dispersions is keeping the internal phase uniformly distributed during storage and consumption [6, 8-16]. This has led the food industry and many researchers to investigate the ability of hydrocolloids and proteins to stabilize emulsion and foam against creaming, flocculation, coalescence, drainage and coarsening, depending on their intended application [13-15, 17-19]. New ingredients are regularly incorporated into food systems to improve their rheological and physicochemical

properties. Therefore, understanding and monitoring the factors that influence the stability and shelf-life of prepared dispersion is critical for their continued success in the market place.

## **Material and methods**

The material of this research was articles of the international scientific journals published during 2000 and 2012 years, thesis and monographs of scientists of dispersion science. Methodology of the investigation is based upon the use of the methods of analysis, comparison and synthesis.

## **Results and discussions**

An emulsion may be defined as an intimate dispersion of at least one immiscible liquid in another in the form of discrete droplets (diameter in general ranges from 0.1 to 100  $\mu\text{m}$ ). A foam is a fine dispersion of gas bubbles in a liquid [20]. An interfacial layer between the two phases is occupied by some surface-active agents, such as proteins, polysaccharides, phospholipids, monoacyl glycerol esters etc. [6, 14, 17, 19]. The behaviour of foam and emulsion in foods is defined by these three parts of the system: the continuous phase, the internal phase and the interfacial layer [6, 16, 21].

Basically, there are three types of emulsions: oil-in-water (O/W), water-in-oil (W/O) and multiple emulsions i.e. oil-in-water-in-oil (O/W/O) emulsion or water-in-oil-in-water (W/O/W) [6, 20, 21]. O/W emulsion refers to the type of dispersion in which oil is dispersed as droplets in the continuous aqueous phase. Milk and cream are best-known oil-in-water emulsions, in which the milk fat globules are dispersed in aqueous phase containing milk proteins, lactose, salts and minerals. The fat globules are stabilized by natural surfactants i.e. lipoprotein membrane, phospholipids and adsorbed casein. Another food O/W emulsions are coffee whiteners, mayonnaise and salad dressing. In case of W/O emulsion, oil forms the continuous phase and water exists as the dispersed phase. Butter and margarine are common water-in-oil emulsions, in which aqueous phase, which consists of milk proteins, phospholipids, sugar and salts, is dispersed in fat cream or oils.

Milkshakes, beer, bread, cakes, meringue, marshmallow, aerated chocolate bars, vegetable paste foams, sorbet are examples of food foams. Moreover, food industry produces aerated emulsions (ice cream, whipped cream, toppings, etc.), in which air cells are covered with clusters of partially coalesced fat globules and adsorbed fat crystals together with proteins, stabilizing the foam. [6, 22].

Methods of the formation of emulsion and foam. Generally, food emulsions are prepared by using high shear equipment items, such as colloid mills, high speed blenders, high pressure valve homogenizers that emulsify an oil phase and an aqueous phase together in the presence of a surface active agent [6, 17, 19, 21].

The basic procedure is to force a coarse mixture of oil and aqueous phases through a narrow slit under the action of high pressure, resulting in cavitation, intense laminar shear flow and turbulence. Input of mechanical energy subdivides the droplets of internal phase until they reach the final average droplet diameter, in the range 1-100  $\mu\text{m}$  [6, 19, 20]. Mechanical stirring of an oil-water mixture forms drops of liquid that are distorted into cylinders (along the lines of flow) and that break up into smaller droplets. The process is repeated until the droplets are so small they cannot be further distorted and subdivided ceases. A suspended liquid drop forms a sphere, because this shape has minimum surface area (hence minimum interfacial free energy)

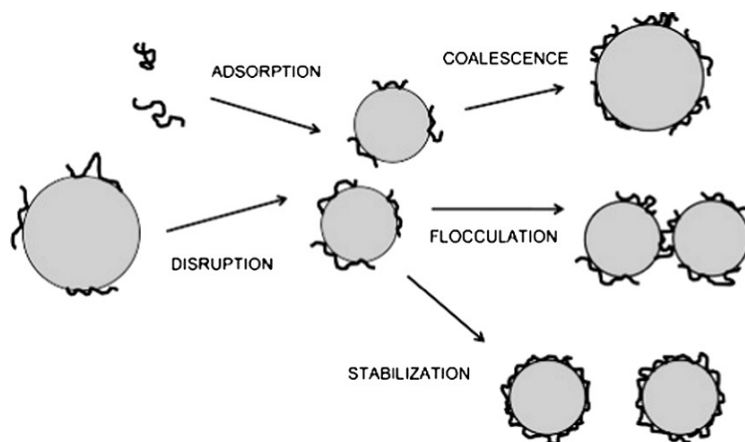
for a given volume. At the same time, the surface active agents, such as emulsifiers being structurally amphiphilic molecules (having both hydrophobic and hydrophilic moieties), are adsorbed at the oil-water interface, creating a stabilizing interfacial layer [6-8, 14,17].

Concerning the energetics involved, foam is nearly identical to an o/w emulsion. The mechanism of air incorporation and subdivision in a foam is the same as for an emulsion: large bubbles are elongated, and the unstable cylinders spontaneously divide [20].

Bubbling and stirring are the two main categories of mechanical methods for foam formation [1, 16, 20]. In the bubbling methods the foam is generated by bubbling gas through the foaming solution. Bubbling can be realized through a single capillary, a set of capillaries, or a porous plate placed in the lower part of the foam generator.

In the stirring methods foam is generated by mechanical mixing of the gas and liquid phases, e.g. by whipping or by mixing with a stirrer, by shaking a vessel partially filled with solution, by simultaneous flow of gas and liquid in a tube, by pouring liquid on the surface of the same solution, etc [1, 20].

Interaction between surfaces. An emulsion having been formed, the oil droplets tend to flocculate and coalesce due to attractive forces. Flocculation has been described as the reversible aggregation mechanism, which arises when droplets associate, due to unbalanced inter-atomic attractive and repulsive forces [6, 18, 20]. On the other hand, coalescence refers to a completely irreversible increase in droplet size gradually leading to the separation of the oil and the aqueous phase (fig. 1).



**Fig. 1. Illustration of main physicochemical processes involved in making of emulsions [18]**

One of the keys in preparing a stable emulsion is to form small oil droplets in a continuous aqueous phase with sufficiently high viscosity to prevent coalescence of the oil droplets [6, 12, 14, 19]. A thermodynamical balance between the emulsion phases is assured by an emulsifier (proteins, polysaccharides, phospholipids), which decreases the interfacial tension and keeps the emulsion stable. An emulsifier should have sufficient hydrophobic groups to strongly adsorb onto the oil-surface and hydrophilic groups to spread out in the aqueous continuous phase, and thus reduce the interfacial tension [19, 17]. The ability of an emulsion to resist any alteration in its properties over the time scale is named the term «emulsion stability» [6, 8, 21].

Foam stability is governed by similar factors as emulsion stability. After a foam formation several processes occur each of them leading to foam destruction [16, 23, 24]:

liquid drainage;  
bubble coalescence;  
bubble disproportionation.

The incorporated bubbles are usually stabilized by proteins and other food macromolecules which, being surface active, adsorb onto the bubble surface and prevent coarsening or drainage due to coalescence by modifying the interparticle forces as well as by providing interfacial rheological properties [16, 23, 24].

Thus, the protein molecules unfold with the hydrophobic side chains entering the air phase and the hydrophilic chains remaining in the water phase. The portion of the proteins located in the aqueous phase hold water, preventing it from draining away from this region and hence preventing the air bubbles from coalescing and destabilizing the foam.

Many polysaccharides being hydrophilic, they do not adsorb at the interface. However, they can enhance the stability of foam by a thickening or a gelling effect of the aqueous solution [24]. Some studies have evidenced an additional role of polysaccharides at the interfacial film [25]. Polysaccharides can interact with adsorbed proteins to form protein-polysaccharide complexes which can increase both the rigidity of the interface and the surface activity of the protein [25, 27]. Aqueous mixtures of proteins and polysaccharides can exhibit various phenomena including complex coacervation, miscibility and segregation [25, 27]. Complex coacervation mainly occurs below the protein isoelectric point as a result of net electrostatic interactions between the biopolymers carrying opposite charges and implies the separation of two phases, one rich in complexes biopolymers and the other phase depleted in both [26].

The stability of aerated emulsions e.g. ice cream, whipped cream is related both to the amount of fat globules adsorbed around the air cells and to the formation of clusters of fat globules between air cells, linking them together in a structural matrix [22].

Emulsifiers and stabilizers for the food industry. Milk proteins and particularly whey proteins are widely used as emulsifying and foaming agents in diverse food products thanks to their unique interfacial properties. Milk proteins in soluble and dispersed forms have excellent surface-active and emulsion-stabilizing properties (film forming, water binding and whipping abilities) [3, 13, 18, 23, 28].

Proteins form different interfacial films and do not show the same behaviour. Differences in the abilities of milk proteins arise largely from the differences in structure, flexibility, state of aggregation, and composition of the proteins. The sequence of surface activity for milk proteins is  $\beta$ -casein > monodispersed casein micelle > serum albumin >  $\alpha$ -lactalbumin >  $\alpha$ s casein =  $\kappa$ -casein >  $\beta$ -lactoglobulin > euglobulins [28]. The  $\beta$ -casein is the most important milk protein fraction because of its high surface activity and flexible nature, due to numerous proline residues, little ordered structure and negligible intermolecular cross-links [13, 28].

Protein molecules change their charging and surface activity with pH and accordingly their foamability and emulsifying properties are also altered.

Thus, whey proteins enable the formation of very small air bubbles (average diameter of 15  $\mu\text{m}$ ) which do not evolve significantly during the first day following the foam formation: no coalescence, no ripening, and no drainage during the first 24 h. On the contrary, the evolution of sodium caseinate stabilised foams is quite different: the average bubble size grows very quickly, and after only a few hours, the foams do not exist anymore. All the liquid drained and the bubbles disappeared. A clear relationship between surface elasticity and foam stability has been found. At least in the case of whey protein aerated systems a high surface elasticity improves foam stability, interfacial films being more resistant and the protein network constituting a mechanical barrier towards rupture of the bubbles and coalescence [29].

It has been studied that there is little differentiation between the products containing the aggregated and non-aggregated casein (i.e. milk protein concentrate and skim milk powder) for emulsifying ability, creaming stability, surface coverage and composition of the interfacial layer. The non-aggregated sodium caseinate and whey proteins have similar emulsifying abilities, which are greater than the aggregated casein. The surface coverages for emulsions made with sodium caseinate and whey protein are approximately 10 times lower than the aggregated casein samples. The casein composition of the interfacial layer in emulsions made with milk protein concentrate and skim milk powder is independent of protein concentration. For sodium caseinate,  $\alpha$ -casein replaces  $\beta$ -casein at the interface as the total protein concentration is increased. The creaming stability of the emulsions shows large differences between the aggregated caseins, the non-aggregated caseins and the whey proteins. The behaviour of sodium caseinate, in particular, is anomalous [13, 18, 31]. It has been proved that the surface tension behavior of sodium and calcium caseinates is similar but the foaming properties are differed. Sodium caseinate presents better foaming properties than calcium caseinate [12, 30, 31].

The addition of monoglycerides reduces the amount of adsorbed protein, except for emulsions produced from heated protein solutions containing high proportion of whey protein, for which an increasing has been observed. Monoglycerides are also effective in reducing coalescence of emulsions containing casein. Pure whey protein emulsions have no coalescence but considerable creaming upon storage. However, emulsions containing casein show extensive creaming and coalescence upon storage. [32] It was found that the interfacial layer forming surfactants such as the sodium stearoyl lactylate or the mono-, diglyceride induced a better foam stability and a lower gas permeability coefficient through a gas/liquid interface than a whey protein isolate [33].

It has been documented that heating has an impact on the particle size of emulsions stabilized with milk proteins [28]. Thus, the particle size distribution (pH 6.8) shifted from below 1  $\mu\text{m}$  prior to heating to 1-10  $\mu\text{m}$ , when heated at 140  $^{\circ}\text{C}$  for 80 s. This increase in particle size distribution is attributed to fat globules aggregation, which resulted from interactions between non-adsorbed protein molecules in the serum phase and proteins adsorbed at the interface of fat globules [34].

The impact of thermal processing on the milk protein structure concerns mainly the whey proteins, whereas caseins seem to have a protective effect against denaturation of the serum proteins. Heat treatment of milk proteins prior to emulsion formation is proved to reduce the protein ability to form stable coarse particles, when whey proteins are involved in the process. However, the addition of small amounts of sodium caseinate can substantially improve the heat stability of a protein-based emulsion system [9, 12].

Whey proteins are less surface-active than caseins, mainly because of their globular structure. Although their solubility characteristics are good, their ability to stabilize emulsions and foams are poor, and this limits their use as food ingredients. Application of enzymatic hydrolysis improves surface properties of whey proteins. However, if the degree of protein hydrolysis is not controlled, foam and emulsion stability is decreased drastically. The literature indicates that large molecular size and hydrophobicity of peptides produced by enzymatic proteolysis are important factors to consider for the improvement of the surface activities of proteins [10,11]. As estimated by the particle sizes, the maximum emulsifying capacity has been obtained from hydrolyzates with a 10 or 20% degree of hydrolysis. Higher hydrolysis results in peptides that were too short to act as effective emulsifiers, and, at lower proteolysis, the somewhat reduces solubility of the hydrolyzates slightly decreases their emulsifying power. All of the emulsions are unstable when they are subjected to heat treatment at high

temperatures (122°C), but emulsions prepared from the less hydrolyzed peptide mixtures are stable to heat treatment at 90°C for 30 min [35].

Non-ionic food-grade emulsifiers as well as proteins are commonly used in food industry e.g. in soft baked products. However, the presence of emulsifiers leads to different foam behaviour. Both foams stabilised by sucrose stearate and by monodiglyceride contain small bubbles, shortly after their formation, with quite a certain polydispersity of the bubble size. After 1 day however, the samples are not any more similar. Whereas the average bubble size of foams stabilised by monodiglyceride doubled in 24 h, the one of foams stabilised by sucrose stearate remained quite the same [29].

Compared to the other emulsifiers and proteins, monodiglyceride in  $\alpha$ -gel is the most effective in terms of foamability (Table 1).

**Table 1. Gas volume fraction of foam stabilised by different kinds of surfactants [29]**

<i>Surface active agents (concentration is 0,5 wt %)</i>	<i>Micellar caseins</i>	<i>Sucrose stearate</i>	<i>Sodium caseinate</i>	<i>Whey proteins</i>	<i>Monodiglyceride in <math>\alpha</math>-gel</i>
Gas volume fraction (%)	10	50	50	60-65	80

When both proteins and non-ionic emulsifier molecules coexist in the bulk, the two kinds of molecules compete at interfaces. The effects of low-molecular-weight surfactants on the interfacial rheology of protein films depend on their nature and their concentration relative to protein concentration. The sucrose ester, which is water-soluble, appears to be more effective in adsorbing at the interface and displacing proteins than those which are oil-soluble e.g. lactylated monodiglyceride [12, 29].

Recently, the structure of complexes an aqueous mixture of pectin and a protein, lysozyme, was described in detail. The globular complexes were characterized and showed a strong similarity with aqueous mixtures of lysozyme with a synthetic polymer, sodium polystyrene sulfonate [26].

A protein-polysaccharide coacervation at the air/water interface is an efficient process to increase foam stability. Carrageenans, gum arabic, tragacanth gum have been reported as effective thickeners, stabilizing and gelling agents in food and beverages [14, 15, 36]. It has been noted that egg-albumin/ $\kappa$ -carrageenan at pH below the protein isoelectric point are the most efficient systems to stabilize air/water interfaces in food foams such as marshmallow, Chantilly and mousses [37]. However, the relatively high cost, large quantity required, and problems associated with obtaining a reliable source of consistently high-quality gums and carrageenans have led many food scientists to investigate alternative sources of biopolymer emulsifiers. Hydrophobically modified starches have been identified as one of the most promising replacements. It consists primarily of amylopectin that has been chemically modified to contain nonpolar side groups. These side groups anchor the molecule to the bubble surface, while the hydrophilic starch chains protrude into the aqueous phase and protect air bubbles against aggregation through steric repulsion [36].

The presence of polysaccharides in protein stabilized emulsions can have variable effect on stability and rheological properties. Hydrocolloids are added to increase the stability of the interfacial film separating the droplets that prevent coalescence. Moreover, there is no effect of pH, calcium chloride concentration, or temperature on emulsions stabilized by gum arabic or modified starch. In contrast, droplet aggregation of whey protein-stabilized emulsions is strongly dependent on pH, calcium chloride concentration, and temperature [36, 38].

The carbohydrate addition (glucose, sucrose, starch and inulin) in whey protein suspensions significantly enhances foam stability. Similarly, the emulsion stability increases in suspensions prepared with whey protein isolate and  $\beta$ -lactoglobulin in combination with mono and disaccharides, while significant decrease is remarked in model suspensions prepared with inulin and starch addition. [39].

## Conclusions

Being the most desirable feature for the consumer the emulsion and foam stability significantly influences on the product quality. Up to now, both proteins and polysaccharides are in a scope of interest of the dispersion science. Proteins being an indispensable component of all processed foods have proved to be effective functionally, providing the necessary stability and rheological properties to the final food products, because of their naturally amphiphilic nature and surface active. The combined presence of proteins and polysaccharides strongly increases the emulsion and foam stability. The conditions and treatments of formation of multicomponent foam and emulsion which are stabilized by protein-polysaccharide complexes, should be more investigated.

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