FOOD EMULSIONS

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Contents

Summary

Food emulsions are very complex in composition and structure. They consist of an oil phase containing hydrophobic compounds and an aqueous phase containing water-soluble components. One is dispersed into the other, defined as oil-in-water (O/W) emulsions or water-in-oil (W/O) emulsions, in which the aqueous solution and oil are the continuous phase, respectively. Amphiphilic components such as proteins or low molecular weight surfactants are located at the oil-water interface, thereby decreasing the interfacial tension and forming films in which the structure, thickness, solvatation degree, and mechanical behavior greatly affect emulsion stability and properties. Emulsions are thermodynamically unstable, and phase separation can be prevented through kinetic factors. Destabilization is due to the action of different range forces: gravitational forces, interparticle repulsive and attractive forces, flow forces, and molecular forces. To a differing degree, these are responsible for the action of destabilization mechanisms. The primary processes leading to instability are creaming, flocculation, and coalescence. In addition to these, emulsion phase inversion and

Ostwald ripening must sometimes be considered. Creaming (settling) is a phase separation caused by the upward (or sometimes downward) motion of droplets due to the density difference between phases. Flocculation occurs when droplets aggregate as they collide, due to the prevailing attractive forces at a determined distance between them. Coalescence is the merging of droplets and their loss of identity. The texture of food emulsions depends on their rheological properties, which are greatly affected by the rheology of the continuous phase and the volume fraction of the droplets (See *Newtonian and Non-Newtonian Flow*), although other factors, such as flocculation degree, droplet size, rheology of droplet liquid and interface, etc., also play an important role in emulsion consistency. Due to the complexity of such systems, no universal theory describing the destabilization process exists, and empirical approaches continue to be required in tackling the problem of food emulsion formulation.

1. Introduction

Emulsions are colloidal dispersions of liquid droplets in another non-miscible continuous liquid phase. Nevertheless, the terms colloidal and liquid must not be taken literally, since many food lipids (sometimes the aqueous phase) may be liquid or partially crystallized, depending on the handling/consumption temperature, as in whipped cream, butter or ice cream. Dispersed particles in food emulsions can be of various shapes and sizes, depending on the composition and process conditions. A large portion of the particle or droplet in dairy emulsions or salad dressings is in the colloidal range (lower than $1\,\mu m$), whereas in meat emulsions, fat particles of visible dimensions can be found. Different kinds of emulsions are shown in Figure 1: lipid droplets in aqueous media, called oil-in-water (O/W) emulsions, and aqueous solution droplets in a continuous lipid phase or water-in-oil (W/O) emulsions. Multiple emulsions can also be obtained, when bigger droplets dispersed in a media contain smaller droplets from another liquid phase $(W/O/W$ or $O/W/O)$. Most of the food emulsions are O/W systems (e.g. milk, cream, mayonnaise, salad dressings, cake batter, and cream liqueur). Some exceptions are butter, margarine, and dairy spreads.
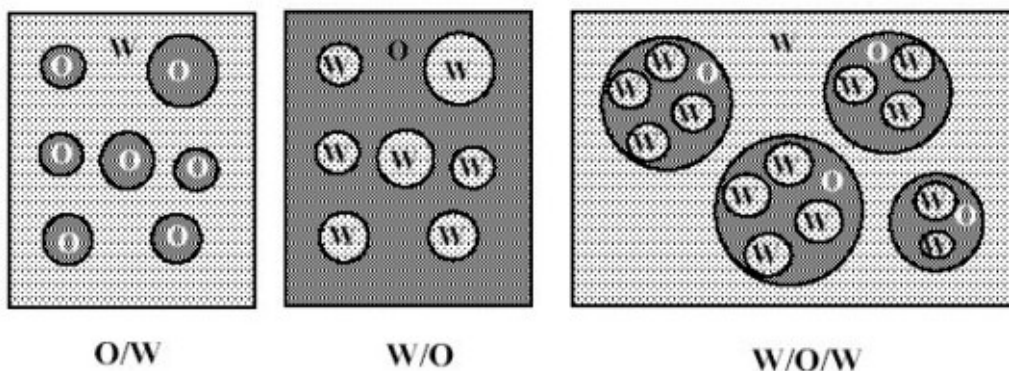

Figure 1. Structure of oil-in-water O/W, water-in-oil (W/O), and multiple emulsions.

Emulsions are by definition unstable. Therefore, developing a "stable emulsion" implies controlling the kinetics of the processes leading to breakdown of the emulsion structure.

This work discusses food emulsion structure, and the stability problems and factors involved in destabilization kinetics. Likewise, some aspects related to emulsion texture or rheological properties are addressed.

2. Structure of Food Emulsions

Food emulsions are very complex in composition and structure. Besides lipids and water, they contain proteins, polysaccharides, small surfactant molecules, and molecular and ionic solutes (sugar, alcohol, salts, preservatives, colorants, flavorings, etc.). Distribution and arrangement of these components, determined in part by their respective chemical affinity, are such that they permit a partial reduction of the systems free energy. Some proteins and surfactants (amphiphilic compounds) are in the O-W interface. Water-soluble polysaccharides are mainly solvated in the continuous phase, contributing to its viscosity, which affects product stability. At the O/W interface, solid particles (such as caseins in milk fat globules), and small surfactant molecules or proteins arranged in mono or multi-layers may be found. In many food emulsions, other dispersed phases (proteins, gas bubbles, starch granules, fat or ice crystals, jellified zones, etc.) coexist with droplets, interacting in different ways and contributing to its structural complexity. In many cases, structural arrangement controls product stability, e.g., in whipped dairy cream, fat globules form a network layer around the gas bubbles, which are in turn linked by bridges in a three-dimensional structure with semisolid consistency. The degree of fat crystallization plays an important role in the stability of such a system.

2.1. Oil-water Interface

Water-air interface	γ (mNm^{-1})	Oil-air interface	γ (mNm^{-1})	Oil-water interface	γ (mNm^{-1})
Water	72	n-octane	22	Milk plasma-liquid milk fat	15
Sodium laurate, 22 mM	43	Liquid-milk fat	34	Water- liquid milk fat	20
Sodium estearate, 0.3 mM	43	Cotton seed oil	33.4	Water-n octane	51
Milk plasma	48	Coconut oil	33.4	Water -triglycerides	25
	14	Olive oil	33.0	Fat globule-milk plasma	1-2.5
				Peanut oil-water	18.5
				Olive oil-water	17.6

Table 1. Values for interfacial tension ranging from 20 to 40ºC in different systems.

The properties and stability of emulsions are largely determined by the droplet surface composition, due to the fact that it is responsible for surface interactions that greatly affect destabilization kinetics. O/W interface usually contains a high concentration of amphiphilic molecules (surfactants or emulsifiers). Both low molecular weight surface-active lipids and a wide range of more or less surface-active proteins and

polysaccharides can be located at the interface. These are arranged as an adsorbed layer at the surface with different thicknesses, as shown in Figure 2. Surface adsorption implies a notable decrease in oil-water surface tension (Table 1) and thus the systems free energy through a decrease of surface energy. The amount of amphiphiles (i) at the interface is quantified through their surface excess concentration (Γ_i: molecules per surface unit), which determines the requirements for complete droplet surface coverage with these molecules. The surface excess concentration of an emulsifier may be determined by measuring the O/W interfacial tension for different emulsifier concentrations in the system. In homogenized milk, the amount of proteins (mainly caseins) at the fat globule surface is $\Gamma_i = 10$ mg dry matter m^{-2}, defining an adsorbed layer as 15 nm thick. Lower protein surface concentrations imply that fat globules are partially uncovered, which will cause globule bridging. Concerning macromolecular emulsifier adsorption, it must be considered that flexible molecules exist, anchored to the surface at several points or zones. So, desorption requires that all contact points be separated simultaneously, which is an unlikely event. Once adsorbed onto a surface, a polymer may undergo slow conformational changes, causing changes in the adsorbed amount and surface properties. This is observed as an ageing effect. Ageing causes the interfacial tension to decrease slowly over a period of several hours, together with a change in the surface rheological properties. When low molecular weight emulsifiers are adsorbed at the interface, these changes occur faster, due to their greater molecular mobility.

In systems containing several surface-active components, three types of adsorbed layers can be identified, based on how the layers are formed:

a) *Monolayer containing a predominant type of molecule at the interface*. This is usually built-up through competitive adsorption with other less surface-active components present in the system. If a more surface-active component is added to an emulsion where droplets are initially covered with adsorbed material, the added component may adsorb by replacing the initial component at the interface segment by segment. Competitive adsorption between various proteins and surface-active lipids has been investigated. It has also been observed that large flexible proteins are able to dominate the interface over smaller and/or globular proteins. From these studies, it is possible to generalize the order of surface activity for common food ingredients: lipid emulsifiers > large flexible hydrophobic proteins (e.g. β-casein) > small hydrophilic proteins (e.g. lactalbumin) > gelatin > surface active polysaccharides (e.g. gum arabic) > starch.

b) *Monolayer containing a mixture of several surface-active components* (Figure 2). This is built-up by associative adsorption, forming a mixed surface that has the average properties of the emulsifiers present. Typical associative systems are those obtained from a blend of surfactant lipids with a different hydrophilic-lipophilic balance (HLB), in which case the packaging degree at the interface is higher than that reached separately. The surface energy is then reduced, and the surface activity enhanced. In the case of associative adsorption, both components are assumed present at the surface. The adsorption of the second component should either be enhanced by the presence of the first component, or

    not influenced at all. The total amount of adsorbed material should be greater than or equal to the sum of both components.

c) *Adsorbed multi-layer*. One component adsorbs on top of the other. Adsorption in layers is possible when surface-active components that are very different in character are present in the system. The second component adsorbs to a particle displaying the properties of the primary adsorbing emulsifier, which usually means a more hydrophilic character than the direct oil surface (Figure 3).

When a mixture of surface-active compounds are present, as occurs in the major part of food emulsions, their relative surface activity determines to a great extent the type of adsorbed layer formed, which in turn results in different types of droplet interactions and emulsion stability properties.
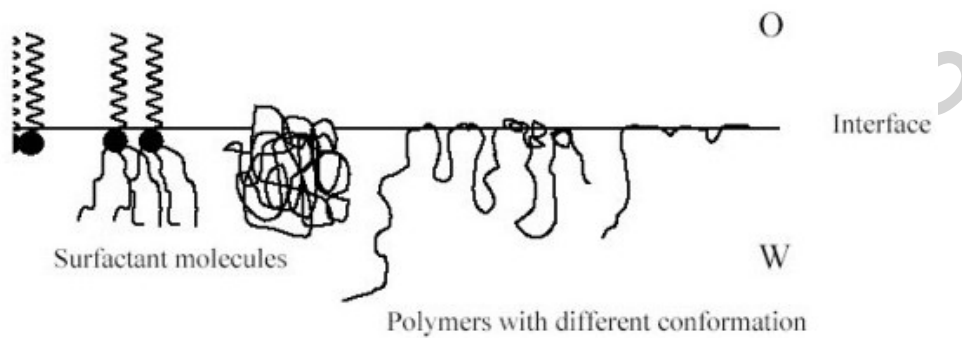

Figure 2. Component arrangement at O/W interface.

Figure 3. Microstructure of O/W emulsion containing skim milk powder (4 percent) and locust bean gum (LBG, 0.35 percent), sunflower oil (30 percent), NaCl (1.5 percent), sucrose (2.5 percent) and acetic acid (0.45 percent). Multilayers of adsorbed material and gelled zones can be observed, as well as droplet flocculation.

3. Emulsion Stability. Destabilization Mechanisms

Emulsions are potentially unstable, since liquid phases are non-miscible and the density difference between them leads to a fast phase separation if there are no kinetic factors to

prevent it. Destabilization is due to the action of different range forces: gravitational forces, interparticle repulsive and attractive forces, flow forces, and molecular forces. To a differing degree, these are responsible for the action of destabilization mechanisms (Figure 4). Even in a system that appears to be perfectly stable, with a shelf life of several years, the total number of droplets, their size distribution, and their arrangement in space are all changing imperceptibly with time. The primary processes leading to instability are creaming, flocculation, and coalescence, and sometimes emulsion phase inversion and Ostwald ripening are considered. Each process consists of the following:

- Creaming (settling): separation caused by upward (or sometimes downward) motion of emulsion droplets, due to the density difference between the droplets and the continuous phase.
- Flocculation: droplets aggregate as they collide, due to the prevailing attractive forces that exist at a determined distance between them.
- Coalescence: merging of droplets and their loss of identity.
- Ostwald ripening: diffusion transport during the dispersed phase of small droplets into larger ones.
- Phase inversion: conversion of an W/O emulsion into a W/O emulsion, or vice versa.
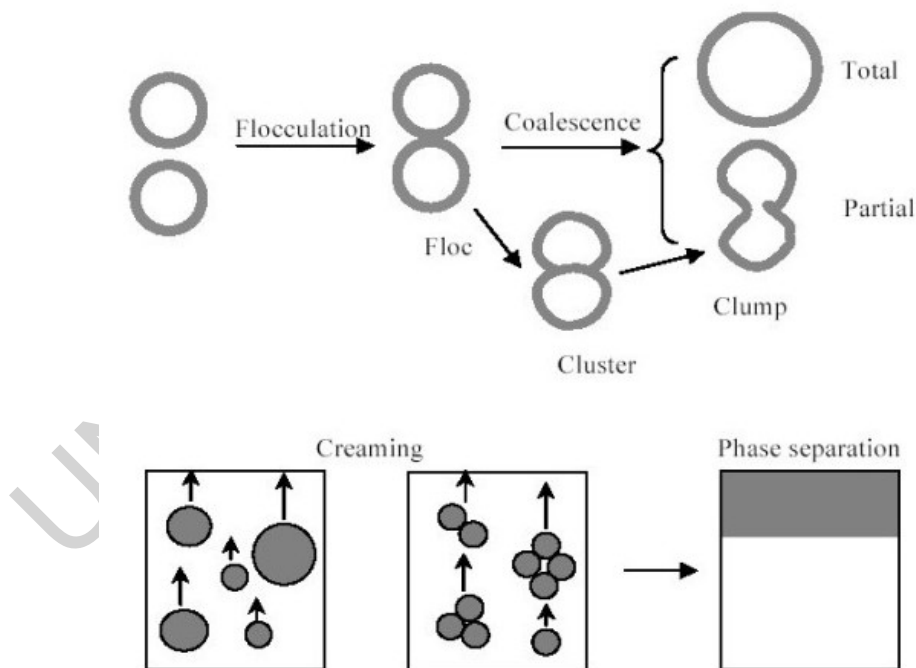

Figure 4. Scheme of action of destabilization mechanisms responsible for emulsion breakdown.

3.1. Creaming

Creaming results in the formation of a concentrated layer of oil droplets at the top of an oil-in-water emulsion sample. In the early stages, there is merely a concentration gradient of droplets, but later a distinct boundary may appear between an upper cream

layer and a lower depleted layer. Stokes' Law gives the creaming (or settling) rate v_s for an isolated, rigid, uncharged droplet of mass m, radius a, and density ρ, in an infinite fluid medium of density ρ_o and viscosity η_o. Equation (1) is deduced from the balance of gravitational and friction forces on the droplet when it reaches a constant rate. In Equation (1), g is local acceleration of free fall.

$$v_s = \frac{2a^2(\rho_0 - \rho)g}{9\eta_0} \tag{1}$$

In homogenized milk containing fat globules with $a = 1\,\mu m, v_s = 1mm/h$, which is low enough to prevent visible creaming over a period of one or two days. Creaming may be described as negligible compared with Brownian motion when v_s is less than 1 mm day^{-1}.

Stokes' Law permits observation of the different factors that can prevent or minimize creaming:

a) *Reduction of average droplet size*. This usually requires the use of valve homogenizers at high operating pressure and the incorporation of a generous ratio of emulsifiers to facilitate an increase of the interfacial surface. However, even under the most intense homogenization conditions, it is impossible to eliminate a small portion of micron-sized droplets, in which creaming occurs after a few days.

b) *Reduction of density differences between the phases*. In this sense, there is little room to maneuver when taking into account the chemical, legal, and toxicological constraints. Density difference between the oil phase and water phase is about 50 kg m^{-3}, although significant changes in the aqueous phase density can be provoked when sugar, protein, etc., are present. Droplet size reductions in emulsions stabilized with proteins adsorbed at the interface contribute to matching of densities, due to an increase in the overall oil droplet density in line with the (ratio) protein layer-oil volume increase. While the effective density of large droplets is very close to the oil phase, the smallest droplets may have a density closer to or even greater than that of the aqueous phase, due to the dominating effect of the adsorbed layer.

c) *Adjusting the viscosity of the continuous phase*. This is usually achieved in practice by adding hydrocolloids (thickeners), such as gums or modified starches. The rheological behavior of hydrocolloid solutions is pseudo-plastic and shows very high viscosity at the shear rates involved in the gravitational motion of the droplets $(\approx v_s/a: 10^{-4} \text{ to} 10^{-1}\ s^{-1})$. So, hydrocolloids contribute substantially towards extending the shelf life of many commercial food emulsions (e.g. milk chocolate beverages, fruit juices, etc.).

Aside from the dilution limit, Stokes' Law is not strictly applicable. Up to moderate droplet volume fractions $(0 < \phi < 0.05)$, the mean creaming speed (v) is less than the Stokes' value (v_s) by an amount proportional to ϕ (Equation 2). Change in the single particle settling speed, caused by the presence of other particles, is not solely due to an increase in the effective viscosity of the surrounding fluid, but also to the predominant

contribution of the downward movement of an equivalent volume in the continuous phase, simultaneous to the upward movement of the droplet. This fluid backflow leads to a general retardation of the single particle settling speed. Rigorous treatments of creaming kinetics are not available at volume fractions greater than a few percent, due to the complexity of the handling of inter-particle hydrodynamic interactions. Equation (3) allows a semi-empirical calculation of the settling speed, which is lowered with respect to v_s, as a function of ϕ (e.g. in a salad dressing with $\phi = 0.4$, the predicted lowering is 10 percent of v_s). Settling is reduced to almost zero in a dispersed phase by about 40 percent.

$$v = v_s (1 - 6.65\varphi) \tag{2}$$

$$v = \frac{v_S (1 - \varphi)}{\left(1 + \varphi^{1/3}\right) \exp\left[\dfrac{5\varphi}{3(1 - \varphi)}\right]} \tag{3}$$

From the expression for volume flux density, it is possible to deduce that mass transport by creaming is maximized when the volume fraction is about 0.17. This droplet concentration should be employed to optimize the centrifugal separation of emulsions by creaming.

Flocculation of droplets in diluted emulsion results in enhanced creaming, since it supposes an increase in the effective size of the particles. In concentrated emulsions, flocculation leads to the formation of an extensive network structure, which permeates throughout the whole system and behaves like a gel structure, showing syneresis instead of creaming.

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Bibliography

Becher P. (1983). *Encyclopedia of emulsion technology*, Vol. 1, 725 pp., Vol. 2, 521 pp., Vol. 3, 437 pp. New York, NY: Marcel Dekker. [A complete overview of basic theory, applications, and different experimental methodologies used to study emulsion stability and properties]

Becher P. (1990). *Dictionary of colloid and surface science*, 202 pp. New York, NY: Marcel Dekker. [Definitions and concepts for a wide collection of specific terms in colloidal science]

Dickinson E. (1992). *An introduction to food colloids*, 207 pp. Oxford, UK: Oxford Science Publications. [This book analyzes the physico-chemical aspects of food colloids]

Dickinson E., Mcclements D.J. (1996). *Advances in food colloids*, 333 pp. London, UK: Blackie Academic Professional. An imprint of Chapman & Hall. [This work describes some recent experimental and theoretical developments in the field of food colloids]

Dickinson E., Stainsby G. (1982). *Colloids in foods*, 533 pp. London, UK: Elsevier Applied Science Publishers. LTD. [Describes the current state of experimental and theoretical colloid science and the colloidal complexity of food materials]

Dickinson E., Stainsby G. (1988). *Advances in food emulsions and foams*, 397 pp. London, UK: Elsevier Applied Science Publishers. LTD. [A collection of chapters by prominent researchers in the field, on basic principles, adsorption of proteins, and optimization of the functional properties of food macromolecules]

Ferragut V., Chiralt A. (1996). Microstructure of oil-in-water low-fat emulsions containing skim milk powder and locust bean gum. *Lebensmittel-Wissenschaft und Technology* **29**, 654-658. [Some examples showing the influence of emulsion composition on its microstructure and rheology are presented]

Larsson K., Friberg S.E. (1990). *Food emulsions*, 510 pp. New York, NY: Marcel Dekker. [This work presents a broad understanding of surface and colloid science, related to the components of food emulsions]

Mitchell J.R. and Ledward D.A. (1986). *Functional properties of food macromolecules*, 394 pp. London, UK: Elsevier Applied Science Publishers. LTD. [This book describes the ability of macromolecules to dictate or modify the structure of a food, and to a large extent, its texture]

Biographical Sketch

Amparo Chiralt is Professor of Food Science in the Department of Food Technology at the Polytechnical University of Valencia, Spain. Professor Chiralt's research and teaching interests are focused on the physiochemical aspects of food processes. She has conducted numerous studies in the flow area: physical properties of colloidal food systems as related to composition, and structural and physicochemical changes that occur during fruit processing, especially dehydration.