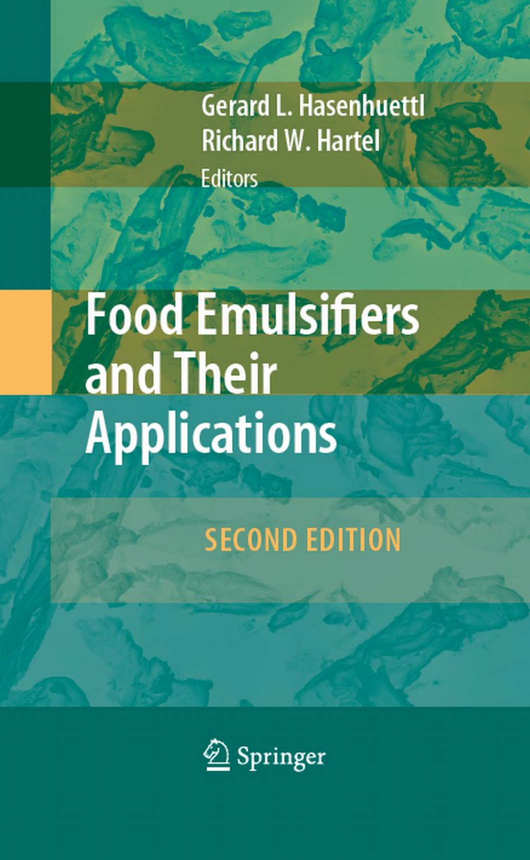

Gerard L. Hasenhuettl
Richard W. Hartel
Editors

Food Emulsifiers and Their Applications

SECOND EDITION

Springer

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Second Edition

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To our wives and children, whose continued patience and understanding are greatly appreciated.

A special dedication is made to Niels Krog and Kare Larsson to recognize their valuable contributions to food emulsifier technology.

Preface

Emulsifiers have traditionally been described as ingredients that assist in formation and stabilization of emulsions. The definition, however, may be expanded to include mixing of mutually insoluble phases. Foams (gas in liquid or solid) and dispersions (solids in liquids or other solids) may be stabilized by emulsifiers. For this reason, the terms emulsifier and surfactant are used interchangeably.

The first emulsifiers were naturally occurring surface-active proteins, such as egg or casein. With advances in chemical and engineering technologies, the array of emulsifiers has been greatly expanded. Applications to food products have enabled the widespread distribution of packaged foods. Selection and design of emulsifiers was done by experienced product developers who were familiar with the behavior and interactions of each emulsifier. Over the past few decades, tremendous progress has been accomplished in the fundamental understanding of emulsions, dispersions and foams.

This book has focused on the design and application of emulsifiers as versatile food ingredients. The second edition has updated and expanded applications, from both theoretical and practical perspectives. The first three chapters describe design, synthesis, analysis, and commercial preparation of emulsifiers. Synergistic and antagonistic interactions with other food ingredients, such as carbohydrates, proteins, and water, are discussed in the next three chapters. The remainder of the book provides detailed descriptions of food product categories and quality benefits obtained by emulsifier systems. Dairy, infant nutrition, bakery, confectionery, and margarine products are included. Chapters on nutrition improvement (e.g., fat reduction) and processing techniques have been included.

Innovation in the food industry is progressing rapidly in response to economic, demographic, nutritional, and regulatory pressures. Many third world countries are undergoing dramatic economic development. This could stimulate demand for convenient packaged food products. At the same time, a contrarian trend toward natural, minimally processed foods is occurring in developed countries. An aging population has created a demand for functional foods. Some products (e.g., yogurt) are delivery vehicles for therapeutic agents. Global trade has stimulated calls for uniform safety and nutrition regulations. Food emulsifiers are versatile ingredients that may be valuable tools to address these challenges.

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Chapter 1
Overview of Food Emulsifiers

Gerard L. Hasenhuettl

1.1 Introduction

Food colloids, emulsions and foams have their origins in nature and have evolved with advances in food processing techniques. Milk, for example, has a naturally occurring membrane, which allows solid fat to be dispersed into an aqueous phase. Early food formulations for butter, cheese, whipped cream and ice cream took advantage of these natural emulsifiers. The invention of mayonnaise as a cold sauce in France utilizes egg lipoproteins and phospholipids to disperse oil into an acidified aqueous phase. The emulsifying power of these lipoproteins is still impressive by today's standards, because up to 80% oil could be dispersed without inversion to an oil continuous emulsion. In 1889, the French chemist Hippolyte Mege-Mouries invented margarine as a low-cost substitute for butter. An aqueous phase was dispersed into a molten tallow to form an oil continuous emulsion. Subsequent discovery of the hydrogenation process allowed the substitution of partially hydrogenated oil for the tallow. In this application, the emulsion only had to be stable long enough to solidify the fat and fill into containers.

Synthetic emulsifiers have only come into wide commercial use in the second half of the twentieth century. Their development was driven by the processed food industry, which needed shelf-stable products for distribution through mass-market channels. For example, creamy salad dressings may be stored for up to a year without visible separation. Other factors, such as rancidity, are now more important factors in predicting product stability.

Detailed knowledge of the physical chemistry of emulsions is best obtained when pure oil, water, and emulsifiers are used. Food emulsions, by contrast, are extraordinarily complex systems. Commercial fats and oils are rich mixtures of triacylglycerols that also contain small amounts of highly surface-active materials; Salt content and pH in food emulsions vary widely enough to have significant effects on their stability. Natural and commercial emulsifiers are often complex mixtures that vary in composition between different manufacturers. Other food ingredients, such as proteins and particulates, contribute surface activity that may dramatically alter the character of the emulsion. Processing conditions can affect emulsion stability. For example, high temperatures, with or without agitation, may be used for

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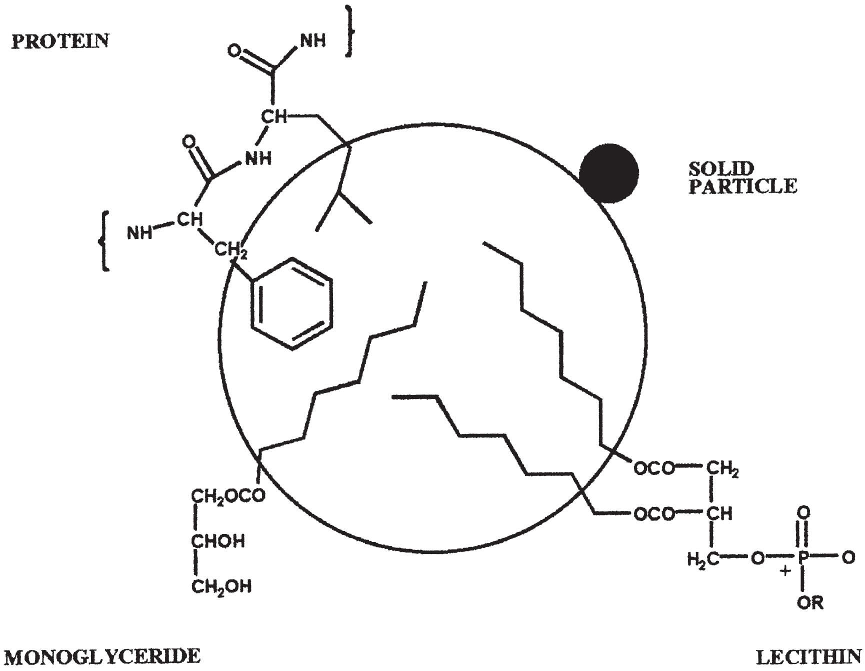

Fig. 1.1 Schematic representation of an Emulsified oil droplet

pasteurization. Because of all these complex relationships, the formulation of food emulsions grew up as an art, dominated by individuals having a great deal of experience. The gradual development of sophisticated techniques such as electron microscopy, rheology, nuclear magnetic resonance, and chromatography/mass spectrometry has solidified the art with a scientific dimension. The orientation of some typical food emulsifiers at the water/oil interface is displayed in Fig. 1.1.

The science of food emulsions has been extensively covered by other authors (Dickinson and Rodriguez-Patino, 1999; Friberg et al., 2003; McClements 2004). This book will concentrate on the structure, preparation, analysis, interactions, and applications of emulsifiers.

1.2 Emulsifiers as Food Additives

Approximately 500,000 metric tons of emulsifiers are produced and sold worldwide. Sales in the European Union and the United States are estimated to be 200–300 million EUROD and 225–275 million USD respectively. However, since the value/volume ratio of these products is low and local regulations vary, very little truly global trade has yet developed. Products, which are solids at room temperature, may be packaged as beads or flakes. Semisolids may be available in plastic lined cartons or drums. In some cases, bulk quantities may be delivered in tank trucks or rail cars.

In the United States, food emulsifiers, along with other additives, are regulated by the Food and Drug Administration (Federal Register, 2003). Two sections of the regulations govern their use: substances Affirmed as GRAS, that is, Generally Recognized as Safe, (21CFR184) and Direct Food Additives (21CFR172). Substances that have been affirmed as GRAS usually have less stringent regulations attached to their use. However, Food and Drug Administration Standards of Identity may preclude their use in certain standardized foods. In comparison, direct food additives may be allowed only in certain specific foods at low maximum allowable levels. The method of manufacture and analytical constants may also be defined. Tables 1.1 and 1.2 reference Food and Drug regulations.

Table 1.1 Food emulsifiers affirmed as GRAS

Emulsifier	U.S. FDA (21CFR)	EEC (E No.)
Diacetyltartaric esters of monoglycerides (DATEM)	184.1101	E472e
Lecithin	184.1400	E322
Mono- and diglycerides	184.1505	E471
Monosodium phosphate derivatives of mono and diglycerides	184.1521	–

Table 1.2 Emulsifiers—Direct food additives

Emulsifier	U.S. FDA (21CFR)	EEC (E No.)
Acetylated mono- and diglycerides	172.828	E472a
Calcium stearoyl lactylate	172.844	E482
Citric acid esters of mono- and diglycerides	172.832	E472c
Ethoxylated mono- and diglycerides	172.834	–
Lactic acid esters of mono-and diglycerides	172.850	E472b
Magnesium salts of fatty acids	172.863	E470b
Polyglycerol polyricinoleate	–	E476
Polysorbate 60	172.836	–
Polysorbate 65	172.838	–
Polysorbate 80	172.840	–
Propylene glycol esters of fatty acids	172.856	E477
Salts of fatty acids	172.863	E470a
Sodium stearoyl lactylate	172.846	E481
Sodium stearoyl fumarate	172.826	–
Sorbitan monolaurate	–	E493
Sorbitan monooleate	–	E494
Sorbitan monopalmitate	–	E495
Sorbitan monostearate	172.842	E491
Sorbitan tristearate	–	E492
Stearyl tartrate	–	E483
Succinylated mono-and diglycerides	172.830	–
Sucrose acetate isobutyrate (SAIB)	172.833	–
Sucrose esters of fatty acids	172.859	E473
Tartaric acid esters of mono-and diglycerides	–	E472d

The European Economic Community (EEC) regulates food emulsifiers in an analogous fashion to United States regulations. E-numbers are also listed in Tables 1.1 and 1.2. Specific regulations, however, must be consulted before food products are designed for international markets. For example, polyglycerol esters up to a degree of polymerization of 10 are widely accepted in the United States. For the EEC, this value may not exceed 4. Standards of identity may also differ significantly.

Other countries, which have not formed trading communities, may have regulations, which are unique. Careful translation from the local language is often difficult and time consuming.

As with any other totally new food additive, the need to prove safety of the product in foods at high levels of consumption requires extensive toxicity studies and enormous documentation. The consequent financial and time commitment make development of totally new synthetic emulsifiers unattractive for emulsifier manufacturers. A somewhat easier development approach is to petition for expanded use (new applications or higher permitted levels) of emulsifiers that are already approved. However, even this tactic may require several years of review. In addition to national regulations, many food processors require their ingredients, including food emulsifiers, to be Kosher so that their products are acceptable to Jewish and many Islamic consumers. For emulsifiers to be considered Kosher, they must be produced from Kosher-certified raw materials. This requirement precludes the use of almost all animal fats. This is not much of a problem since emulsifiers are easily produced from vegetable fats that can be blended to give similar fatty acid compositions. The major concern in Kosher certification is to determine in advance whether the customer's rabbinical council recognizes the Hekhsher (Kosher symbol) of the producer's rabbi.

Products labeled, as "all natural" must contain ingredients that have not been chemically processed or modified. Only lecithin or other naturally occurring materials such as proteins and gums, would be acceptable for these products.

1.3 Emulsifier Structure

Since food emulsifiers do more than simply stabilize emulsions, they are more accurately termed surfactants. However, because the term emulsifier has been used so extensively in the food industry, both terms will be used interchangeably in this book. Surface-active compounds operate through a hydrophilic head group that is attracted to the aqueous phase, and an often-larger lipophilic tail that prefers to be in the oil phase. The surfactant therefore positions itself to some extent, at the air/water or oil/water interface where it can act to lower surface or interfacial tension, respectively. Lipophilic tails are composed of C16 (palmitic) or longer fatty acids. Shorter chains, such as C12 (lauric), even though they can be excellent emulsifiers, can hydrolyze to give soapy or other undesirable flavors. Unsaturated fatty acids are molecules having one (oleic) or two (linoleic) cis (Z) double bonds. Linoleic acid is usually avoided since it is easily oxidized and may produce an oxidized rancid off-flavor in the finished food. Fats may be hydrogenated to produce a mixture of saturated and unsaturated fatty acids. Emulsifiers produced from these fatty acids may have an intermediate consistency (often referred to as “plastic”) between liquid and solid. These products also contain measurable concentrations of trans (E) unsaturated fatty acids that have higher melting points than the cis (Z) fatty acids.

Polar head groups may be present in a variety of functional groups. They may be incorporated to produce anionic, cationic, amphoteric, or nonionic surfactants. Mono- and diacylglycerols (more commonly known as mono- and diglycerides), which contain an -OH functional group, are the most widely used nonionic emulsifiers. Sodium stearoyl lactylate is an anionic surfactant used widely in bakery products. Lecithin, whose head group is a mixture of phosphatides, may be visualized as amphoteric or cationic, depending on the pH of the product.

Proteins may also be surface active due to the occurrence of lipophilic amino acids such as phenylalanine, leucine, and isoleucine. Interfacially active proteins will fold so that lipophilic groups penetrate into the oil droplet while hydrophilic portions of the chain extend into the aqueous phase. Proteins in this configuration may produce a looped structure that provides steric hindrance to oil droplet flocculation and coalescence. Charged proteins may also stabilize emulsions due to repulsion of like charged droplets. Proteins may also destabilize water-in-oil emulsions, such as reduced fat margarines, by causing the emulsion to invert.

Food emulsifiers may be thought of as designer molecules because the structure and number of heads and tails may be independently varied. A very useful conceptual tool is hydrophile-lipophile balance (HLB). The topic has been extensively reviewed by Becher (2001) so only a brief description will be presented here. The number and relative polarity of functional groups in a surface-active molecule determine whether the molecule will be water or oil soluble (or dispersible). This concept has been quantitated by calculation of an HLB value to describe a given emulsifier. High HLB values are associated with easy water dispensability. Since conventional practice is to disperse the surfactant into the continuous phase, high HLB emulsifiers are useful for preparing and stabilizing oil-in-water (O/W) emulsions. Low HLB emulsifiers are useful for formulation of water-in-oil (W/O) emulsions, such as margarine. Extreme high or low values are not functional as emulsifiers since almost all of the molecule will be solubilized in the continuous phase. They would, however, be very useful for full solubilization of another ingredient, such as a flavor oil or vitamin, in the continuous phase. At some intermediate values of HLB, the molecule may not be stable in either phase and will result in high concentration at the interface. The practice of adding surfactant to the continuous phase is known as Bancroft’s Rule. One notable exception is the formulation of creamy salad dressings by adding polysorbate 60, a high HLB emulsifier, to the oil phase.

Surfactants may assemble into organized structures described as mesophases or liquid crystals. These bilayer structures adopt several geometric forms: (1) Lamellar—sheets of bilayers where the hydrophilic groups are paired. Large amounts of water may be trapped in this mesophase, thereby reducing its concentration in the bulk phase. (2) Hexagonal—two cylindrical types. In Type I, the lipophilic tails are contained inside the cylinder and the hydrophilic groups are on the surface. For Type II, the geometry is reversed, with the lipophilic tails on the outside and hydrophilic groups inside the cylinder. (3) Vesicles (liposomes)—Spherical bilayer structures.

The most common are large unilamellar vesicles (LUV) and small unilamellar vesicles (SUV). These mesophases have received a good deal of attention in the science of drug delivery. (4) Cubic—Complex three-dimensional structures which are difficult to characterize.

Israelachvili (1992) has described a predictive model based on the critical packing coefficient. As shown in Fig. 1.2, packing into the mesophase structure is predicted based on the hydrodynamic radius of the head group and the number and effective length of the lipophilic tails. For example, a double tail surfactant with a small head group, like lecithin, can readily pack into a liposome. Predictions based on this model are summarized in Table 1.3.

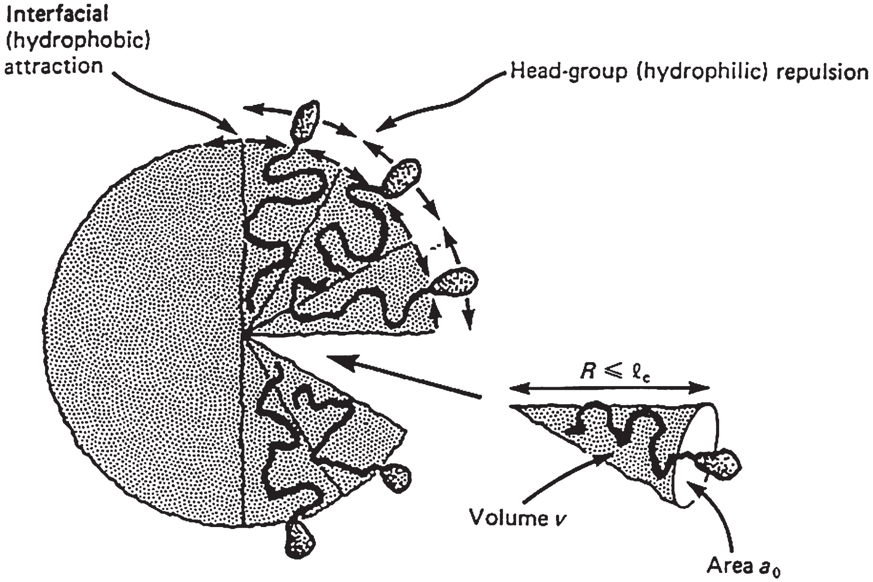

Fig. 1.2 Critical packing parameter for prediction of mesophase structure (Israelachvili, 1992, p. 368). Reproduced with permission of Elsevier Ltd

Table 1.3 Prediction of mesophase structure using critical packing parameters

Molecular structure	Packing parameter	Shape	Mesophase
Small single-tail lipid; Large polar head group	<1/3	Cone	Micelle
Single-tail lipid; Small polar head group	1/3–1/2	Truncated cone	Hexagonal
Double-tail lipid; Large polar head group	1/2–1	Truncated cone	Vesicle
Double-tail lipid; Small polar head group	~1	Cylinder	Lamellar
Double-tail lipid; Small polar head group	>1	Inverted truncated cone	Inverted micelle

Adapted from Israelachvili (1992, p. 381).

1.4 Surface Active Hydrocolloids

Traditionally, hydrocolloids such as gums and starches have been regarded as thickeners. Their stabilizing effect on emulsions derives from an increase in viscosity of the aqueous phase. The kinetic motion of the droplets is reduced, resulting in a lower rate of flocculation and coalescence. Because of their relatively high oxygen/carbon ratio, these molecules are polar, with an affinity for the aqueous phase. In addition, some, such as sodium alginate, carry a negative charge, which enhances the hydrophilic character. Some commercial gums, however, contain surface-active proteins. As a result, these hydrocolloids demonstrate interfacial activity in some applications.

Starches and gums may be chemically or enzymatically modified to insert a lipophilic group. For example, alginic acid may be esterified with propylene glycol to yield propylene glycol alginate. The pendant methyl group can facilitate coupling with the oil phase. Saccharides, starches, and gums may interact with emulsifiers to produce enhanced functionality. This will be discussed further in Chap. 4.

1.5 Emulsifier Functionality

In addition to their major function of producing and stabilizing emulsions, food emulsifiers (or surfactants) contribute to numerous other functional roles, as shown in Table 1.4 Some foods, notably chocolate and peanut butter, are actually dispersions of solid particles in a continuous fat or oil phase. Chocolate viscosity is controlled by the addition of soy lecithin or polyglycerol ricinoleate (PGPR). Oil separation in peanut butter is prevented by use of a monoglyceride or high melting

Table 1.4 Functionality of surfactants in some foods

Functionality	Surfactant	Food example(s)
Foam aeration/stabilization	Propylene glycol esters	Cakes, whipped toppings
Dispersion stabilization	Mono/diglycerides	Peanut butter
Dough strengthening	DATEM	Bread, rolls
Starch comlexation (anti-staling)	SSL, CSL	Bread, other baked goods
Clouding (weighting)	Polyglycerol esters, SAIB	Citrus beverages
Crystal inhibition	Polyglycerol esters, oxystearin	Salad oils
Antisticking	Lecithin	Candies, grill shortenings
Viscosity modification	Lecithin	Chocolate
Controlled fat agglomeration	Polysorbate 80, polyglycerol esters	Ice cream, whipped toppings
Freeze-thaw stabilization	SSL, polysorbate 60	Whipped toppings, coffee whiteners
Gloss enhancement	Sorbitan monostearate, polyglycerol esters	Confectionery coatings, canned and moist pet foods

fat. In some products, such as ice cream and whipped toppings, one of the dispersed phases is air. Foam stability is a critical functional property in these systems. In some cases the secondary effect may be of greater concern than formation of the emulsion. Strengthening of dough and retardation of staling are vital considerations to processors who bake bread.

A common practice in the food industry is to use two or three component emulsifier blends to achieve multiple functionalities. In a cake emulsion, for example, aeration to produce high volume, foam stabilization, softness, and moisture retention are achieved by using an emulsifier blend. One useful statistical method to optimize emulsifier blends is the full factorial experimental design using a zero or low level and a higher level of each ingredient. The major advantage of this design is that it will detect two and three factor interactions that are not uncommon in complex food systems. Response surface methodology (RSM) and fractional factorial designs are also very useful techniques because they reduce the number of experiments necessary to obtain optimal concentrations. Robust design is recommended for products that require the consumer to mix ingredients. This approach results in a quality product, even if measurements are slightly inaccurate.

Small molecule emulsifiers (e.g., monoglycerides) may exert their effect by partially or totally displacing proteins from an oil/water interface. This replacement is entropically favored because of the difference in size and mobility of the species. Direct interaction of emulsifiers and proteins may be visualized through electrostatic and hydrogen bonding, although it is difficult to observe in a system that contains appreciable amounts of oil. Chapter 5 on emulsifier/protein interactions will elaborate on these concepts.

Emulsifier suppliers generally employ knowledgeable technical service professionals to support their customer's product development efforts. Their experience in selecting emulsifiers for a functional response is a valuable initial source of information. However, food processors may want to develop unique products that have no close relationship to a product currently in commerce. In this case, the supplier may have some general ideas for emulsifier selection. However, it may be necessary for product developers to define their own criteria for emulsifiers based on critical functions required in the product.

The objective of this book is to provide the food industry professional or interested technical professional with an overview of what emulsifiers are, how they are prepared, and how they are utilized in food products. Although in many senses food emulsifiers have become commodity ingredients, sophisticated understanding and application in processed foods is likely to continue to advance.

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