Gerard L. Hasenhuettl
Richard W. Hartel *Editors*

Food Emulsifiers and Their Applications

Third Edition

Springer

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Editors
Gerard L. Hasenhuettl
Cheetahtech International, LLC
Port Saint Lucie, FL, USA

Richard W. Hartel
Department of Food Science
University of Wisconsin
Madison, WI, USA

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Preface to the Third Edition

Next to water, food is the most critical resource to ensure life. The gold standard for good food has been an appetizing meal, prepared from fresh ingredients. Unfortunately, ingredients do not remain fresh for long. The quality of prepared foods is likewise fleeting. Packaged foods have been developed to fill in when fresh ingredients are unavailable, or convenience is essential.

Food additives were developed in the twentieth century to improve the stability, texture, and flavor of foods. Food emulsifiers have been classically defined as ingredients that promote the formation of or maintain the stability of emulsions. The definition may be generalized further to mixing of insoluble phases. Foams are mixtures of gas and liquid, and dispersions are mixtures of liquids and solids. The action of these ingredients occurs at an interface or surface. For this reason, the terms emulsifier and surfactant have been used interchangeably.

The first emulsifiers were naturally occurring ingredients, such as egg or casein. Advances in chemistry and engineering led to synthesis of surfactants that produced superior and more economical effects. The wide selection of food emulsifiers has led to wide geographical distribution of packaged foods. This capability improves scale economies, which allows more economical pricing for consumers. Lecithin, egg yolk and white proteins, and protein-containing hydrocolloids are naturally occurring emulsifiers, with long histories of use in food applications. Other surfactants are produced by chemical reaction of fats, oils, or fatty acids with other well-known biological molecules. Emulsifiers as well as other food additives are regulated by government agencies, such as the U.S. Food and Drug Administration and the European Economic Community.

Surfactants are amphiphilic molecules, having one or more hydrophobic regions, and one or more functional groups. They promote and stabilize emulsions by orienting themselves at the oil-water interface and lowering the interfacial tension. Interactions with other food components, such as water, carbohydrates, and proteins, are important to promote other functions. Mechanisms of these interactions are discussed in Chaps. 4, 5, and 6.

Applications in food products are discussed in Chaps. 7–16. Chapters describing dressings and sauces and processed meats are new in the Third Edition.

Consumers have favored natural foods and have resisted chemical additives. Affluent consumers have been willing and able to pay the higher cost for these foods. Lower income consumers may attempt to grow their own food, but are limited to growing seasons and access to arable land. The challenge for processed food manufacturers is to produce nutritious foods having good flavor and texture with minimal chemical additives. Scientists, product developers, engineers, and students may find this book useful for addressing this challenge.

Port Saint Lucie, FL, USA Gerard L. Hasenhuettl
Madison, WI, USA Richard W. Hartel

Contents

Contributors

Thomas Arnebrant Faculty of Health and Society, Department of Biomedical Sciences, Malmö University, Malmö, Sweden

Bjorn Bergenståhl Department of Food Technology, Lund University, Lund, Sweden

Martin Bos Bosstamps, Wageningen, The Netherlands

Bruce Campbell Independent Researcher, Glenview, IL, USA

Marité Cárdenas Faculty of Health and Society, Department of Biomedical Sciences, Malmö University, Malmö, Sweden

Lynn B. Deffenbaugh Kemin Industries, Inc., Des Moines, IA, USA

Stephen R. Euston School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, Scotland, UK

Hassan Firoozmand University of Wisconsin, Madison, WI, USA

H. Douglas Goff Department of Food Science, University of Guelph, Guelph, ON, Canada

Matt Golding School of Food and Advanced Technology, Massey University, Palmerston North, New Zealand

Richard W. Hartel Department of Food Science, University of Wisconsin, Madison, WI, USA

Gerard L. Hasenhuettl Cheetahtech International, LLC, Port Saint Lucie, FL, USA

Dennis Kim Mondelez International, East Hanover, NJ, USA

Séamus L. McSweeney Nestle Development Centre, Wyeth Nutritionals Ireland Limited, Askeaton, Limerick, Ireland

Ganesan Narsimhan Department of Agricultural and Biological Engineering, Purdue University, West Lafayette, IN, USA

Tommy Nylander Physical Chemistry, Department of Chemistry, Lund University, Lund, Sweden

Frank Orthoefer Lenoir City, TN, USA

Eddie Pelan School of Chemical Engineering, University of Birmingham, Birmingham, UK

M. Wes Schilling Department of Food Science, Nutrition and Health Promotion, Mississippi State University, Mississippi State, MS, USA

Patrick T. Spicer School of Chemical Engineering, UNSW Sydney, Sydney, NSW, Australia

Zebin Wang Dupont Nutrition and Health, St. Louis, MO, USA

Paul Wassell Golden Agri-Resources (GAR), PT SMART (R&D) Marunda Centre, Jakarta, Jawa Barat, Indonesia

Peter Wilde Food Innovation and Health, Quadram Institute Bioscience, Norwich Research Park, UK

Ning Xiang Department of Agricultural and Biological Engineering, Purdue University, West Lafayette, IN, USA

Department of Food Science and Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang, China

Niall W. G. Young DuPont Nutrition and Health, Physical Food Science, Brabrand, Denmark

Chapter 1
Overview of Food Emulsifiers

Gerard L. Hasenhuettl

1.1 Introduction

Spoilage has been a serious problem throughout history. Innovations in processing, preservation and packaging have dramatically increased the capability to distribute food around the world.

Many processed packaged foods contain mixtures of mutually insoluble phases, such as gas, liquid, and solids. Table 1.1 shows examples of these foods. Mixtures of insoluble phases are thermo dynamically unstable, and will eventually separate. Separation of these phases can cause problems with texture and appearance, flavor, and microbial stasis. For example, a creamy salad dressing may turn from white to gray, after storage on a shelf for a few months. Food emulsifiers can help to retard separation. A competing approach is to increase the viscosity of the continuous phase, in order to reduce mobility of dispersed phase (particles, droplets, or bubbles). For water-continuous products, starches and gums (also referred to as hydrocolloids) can exert this thickening effect. Additives for oil-continuous systems are solid fats, waxes, and calcium salts.

Emulsifiers may be defined as additives that promote the formation, or enhance the stability of emulsions. Food emulsifiers often provide technical benefits, such as viscosity reduction, starch complexation, or inhibition of crystallization. These additives may be more correctly defined as surfactants. Because of widespread usage of the term emulsifier in the literature, it will be preserved in this book, as an interchangeable term with surfactant.

G. L. Hasenhuettl (✉)
Cheetahtech International, LLC, Port Saint Lucie, FL, USA

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Table 1.1 Multiple phase mixtures in food products

	Continuous phase			
	Phases	Solid	Liquid	Gas
Dispersed phase	Solid	Alloy/solid solution Chocolate	Dispersion Chocolate beverage	Solid aerosol Spray icings
	Liquid	Semi-solid emulsion Margarine	Emulsion Creamy dressing	Liquid aerosol Spray oil
	Gas	Foam Whipped topping	Gas dispersion Carbonated beverage	Gas mixture Air

A detailed discussion of food emulsions, dispersions, and foams is far beyond the scope of this book. There are several excellent sources in the literature (McClements 2004; Sjobiom 2013; Phillips 2009).

The earliest known emulsions were based on natural occurring materials. Milk, for example, is a dispersion of fat droplets in an aqueous media, stabilized by milk proteins and phospholipids. Early formulations for butter, cheese, and whipped cream took advantage of these naturally occurring emulsifiers. The invention of mayonnaise in France dispersed oil into an acidified aqueous phase, using egg yolk to stabilize the emulsion. The functionality of egg lipoproteins is still impressive by today's standards. Up to 80% oil can be emulsified without inversion to a water-in-oil emulsion.

In 1889, French chemist Hippolyte Mege-Mouries invented margarine as a low-cost substitute for butter. He dispersed an aqueous phase into molten tallow, followed by cooling. In this case, stability is maintained by restricted motion of water droplets by the solid tallow phase. Discovery of the hydrogenation process allowed semi-solid vegetable fat to be substituted for the tallow. Synthetic food emulsifiers were developed during the second half of the Twentieth Century, in response to the need for shelf-stable foods for mass market distribution. For example, creamy salad dressing can now remain stable for a year without phase separation. Rancidity and flavor degradation are now the factors which limit shelf life. Synthetic food emulsifiers are less expensive than gums, but bear the stigma of chemical-sounding names.

Food emulsifiers are amphiphilic molecules, having a hydrophilic (water loving) head group and a lipophilic (oil or lipoid loving tail. The lipophilic tails are even-numbered straight-chain fatty acids. They are derived from animal or vegetable fats and oils. Hydrophilic groups are ionic or dipolar. They are derived from molecules that are edible. Proteins can also be surface-active if they contain both hydrophilic and lipophilic amino acid residues. Figure 1.1 shows how emulsifiers are oriented at the oil-water interface.

Synthetic food emulsifiers may be produced as liquid, solid, or semi-solid physical states.

Liquids are packaged in buckets, drums, or may be delivered in tank trucks or rail cars. Solids are flaked or spray-chilled into beads, and delivered in plastic-lined cartons or drums. Emulsifiers may also be blended with stabilizers or other ingredients for convenient addition of the customer.

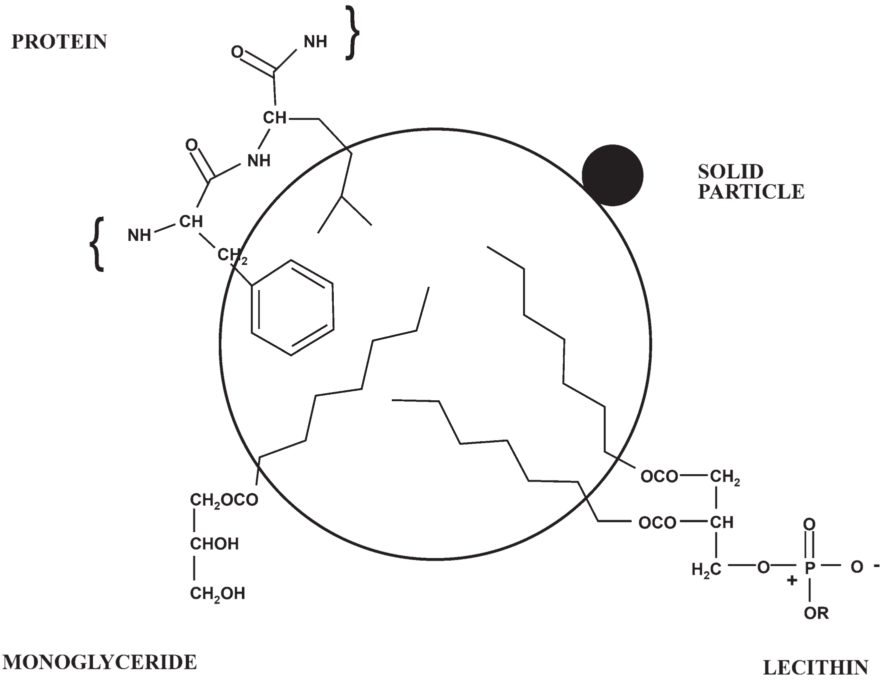

Fig. 1.1 Orientation of surfactants at the oil/water interface

1.2 Food Additive Regulations

Food emulsifiers are regulated as food additives in almost all major countries around the world. In the United States, the Food and Drug Administration (Federal Register 2013) regulates the composition of foods, drugs and cosmetics. Food regulations may be found on Title 21 of the Code of Federal Regulations (21 CFR). The most lightly regulated additives are listed in Section 182, Generally Recognized as Safe (GRAS), and Section 184, Affirmed as GRAS. These substances have long histories of use and clean safety records. Table 1.2 lists these emulsifiers. They may be used in foods as long as they are not precluded by a standard of identity.

Other emulsifiers are listed as Direct Food Additives in Section 172. Here the restrictions vary widely. Some emulsifiers are allowed at levels "sufficient to accomplish the desired technical effect." Others are restricted for methods of manufacture, analytical measurements, specified food products, and use levels. Table 1.3 lists these emulsifiers. Companies that produce emulsifiers can petition the FDA for approval of a new food additive, but documentation of safety is expensive and time consuming. It is less burdensome to obtain permission for expanded use for an additive currently approved for a different product, or an additive with a history of safe use in another country. The process, however, still takes several years.

Table 1.2 Food emulsifiers affirmed as GRAS

Emulsifier	U.S. FDA (2ICFR)	EEC (E no__.)
Diacetyltartaric ester 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 1.3 Emulsifiers listed as direct food additives

Emulsifier	U.S._FDA_(21CFR)	E EC (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	–
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 tristerate	–	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) regulations are similar to those in the United States. E-numbers for the commonly used emulsifiers are shown in Tables 1.2 and 1.3. However, when preparing to sell a product in another country, details of the regulations must be examined. For example, polyglycerol esters with a degree of polymerization up to 10 are acceptable in the United States. In EEC countries, the maximum degree of polymerization is 4.

Countries that have not formed trading agreements may have unique food regulations. Translation from the local language may result in misunderstanding. Local consultants or trading partners can provide valuable information and contacts.

In order to reach Jewish and Islamic consumers, many manufacturers require their ingredients to conform to Kosher or Halal requirements. Food emulsifiers must be prepared from kosher certified raw materials, for example, vegetable oils. Manufacturing must also be carried out in a Kosher-certified plant, and not contaminated by non-Kosher materials. The major hurdle to clear is to ensure that the customer's rabbinical council will accept the Heckshire (Kosher symbol) of the supplier's rabbi.

Although standards remain somewhat loose, products that claim to be "all natural" must not contain ingredients that have been chemically processed or modified. Food emulsifiers for these products are limited to lecithin, dairy and egg proteins, surface-active gums, or other naturally occurring materials.

1.3 Food Emulsifier Structure and Function

Emulsifiers are amphiphilic molecules, containing polar and non-polar regions. In most cases, the non-polar units are derived from fatty acid of 16 or more carbon atoms. Shorter chain lengths make excellent emulsifiers, but can react with water to produce soapy or other undesirable off-flavors (hydrolytic rancidity). Unsaturated fatty acids (oleic, linoleic, and linolenic) can react with oxygen to produce cardboard, beany, grassy, or painty off-flavors (oxidative rancidity). Liquid oils may be hydrogenated to produce semi-solid fats, referred to as "plastic."

Polar functional groups are hydroxyl, amino, and carboxylic or phosphoric acids that can be incorporated into the structure to produce anionic (negative charge), cationic (positive charge), amphoteric (positive and negative charges), or nonionic (no formal charge) emulsifiers. Monoacyl glycerols, commonly called monoglycerides, are the most commonly used nonionic surfactants. Calcium and sodium stearoyl lactylates are anionic surfactants widely used in bakery products. Lecithin can function as an amphoteric or cationic surfactant, depending on the pH of the food product.

Proteins can also be surface active if they contain Lipophilic amino acids such as phenylalanine, leucine, and isoleucine. These side groups are attracted to the oil phase, while polar amino acid, such as aspartic or glutamic acids, tend to extend into the aqueous phase. Proteins can form loops around oil droplets and prevent coalescence and separation (steric stabilization). Charged amino acids can stabilize emulsions by electrostatic repulsion of the droplets. However, they can destabilize oil-continuous emulsions, such as low fat spreads, by causing inversion.

Food emulsifiers may be thought of as designer molecules. The size and number of hydrophilic head groups and lipophilic tails can be independently varied. A useful conceptual tool is the hydrophilic-lipophilic balance (HLB). Becher (2001) has extensively reviewed the subject, so it will not be discussed in detail here.

HLB values determine whether hydrophilic or lipophilic groups are dominant. Values for food emulsifiers range from 2 to 16. Low HLB emulsifiers readily dissolve in oil, while high HLB emulsifiers dissolve in water. High HLB emulsifiers are effective emulsifying agents, e.g. for dissolving flavor oils in the aqueous phase. High HLB emulsifiers are useful for preparing oil-in-water (O/W) emulsions, while low HLB emulsifiers are good for water-in-oil (W/O) emulsions. Emulsifiers with intermediate HLB values tend to be poorly soluble in both oil and water, so they tend to accumulate at the interface.

Conventional practices to add the emulsifier to the continuous phase, and then slowly add the dispersed phase with vigorous mixing, this is known as Bancroft's Rule. One exception is to dissolve Polysorbate 60 to the oil phase when preparing a salad dressing. A finer and narrower droplet distribution is achieved.

Surfactants can react with water to form ordered structures called mesophases, sometimes referred to as liquid crystal. The most common of these bilayer systems are lamellar, hexagonal, cubic, and vesicular.

The lamellar phase consists of an infinite bilayer plane where polar head groups are associated with one another. Above the melting point of the alkyl chains (Kraft temperature), large amounts of water can enter the space between the polar head groups. When the system is cooled, the alkyl chains crystallize, trapping the water and reducing its concentration in the continuous phase. The swollen bilayer is called an alpha gel.

The hexagonal phase is an assembly of cylindrical or barrel-like structures. Type I has the fatty acid chains inside the cylinder, with the head groups outside, facing the water-continuous phase. The Type II structure has the reverse arrangement, with the polar head groups inside, and the fatty acid chains protruding into the continuous oil phase.

Cubic phases are complex three-dimensional structures, with single distinct internal and external phases. The tortuous paths inside the cubic phase have recently been investigated for applications in a number of disciplines.

Vesicles, sometimes referred to as liposomes, are spherical bilayer structures. The most common forms are large unilamellar vesicles (LUV) and small unilamellar vesicles (SUV). Vesicles have been explored for controlled release and drug targeting in the pharmaceutical industry.

Israelachvili (1992) has developed a predictive model that relates relative sizes of the lipophilic and hydrophilic groups to the type of mesophase formed when the molecule is dispersed. A critical packing coefficient is calculated by determining the hydrodynamic volume (includes bound water molecules) of the head group and the volume occupied by the lipophilic tail. Figure 1.2 and Table 1.4 shows these relationships. The major limitation of this approach may be the heterogeneous composition of commercial food emulsifiers. This will be discussed further in Chap. 2.

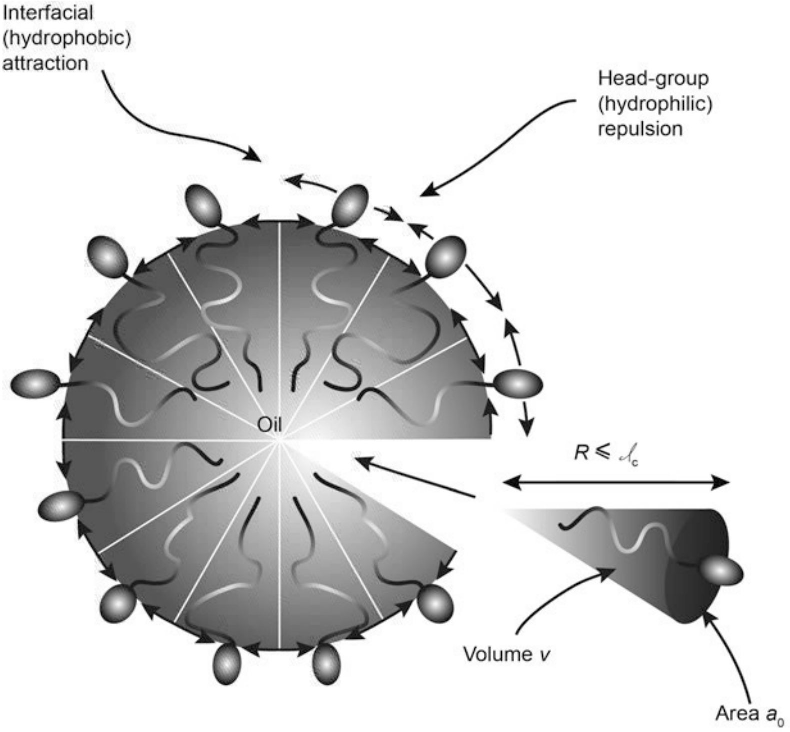

Fig. 1.2 Determination of the critical packing parameter (Israelachvili 1992, p. 368). Reproduced with the kind permission of Elsevier Ltd

Table 1.4 Critical packing parameters predict mesophase structures

Molecular structure	Packing parameter	Shape	Mesophase
Small single-tail lipid Large polar head group	<1/3	Cone	Micelle
Single-tai 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 Functionality of Food Emulsifiers

In addition to their primary functions of forming and stabilizing emulsions, dispersions, and foams, food emulsifiers can provide other functionalities. For example, sodium stearoyl lactylate can form a complex with starch, preventing retrogradation (staling) in bread. Soy lecithin is added to chocolate to reduce its viscosity. Separation of peanut oil from peanut butter may be avoided by addition of a small amount of monoglycerides. The emulsifier forms a network of fine crystals, which immobilize the oil. Table 1.5 describes some specialized functions.

It has been common practice to use blends of emulsifiers to achieve optimum organoleptic properties and stability. Some emulsifiers exhibit synergistic activity, that is, they work better together. One example is the combination of Sorbitan monostearate and Polysorbate 60. In some cases, products require multiple functionalities to be acceptable to consumers. For example, cakes must aerate to produce stable foam, to maintain moisture for good mouth feel, and have a fine even grain for appearance. In the current health-conscious environment, the utility of emulsifier combinations must be balanced against pursuit of a “clean label.” Formulators are attempting to replace the most chemical-sounding names with natural food ingredients, wherever possible.

When developing a new product, information sources can save time. For existing products, literature from emulsifier suppliers can be a good starting point. However, as food emulsifiers have become commodities, suppliers have lower R&D budgets and need to rationalize their customer assistance. Small companies may have difficulty getting research assistance. For new-to-the-world products, the product developer and marketer need to define the critical properties that make the product acceptable to consumers. If emulsifiers may provide a benefit, food

Table 1.5 Functionalities of emulsifiers in some foods

Functionality	Surfactant	Food example
Foam aeration/ stabilization	Propylene glycol esters	Cake, whipped toppings
Dispersion stabilization	Mono/diglycerides	Peanut butter
Dough strengthening	DATEM	Bread, rolls
Starch complexation (anti-staling)	SSL,CSL	Bread, other baked goods
Clouding (weighting)	Polyglycerol esters, SAIB	Citrus beverage
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

regulations should be examined to see which additives would be permitted. A few rough experiments will determine which emulsifiers work.

Statistical experimental designs are very useful when optimizing ingredient composition. A full factorial design should be carried out first. This design can identify two- and three-factor interactions, which are not uncommon in multiphase products. Once the interactions are identified, smaller fractional factorial designs and response surface methodology (RSM) will be useful to optimize the composition. For products that are prepared by the consumer, robust design can result in products that are less sensitive to small measurement errors.

Although food emulsifiers have become commodities, modern technical tools will continue to generate a deeper understanding of how the additives act to perform their function in complex food systems. The objective of this book is to prepare food professionals and other interested parties to understand how food emulsifiers are made, characterized, and formulated into finished foods and beverages.

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Chapter 2
Synthesis and Commercial Preparation of Food Emulsifiers

Gerard L. Hasenhuettl

2.1 Functional Group Design Principles

Emulsifiers (also called surfactants) are amphiphilic molecules, which contain one or more nonpolar (lipophilic), and one or more polar (hydrophilic) functional groups. For food surfactants, lipophilic groups are straight-chain saturated and unsaturated fatty acids, derived from edible fats and oils. Surfactants for non-food applications are often derived from petroleum, and contain branched and cyclic carbon chains.

Hydrophilic polar groups contain electronegative atoms, such as oxygen, nitrogen, and phosphorous. The nature and number of these polar groups determine whether a surfactant is anionic, cationic, amphoteric, or nonionic, as shown in Fig. 2.1. In anionic surfactants, the negatively charged atom is covalently bonded to the large surfactant molecule, and electrostatically associated with a positive counterion. In cationic surfactants, a positively charged functional group is covalently bonded to the large surfactant molecule, and electrostatically bonded to the negative anion. Amphoteric surfactants have both positive and negative functional groups covalently bound to the lipophilic group. Characteristics of charged surfactants are influenced by the pH of the food system. Nonionic surfactants carry no net charge, but have a dipolar carbon-oxygen bond.

Some food products contain naturally occurring surfactants for example, casein protein, and egg components. Lecithin and lipoproteins are excellent emulsifiers. Leucine, isoleucine, and phenylalanine are non-polar amino acids. Arginine, lysine, and tryptophan are amino acids that contain nitrogen atoms that can impart cationic character to a protein at low pH. Aspartic and glutamic acids

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G. L. Hasenhuettl (✉)
Cheetahtech International, LLC, Port Saint Lucie, FL, USA

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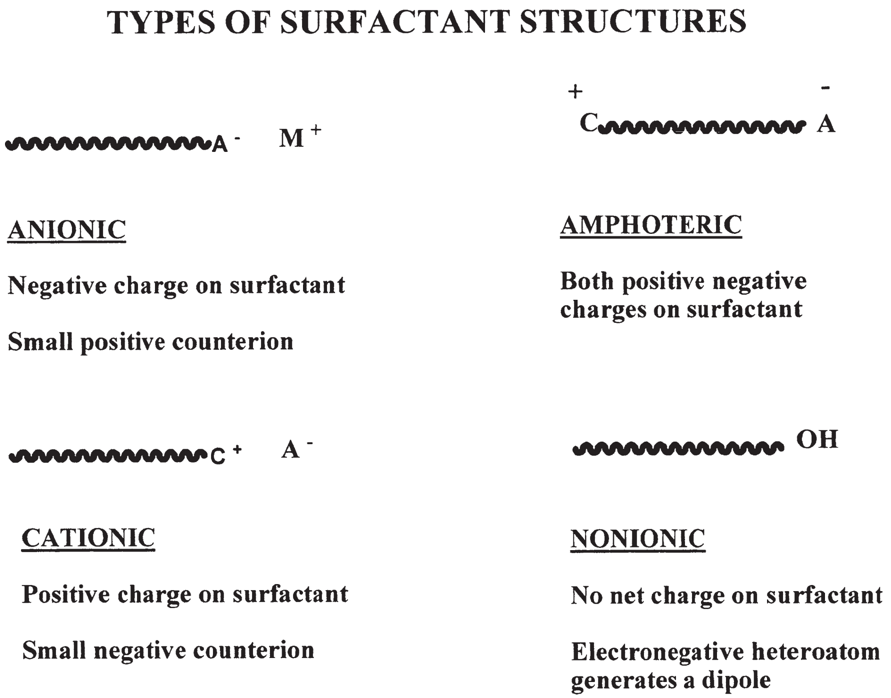


Fig. 2.1 Structures of ionic surfactants

contain carboxyl groups, which contribute anionic character. The nature, number, and location of these charged amino acids determine the isoelectric point of the protein. (The pH at which the protein has a zero net charge) makes the overall molecule amphoteric. Above the isoelectric point, the net charge is negative (anionic). At pH levels below the isoelectric point, the net charge is positive (cationic).

The use of charged surfactants is complicated by their interaction with other charged species, such as calcium and some gums. Proteins may be denatured by high temperatures and shear forces. Egg and soy phospholipids have found many applications in food products. Structurally, these molecules consist of two fatty acids esterified at the 1 and 2 positions, and a phosphates group esterified at the 3-position of the glycerol molecule. Phosphatidyl choline (PC), Phosphatidyl ethanolamine (PE), Phosphatidyl inositol (PI), and Phosphatidyl serine (PS) are the predominant polar functional groups.

Egg and soy lecithin have significantly different structures. They have different PC, PE, PI, and PS distributions. Fatty acids in egg are predominately saturated, while those in soy are mostly unsaturated. This is not surprising, since egg phospholipids are from an animal source, while those from soy are from a vegetable source.

2.2 Chemical Preparation and Modification

A number of synthetic emulsifiers have been used without documented harmful effects. Their chemistry has been developed over a 150 year period (Polouae and Gelis 1844). Early efforts used chemical reactions with fats and oils to produce emulsifiers that were naturally occurring (e.g. mono/diglycerides). Researchers then began to assemble surfactants using building blocks that were used in foods (e.g. acetylated and lactylated monoglycerides). The effort to enlarge the polar head group was accomplished by attaching polyethers to fatty acids (e.g. polyglycerol esters). The fatty acid is cleaved and absorbed in the digestive system, while the polyether passes through the body unchanged.

The lipophilic component of a food surfactant is a fatty acid, obtained from an edible fat or oil. Saturated fatty acids have straight aliphatic chains of 16–22 carbon atoms and no double bonds. Chains of less than 14 carbon atoms, although they are excellent surfactants, contain small quantities of free fatty acids. They impart soapy or goaty off-flavors to finished food products.

Unsaturated fatty acids contain 18–22 carbon atoms and one or two double bonds. More double bonds make the molecule much more susceptible to oxidation. Beany, grassy, and fishy off-flavors are generated by oxidative rancidity. Selective hydrogenation of oils can produce starting fatty acids that are monounsaturated, but also produce trans fatty acids. The trans isomers are undesirable because of their adverse effects on HDL and LDL cholesterol; this can be avoided by using oil that is naturally high in oleic acid, making hydrogenation unnecessary.

2.2.1 Mono/Diacylglycerols

Mono/diacylglycerols, commonly known as mono/diglycerides are the most widely used synthetic surfactants in the food industry. They occur naturally at low levels in fats and oils, due to hydrolysis, an equal concentration of fatty acids are released. Monoglycerides have two free hydroxyl groups, and are more surface-active than diglycerides. There are several chemical reactions that can be used to produce mono/diglycerides in the laboratory. Some involve toxic chemicals, such as acid chlorides and pyridine, that are incompatible with food.

The two most commonly used commercial routes are: (1) Direct esterification of glycerol with a fatty acid and (2) Glycerolysis of a fat or oils shown in Fig. 2.2. Both processes yield a distribution of mono-, di-, and triacylglycerols, free fatty acids, and glycerol. The glycerolysis is more economical, because fats are cheaper than fatty acids, and less glycerol is required. Fats and fatty acids are insoluble in glycerol, and in the absence of solvent, higher temperatures are required to achieve homogeneity.

Direct esterification may be catalyzed either by acids or bases. The ratio of glycerol to fatty acid determines the distribution of mono-, di-, and triacylglycerol's.

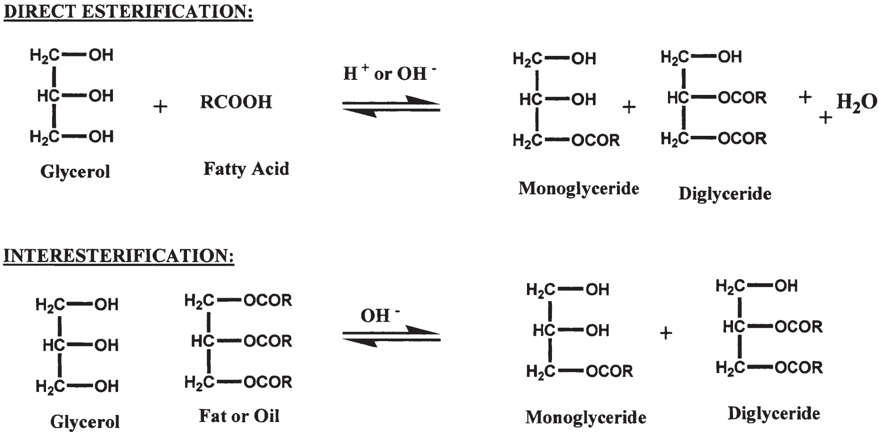


Fig. 2.2 Direct esterification and interesterification

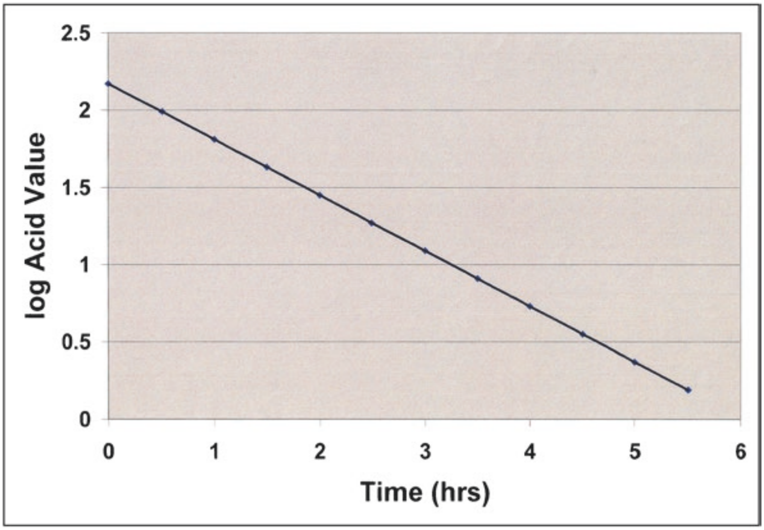


Fig. 2.3 Kinetic plot for direct esterification

Higher glycerol concentrations favor higher levels of monoacylglycerols and free glycerol in the final product. The equilibrium is shifted by continuously removing the water by distillation. Progress of the reaction may be followed by measurement of the acid value (see Chap. 3), or some instrumental method. Figure 2.3 shows the decrease of the log of the acid value versus time. When the reaction is complete, the catalyst is neutralized to stop equilibration. Excess glycerol is then removed by distillation at reduced pressure.

Glycerolysis, also known as interesterification, is accomplished by mixing fat, glycerol, and alkaline catalyst and heating to reaction mixture to high temperatures. Higher glycerol concentrations produce higher yields of monocylglycerols, but also require higher reaction temperatures. The reaction is complete when the reaction is transparent to light. A process has been described in which partial glycerol esters are added to promote homogeneity (Sigfried and Weidner 2005). As with direct esterification, the catalyst is neutralized and excess glycerol is removed. The neutralization step is more critical in a batch process. In a continuous process, glycerol can be flashed off before the mixture can re-equilibrate.

Since these processes are carried out at high temperature, side reactions can occur, which produce dark colors and off-flavors. This can be problematic in many food products. Use of an inert atmosphere, such as nitrogen, can minimize oxidative side reactions. Calcium hydroxide, used as a catalyst at a level of 0.01–0.035%, can produce products with good color and flavor. However, calcium phosphate forms a fine precipitate, which may be difficult to remove with older filters. Low-iron sodium hydroxide (e.g. rayon grade) can also yield products with good quality.

Wee and co-workers (2013) reported a direct esterification method which used hierarchical metal-organic frameworks (MOFS) as heterogeneous catalysts. The process yields monoacylglycerols as the exclusive product. This impressive selectivity is probably due to the small pore of the catalyst. Another advantage to a heterogeneous catalyst is that it can be removed by filtration and re-used. One issue with the cited example is the leaching of small amounts of zinc into the product.

Research using enzymatic reactions to produce emulsifiers, shows that these processes operate at lower temperatures, and can reduce side reactions. Enzymatic reactions will be discussed later in this chapter.

Mono/diglycerides may be produced at concentrations up to 60% by varying the fat/glycerol ratio. The monoglyceride levels can be increased to 90+% by short-path distillation. Mono/diglycerides may be liquid, solid, or semi-solid (also referred to as "plastic"). Liquids may be delivered in pails, drums, tank trucks, or rail cars. Solids may be flaked or beaded. Plastic emulsifiers may be packed into plastic-lined cartons.

2.2.2 Propylene Glycol Esters

Propylene glycol and glycerol have closely related chemical structures. Propylene glycol has one less hydroxyl group, which makes it less polar, lower boiling, and more oil soluble. These differences mean that a lower reaction temperature is required for esterification and transesterification. Figure 2.4 shows direct esterification and interesterification. The processes are similar to those for glycerol, but the distributions are different for the two processes. In addition to propylene glycol mono- and diesters, interesterification also produces mono-, di-, triglycerides, and free glycerol. Some differences in functionality may exist between the two products. Like monoglycerides, the interesterification route is more economical.

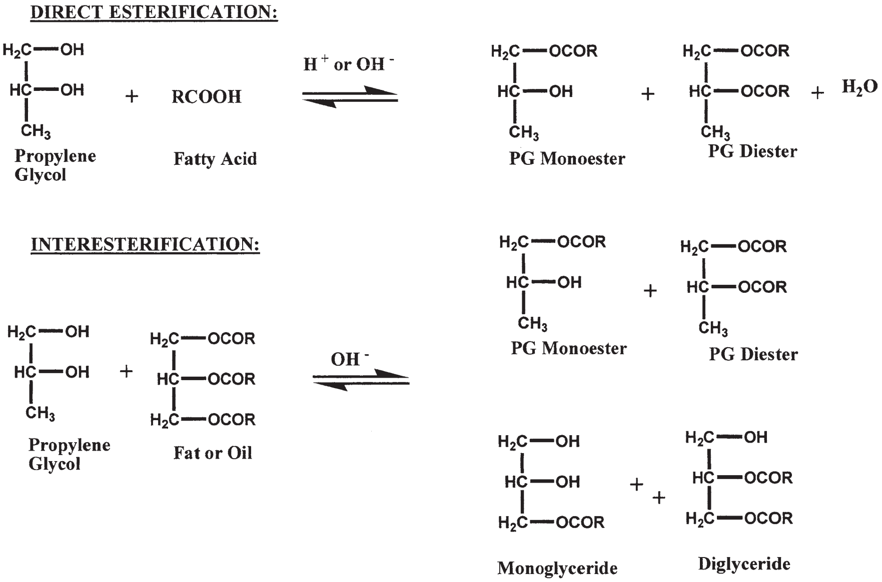


Fig. 2.4 Direct esterification and interesterification to produce propylene glycol esters

Direct esterification of propylene glycol with fatty acids can be catalyzed by acids or bases. As with esterification of glycerol, progress of the reaction is monitored by the decrease in acid value, or an appropriate physical method. After completion, the catalyst is neutralized, and the excess propylene glycol is removed by distillation at reduced pressure. Although fatty acids are expensive, this process may be used where flavor, color, or specific functionality are critical in a finished food product. Propylene glycol monoesters may be separated from diesters by distillation at reduced pressure.

As with glycerolysis, fat, propylene glycol, and an alkaline catalyst are heated in an inert atmosphere. In this process, it is critical to ensure the absence of water, since it retards the reaction. As with monoglycerides, homogeneity (transparency) indicates that the reaction is complete. The concentration of propylene glycol monoesters may be controlled by the ratio of fat to propylene glycol, and measured by gas-liquid chromatography (see Chap. 3).

2.2.3 Polyglycerol Esters of Fatty Acids

Oligomerization of glycerol, followed by esterification with fatty acid, allows the designer to enlarge the size of the polar head group. The hydrophile-lipophile balance (HLB) and mean molecular weight are determined by the degree of polymerization, and the degree of esterification with fatty acid. These factors, along with the

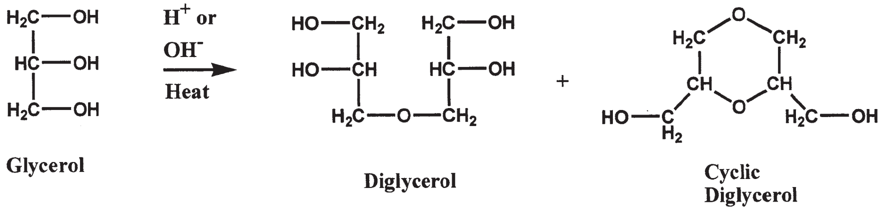


Fig. 2.5 Polymerization of glycerol

nature of the fatty acid, determine whether the product is liquid solid, or semi-solid.

In the first step of this synthesis, shown in Fig. 2.5, glycerol is heated to a high temperature in the presence of an acid or base catalyst under an inert atmosphere. Free hydroxyl groups condense to split out water and form ether linkages. Condensation may be intermolecular to produce linear oligomers, or intramolecular to produce cyclic species. Lower pH and lower temperatures favor the formation of cyclic isomers. When sodium hydroxide is used as the catalyst, the pH declines, as the reaction progresses. Side reactions occur at high temperatures to produce dark colors, off-flavors, and objectionable odors. Processes have been developed using mesoporous (Charles et al. 2003) and zeolite (Esbuis et al. 1984) catalysts under milder conditions. Progress of the reaction may be monitored by refractive index, infrared spectroscopy, or hydroxyl value (see Chap. 3) The viscosity of the polyglycerol increases as the degree of polymerization increases. The degree of polymerization for polyglycerol in the food industry, range from 2 to 12 glycerol units. Polyol distribution can be measured by converting the free hydroxyl groups to trimethylsilyl ethers, followed by gas-liquid chromatography (Sahasrabuddhe and Chadha 1969; Schuetze 1977). Polyglycerol may be used as produced, or stripped of excess glycerol by distillation at reduced pressure (Aoi 1995).

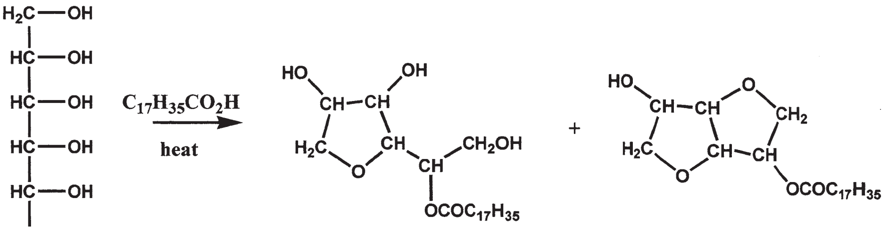
Direct esterification with fatty acids or interesterification with fats or oils can be used to produce polyglycerol esters. For polyglycerols with higher degrees of polymerization, fatty acids are used, to avoid introducing glycerol into the product. Interesterification may be used for polyglycerols, which have been stripped of free glycerol and cyclic diglycerol. The HLB of the surfactant is controlled by the molar ratio of fat (or fatty acid) to polyglycerol. High reaction temperatures cause undesirable side reactions. A lower temperature process, which uses a solid catalyst, has been described (Marquez-Alvarez et al. 2004).

A unique surfactant is produced by the reaction of polyglycerol with bifunctional ricinoleic acid, the predominant fatty acid in castor oil. The carboxyl group of ricinoleic acid may react with a hydroxyl group on the polyglycerol, or with a hydroxyl group of another molecule of ricinoleic acid. The composition of the reaction mixture can be controlled by the order of addition (Aoi 1995).

2.2.4 Sorbitan Monostearate and Tristearate

Despite its simple name, sorbitan monostearate is a complex mixture of molecules. Commercial stearic acid may have a range of 45–90% C18:0, depending on its source. Esterification and dehydration/cyclization reactions occur simultaneously. Cyclization produces a mixture of sorbitol, sorbitan, and isosorbide. Esterification yields a distribution of mono- through hexastearate. Sorbitan monostearate and tristearate are averages of their respective distributions. This is controlled by the fatty acid/sorbitol ratio.

A reaction mixture of stearic acid, sorbitol, and an alkaline catalyst in an inert atmosphere, Fig. 2.6 shows the simultaneous cyclization and esterification reactions. Water is continuously removed by distillation. Sodium hydroxide (Griffin 1945) and zinc stearate (Szabo et al. 1977) have been used as catalysts. Because of the high temperatures required to achieve homogeneity, caramelization side reactions occur, which produce dark colored materials. These side reactions may be reduced by inclusion of a reducing agent, such as sodium hypophosphate (Furuya et al. 1992). An alternative approach uses an acid catalyst to carry out the cyclization reaction at a lower temperature (Stockburger 1981). The polyol mixture is purified and reacted with stearic acid to produce the emulsifier. As with monoacylglycerols, progress of the reaction may be monitored by measurement of the acid value. Infrared spectroscopy can be used to measure disappearance of the free hydroxyl group. Although these methods are fairly rapid, they do not provide any information about the molecular distribution. Gas-liquid chromatography has been shown to provide this information (Sahasrabuddhe and Chadha 1969; Franzke and Knoll 1980).The reaction mixture may also be measured by HPLC (Garti and Asarin 1983). Unfortunately, these instrumental methods are time consuming. The final product must meet tight FDA specifications for saponification and hydroxyl values (see Chap. 3). Sorbitan monostearate and monooleate are used as intermediates in the production of polysorbates, discussed later in this chapter.



Sorbitol **Sorbitan Ester** **Isosorbide Ester**

Fig. 2.6 Preparation of sorbitol and isosorbide esters

2.2.5 Sucrose Esters

Sucrose polyesters have been widely investigated as zero-calorie replacements for fats in food (Akoh and Swanson 1994; Swanson and Swanson 1999). These ingredients are fully esterified sucrose fatty acid esters, and have properties similar to fats and oils. Partially esterified sucrose esters are versatile food emulsifiers. A typical reaction scheme is shown in Fig. 2.7. The distribution of mono-, di-, and triesters, and therefore the HLB, are controlled by the fatty acid methyl ester (FAME)/sucrose ratio in the reaction mixture. The saturation and chain length of the fatty acids also influence physical and functional properties.

Like other polyols, sucrose has low solubility in fats and fatty acids. However, since sucrose undergoes caramelization above 140 °C., high temperatures cannot be used to force homogeneity. One strategy is to carry out a base-catalyzed interesterification in a polar organic solvent, such as dimethylformamide (Wagner et al. 1990) or dimethylsulfoxide (Kasori and Taktabagai 1997). The disadvantage of a solvent based method is the difficulty of complete removal of the toxic low volatility solvent.

Another approach is the use of high levels of soap, or other surfactants, to promote miscibility of the phases (Murakama et al. 1989). Fittermann et al. (2012) has suggested that co-melting of sucrose with a soap of a multivalent cation produces a homogeneous reaction mixture (Zhao et al. 2014). The excess soap may be removed by neutralization to the fatty acid, followed by short path distillation. Alternatively, a volatile solvent, such as ethyl acetate blended with water, can separate the mixture by extraction. Sucrose octaacetate, an oil soluble material, may be reacted with methyl esters in a homogeneous reaction mixture (Elsner et al. 1989). A continuous process, in which a heated reaction mixture is passed through an immobilized catalyst, has been described (Wilson 1999). A mixture of sucrose ester and mono/diglycerides can be produced by interesterification of fats and sucrose (Nakamura et al. 1986).

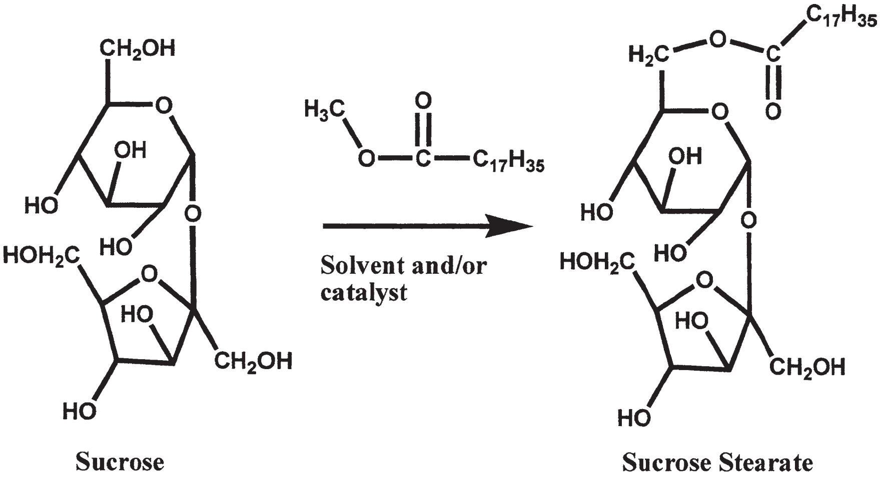


Fig. 2.7 Preparation of sucrose ester surfactants

Reaction of two moles of acetic acid and six moles of isobutyric acid with one mole of sucrose produce an emulsifier with high specific gravity. The resulting additive, sucrose acetate isobutyrate (SAIB), is used as a weighting agent to disperse oils in beverages (Reynold and Chappel 1998).

Composition of reaction products may be obtained by thin layer chromatography (TLC) (Li et al. 2003), or by reverse phase high-performance liquid chromatography (RPHPLC) (Murakama et al. 1989; Okumura et al. 2001). Degree of esterification can also be determined by electrospray mass spectrometry (Schuyl and Platerink 1994).

2.2.6 Sodium and Calcium Stearoyl Lactylate

A surfactant with a carboxylic acid group may be nonionic, or reacted with sodium or calcium hydroxide to form an anionic molecule. Lactic acid is a bifunctional molecule that can self-condense to form an oligomer, or react with stearic acid to give stearoyl lactylic acid (Eng 1972). Figure 2.8 shows the dimeric homolog, commonly known as sodium stearoyl lactylate. In a typical preparation, lactic acid is neutralized with sodium hydroxide, and the excess water is removed by distillation. Iron is highly detrimental to the quality of the product. Consequently, raw materials should contain minimal iron, and the reactor should not contribute leachable iron. Stearic acid is added and esterification is carried out at 160–180 °C. Higher temperatures lead to side reactions, which give rise to off flavors and disagreeable odors and flavors. Water is continuously removed by distillation, and acid value is monitored until the desired value is reached.

The color of the product may be improved by bleaching with 30% hydrogen peroxide, followed by heat treatment to destroy the excess peroxide (Anon. 1983). The final product is characterized by acid value, saponification number, and total lactic acid (Franzke and Knoll 1980).

2.2.7 Derivatives of Mono/Diacylglycerols (Mono/Diglycerides)

Mono and diacylglycerols have a significant mass of lipophilic functionality. The hydroxyl head group is small and nonionic. The size and charge of the head group may be modified by attaching another polar functional group. The result is an increase in the hydrophilicity of the surfactant.

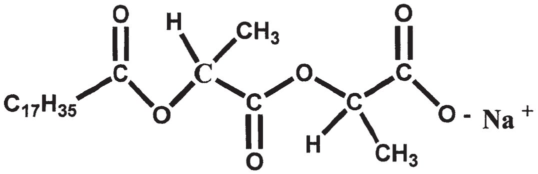


Fig. 2.8 Structure of sodium stearoyl lactylate

2.2.7.1 Acetylated Monoacylglycerols

Reaction of an acetic acid derivative results in replacement of a free hydroxyl group with an acetate group. This change produces a less hydrophilic surfactant, which structurally resembles a fat. Because of their diversity in alkyl chain length, acetylated monoacylglycerols are excellent film formers (Guillard et al. 2004).

Two methods are commonly used for the preparation of acetylated acylmonoglycerols: (1) Monoacylglycerols are reacted with acetic anhydride to produce the acetate ester and one equivalent of acetic acid. The reaction is catalyzed by a strong mineral or organic acid. If the reactor is suitably equipped, the acetic acid may be removed by distillation, and recycled to produce acetic anhydride. (2) Monoacylglycerols can be reacted with glycerol triacetate (triacetin) using an alkaline catalyst. Although acetic acid is not produced as a byproduct of the reaction, glycerol and its mono-, di-, and triacetate esters must be removed by distillation. The advantage of this process is that the reactants and products are less flammable and corrosive.

2.2.7.2 Lactylated Monoacylglycerols

As previously discussed, lactic acid is a bifunctional molecule. Reaction of its carboxyl group with a monoacylglycerol, a lactylated monoacylglycerol is formed. The hydrophilic head group is enlarged, but the nonionic character is maintained. Synthesis is accomplished by heating a monoacylglycerol with lactic acid. The temperature must be kept below 180 °C. to avoid caramelization reactions. Kinetics of the reaction are similar to the direct esterification of glycerol with fatty acids. Water is continuously removed by distillation. The degree of esterification is controlled by the ratio of monoacylglycerols to lactic acid (Shmidt et al. 1976). After the reaction is complete, lactate esters of free glycerol must be removed because they impart off-flavors to the finished food product. Steam distillation or aqueous extraction are useful techniques to accomplish the task. The product may be characterized by acid value, saponification number, water insoluble combined lactic acid (WICLA), and chromatography.

2.2.7.3 Succinylated Monoacylglycerols

Succinic anhydride is similar to acetic anhydride in its esterification of free hydroxyll groups. However, since an alkyl group tethers the two carboxyl groups, the second carboxyl group is retained in the surfactant molecule, rather than expelled as an acid by product. The polar head group is enlarged and can become anionic at the appropriate pH.

In a typical synthesis, a purified monoacylglycerol is reacted with succinic anhydride under an inert atmosphere (Freund 1968; Hadeball et al. 1986). Precautions must be taken while handling succinic anhydride, a suspect carcinogen (Sax and Lewis 1999). Although the reaction is exothermic, heat is initially added to raise the temperature to 150–165 °C. to achieve homogeneity of the mixture. Since succinic acid is bifunctional, it may bind to two monoacylglycerol molecules.