Food Emulsifiers and Their Applications

Second Edition

Gerard L. Hasenhuettl • Richard W. Hartel
Editors

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Springer

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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.

G.L. Hasenhuettl
R.W. Hartel

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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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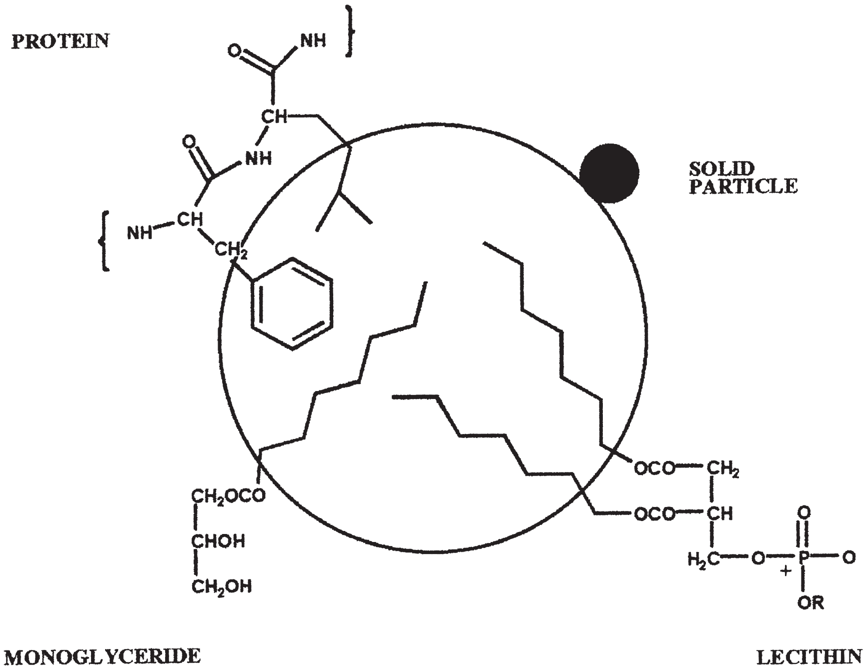

Fig. 1.1 Schematic representation of an Emulsified oil droplet

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.

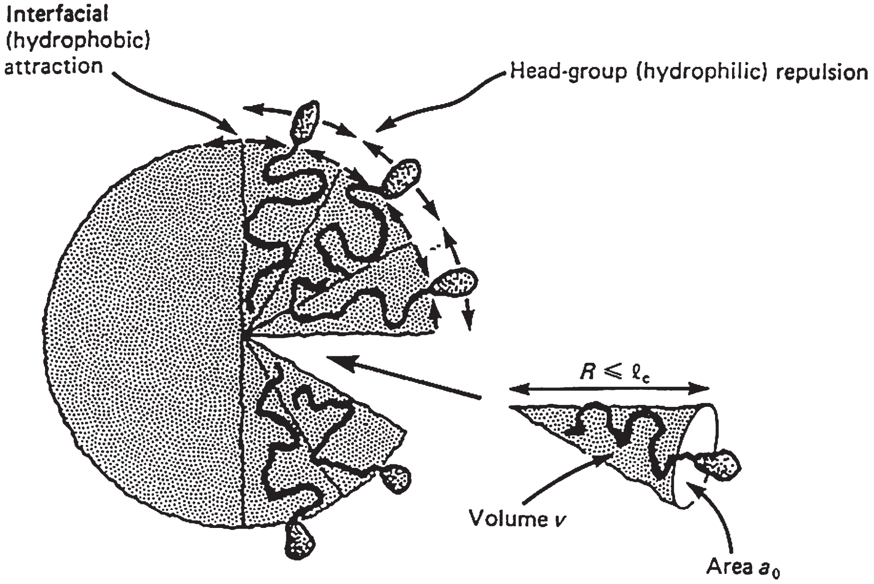

Fig. 1.2 Critical packing parameter for prediction of mesophase structure (Israelachvili, 1992, p. 368). Reproduced with permission of Elsevier Ltd

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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Chapter 2
Synthesis and Commercial Preparation of Food Emulsifiers

Gerard L. Hasenhuettl

2.1 Functional Group Design Principles

Food emulsifiers, more correctly referred to as surfactants, are molecules, which contain a nonpolar, and one or more polar regions. In general, nonpolar groups are aliphatic, alicyclic, or aromatic hydrocarbons. Polar functional groups contain heteroatoms such as oxygen, nitrogen, and sulfur. As shown in Fig. 2.1, the polar functionality makes the emulsifier anionic, cationic, amphoteric, or nonionic. Anionic surfactants contain a negative charge on the bulky molecule, associated with a small positive counterion. Cationics have a positively charged molecule with a negative counterion. Amphoteric surfactants contain both positive and negative charges on the same molecule. A nonionic surfactant contains no formal positive or negative charge, but a polar heteroatom produces a dipole with an electron dense and electron-depleted region.

Many food products use emulsifying agents present in the foods themselves. For example, casein and egg yolk proteins are excellent emulsifiers. Alanine, phenylalanine, leucine and isoleucine contain nonpolar aliphatic and aromatic side chains. Amino acids, such as arginine, lysine and tryptophane, contain amino groups, which promote cationic character to the protein. Aspartic and glutamic acids possess side chains with carboxyl groups, which contribute to anionic character. The nature, number and location of the polar amino acids determine the isoelectric point of a protein; e.g., the pH at which the protein is uncharged. In food systems where the pH is above the isoelectric point, the protein will behave as an anionic emulsifiers, while at pH values below their isoelectric point, it will become cationic. One complicating factor in using emulsifiers is that their charge makes them vulnerable to interactions with other charged species, such as calcium ions and some gums. In addition, proteins may denature under some processing conditions, such as high temperature and shear forces.

Phospholipids from egg and soy have found many applications in food products. Structurally, these molecules contain two fatty acids esterified to glycerol and a phosphatidyl group esterified to a terminal –OH group on the glycerol. Phosphatidylcholine (PC), phosphatidylethanolamine (PE), Phosphatidylinositol (PI), and phosphatidylserine (PS) are the predominant polar functional groups.

G.L. Hasenhuettl and R.W. Hartel (eds.), *Food Emulsifiers and Their Applications*.

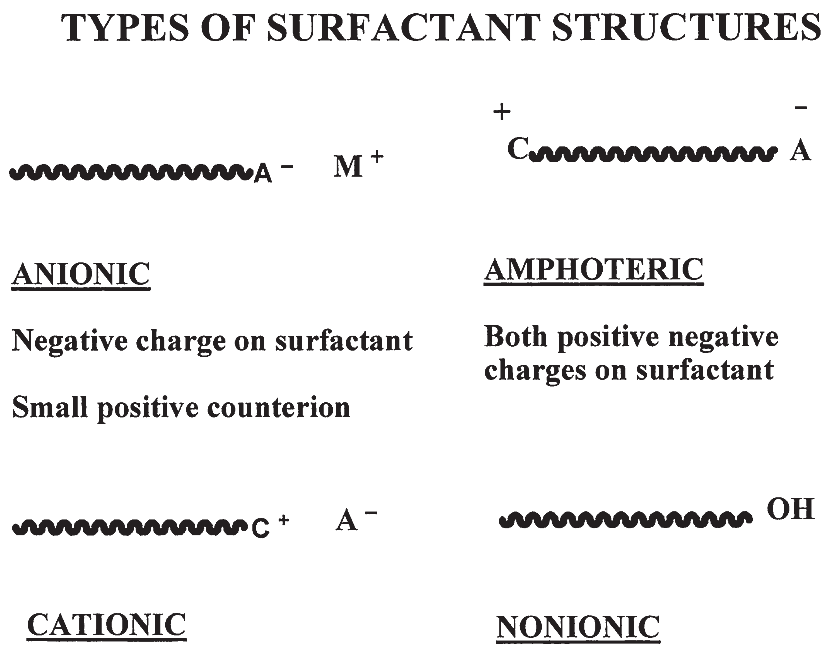

Fig. 2.1 Structures of anionic, cationic, amphoteric, and nonionic surfactants

Egg and soy lecithins differ significantly in their molecular structures. There are significant differences in PC, PE, PI, and PS distributions. Fatty acid chains in soy lecithin are predominately unsaturated. In contrast, alkyl chains are more saturated.

Egg and soy lecithins may be purified and/or modified to improve their properties. Egg lecithin has been studied in the pharmaceutical industry, but purification is much too costly for the food industry. Soy lecithin may be separated from residual triacylglycerols by precipitation. This process yields an emulsifier with a higher HLB value. HLB may also be realized by treatment with Phospholipase A_2 to remove one of the fatty acids. Currently, this process is expensive and the product has not received regulatory approval for use in foods. Reaction with peroxides has also been used to increase the polar character of lecithin.

Many synthetic emulsifiers have been used in the food industry without evidence of harmful effects. Their chemistry is derived from over 150 years of chemical manipulation of fats and oils (Polouze and Gelis, 1844). They have been designed to contain naturally occurring molecules or in the case of non-naturally occurring molecules, to pass through the body without being metabolized. For example, cleavage of polyglycerol esters results in a fatty acid, which is metabolized, and a polyglycerol backbone, which passes through the digestive system without being absorbed.

As shown in Fig. 2.2, lipophilic functional groups are derived from naturally occurring fatty acids approved for food use by the FDA. Saturated fatty acids contain 16–22 carbon atoms. Fatty acids shorter than 14 carbons, although they are excellent emulsifiers, result in soapy or other off-flavors in the finished food

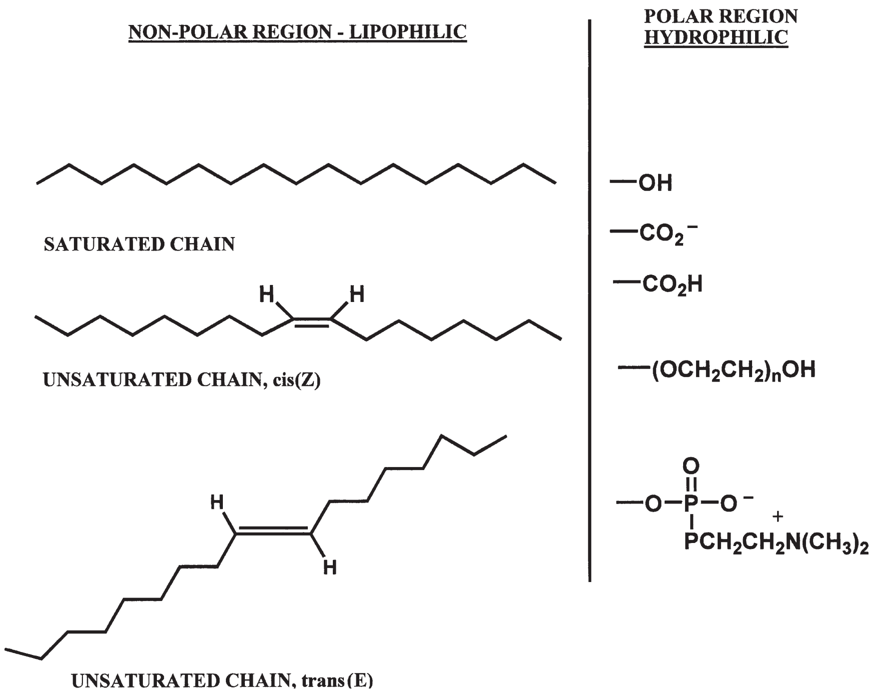

Fig. 2.2 Polar and nonpolar functional groups

product. Unsaturated fatty acids, used as starting materials for food emulsifiers, containing a single double bond. Multiple double bonds would produce an oxidized rancid off-flavor. Trans (E) double bonds result from nickel-catalyzed hydrogenation of unsaturated oils. Based on the model (Israelachvili, 1992), discussed in Chap. 1, cis (Z) double bond chains would be predicted to pack differently than trans (E) chains. Therefore, there may be a difference in emulsifier functionality, depending on whether the starting fat or fatty acid was obtained through hydrogenation or blending.

Polar head groups in food emulsifiers contain oxygen, nitrogen and phosphorus as electronegative heteroatoms. The hydroxyl group is predominant in many nonionic emulsifiers, such as mono- and diacylglycerols, propylene glycol, sorbitan, sucrose and polyglycerol esters of fatty acids. Monoacylglycerols may be esterified with acetic or lactic acid to yield anionic emulsifiers with modified functionalities. Polycarboxylic acids may be reacted with monoacylglycerols to give potential anionic surfactants. Examples are succinate, citrate and diacetyltartarate esters of monoacylglycerols. Fatty acids may be reacted with lactic acid and alkali to produce sodium or calcium stearoyl lactylate. Polyoxyethylene chains may be introduced into sorbitan esters or monoacylglycerols to increase the hydrophilic character of the molecule.

Although many new organic reactions have been developed in other fields, the regulatory difficulties faced by new surface-active molecules are enormous. Current research has focused on enzyme catalyzed reactions and biological modification of starting materials.

2.2 Mono- and Diacylglycerols (Mono- and Diglycerides)

Mono- and diacylglycerols are the most widely used synthetic emulsifiers in the food industry. They are present in small quantities in natural fats and oils as a result of hydrolysis, which also releases fatty acids. Monoacylglycerols, which contain two free hydroxyl groups, exhibit stronger surface activity than diacylglycerols.

In the laboratory, monoacylglycerols may be prepared by reaction of a fatty acyl chloride with glycerol in the presence of pyridine, which acts both as a solvent and an organic base. However, the corrosivity of acyl chlorides and the toxicity of pyridine are problematic for commercial application of this approach. For example, the isopropylidene (acetonide) protective group can block the 1 and 2 positions of glycerol while esterification can be performed on the 3-position (Heidt et al., 1996). Glycidol, an epoxide derivative of glycerol, may also be used as a starting material to produce pure monoacylglycerols (Tamura and Suginuma, 1991). Diacylglycerols may be used as intermediates in the synthesis of regioselective and chiral triacylglycerols and Phospholipids (Dong et al., 1982).

The two most prevalent commercial preparations of mono- and diacylglycerols are (1) Direct esterification of glycerol with a fatty acid, and (2) Glycerolysis of natural or hydrogenated fats and or oils. As shown in Fig. 2.3, both processes yield approximately the same equilibrium distribution of mono- di- and triacylglycerols. The glycerolysis procedure 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; elevated temperatures are required to force the reaction to proceed.

Direct esterification may be catalyzed either by acids or bases. The ratio of glycerol to fatty acid determines the concentrations of mono-, di- and triacylglycerols in the final product. Higher levels of glycerol produce higher concentrations of monoacylglycerols. In a typical batch procedure, fatty acid, glycerol and catalyst

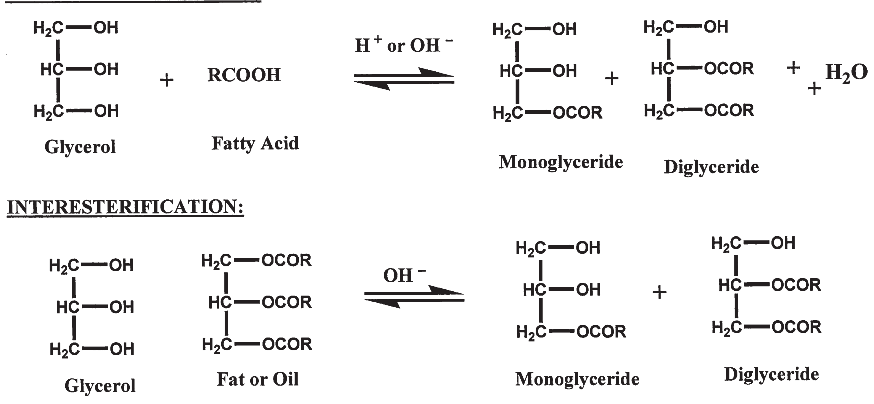

Fig. 2.3 Monoacylglycerol synthesis through direct esterification and interesterification

are stirred at 210–230 °C. Water is continuously removed by distillation, causing the equilibrium to shift toward products. Progress of the reaction is monitored by periodic measurement of the acid value (see Chap. 3). Figure 2.4 shows the linear decrease in the log of the acid value vs. time. Early values on this plot may be extrapolated to predict the reaction end point. When the reaction is complete, the catalyst is neutralized to stop equilibration, and excess glycerol is removed by distillation at reduced pressure. Neutralization is more critical when batch distillation is used than for rapid short path/ short time processes.

For interesterification (glycerolysis), fat, glycerol and alkaline catalyst, such as calcium hydroxides are stirred at high temperature. Higher glycerol/fat ratios require higher reaction temperatures to force the reaction to completion. Recently, a process has been described in which the partial glycerol esters are introduced into the initial reaction mixture to promote homogeneity and increase the rate of the reaction (Sigfried and Eckhard, 2005). The end point of the reaction is determined visually. A sample taken from the reactor is clear. As with direct esterification, the catalyst is neutralized and excess glycerol is removed.

Since these reactions are carried out at high temperatures, side reactions can produce dark colors and off flavors, which can be a problem in a finished food product. Use of an inert atmosphere, such as nitrogen, in the reaction vessel reduces oxidative side reactions. Calcium hydroxide at 0.01–0.035% yields a product with good color. One problem arises when the catalyst is neutralized with phosphoric acid. The calcium phosphate is a fine precipitate that may be difficult to remove with some older filters. Use of a low-iron sodium hydroxide, e.g., rayon grade, may produce products with lighter colors than conventional food grade material.

Some recent investigations have described enzyme-catalyzed esterification as an attractive method for synthesis of monoacylglycerols (Waldinger and Schneider,

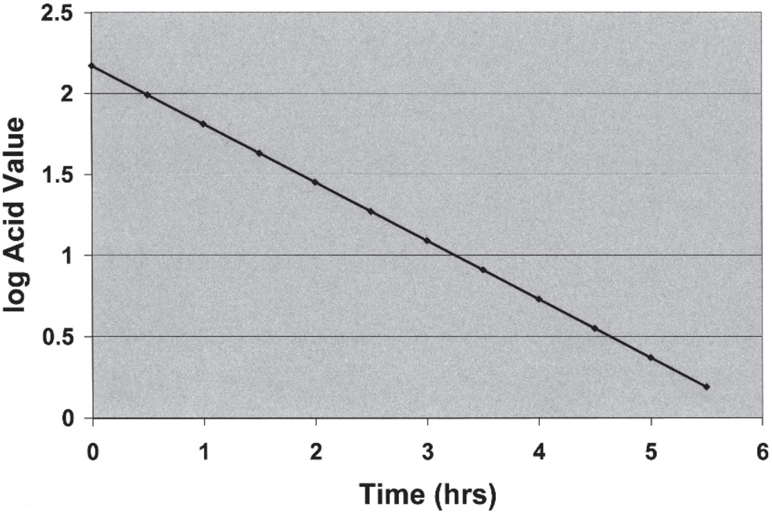

Fig. 2.4 Measurement of direct esterification using acid value

1996; Hari-Krishna and Karanth, 2002; Montiero et al., 2003). Lipase is an enzyme, which breaks down fats into sn-2 monoacylglycerols and fatty acids. Used in reverse, it can catalyze the esterification of glycerol with fatty acids. The ambient to moderate temperatures used in this process minimize the potential side reactions and may allow the preparation of sn-1 monoacylglycerols. Potential problems with the process are high cost and denaturation of the enzyme as well as slow reaction times.

Products having α-monoglyceride concentrations (see Chap. 3) of 10–55% may be produced by esterification and interesterification by adjusting the glycerol/fatty acid ratio. Monoacylglycerols may be further purified by short path distillation. Monoglyceride levels >90% may be produced. Monoacylglycerols may be liquid, solid, or semi-solid (also referred to as "plastic"). Solids may be flaked or spray-chilled into beads. Liquids are shipped in bulk or in metal drums or pails. Semisolids are packed into plastic-lined drums or cartons.

2.3 Propylene Glycol Esters of Fatty Acids

Propylene glycol is similar in structure to glycerol. It is a three-carbon chain but one terminal position does not bear a hydroxyl group. This structural difference causes a shift in physical properties. The boiling point of propylene glycol is lower and its oil solubility is greater than that of glycerol. The impact of these differences is that the temperature required for reaction is lower.

Synthetic processes for producing propylene glycol esters are similar to those used for monoacylglycerols. Figure 2.5 shows direct esterification and interesterification reactions. However in contrast to monoacylglycerols, interesterification produces a more complex mixture than direct esterification. Mono- di- and triacylglycerols are also reaction products of the latter process. Differences in functionality may be expected between products derived from the two processes. As with monoacylglycerol synthesis, the interesterification route is more economical.

Direct esterification is conducted by reacting fatty acids with propylene glycol in the presence of an acid or alkaline catalyst. As with monoacylglycerol synthesis, progress of the reaction may be monitored by the decrease in acid value. After completion, the catalyst is neutralized and excess propylene glycol is separated by fractional distillation at reduced pressure. Although fatty acids are more expensive than fats, esterification does enjoy limited use in the food industry where product color or specific functionality is critical.

Heating propylene glycol, fat and an alkaline catalyst carries out interesterification. The reaction mixture must be dry because water inhibits the onset of reaction. As with monoacylglycerols, completion of the reaction is detected by observation of homogeneity. The concentration of propylene glycol monoester may be controlled by the ratio of the starting materials and measured by gas-liquid chromatography (see Chap. 3).

Since there is only one primary alcohol group in propylene glycol, as compared to two in glycerol, regioselective lipase enzyme-catalyzed esterification should produce high yields of propylene glycol monoester.

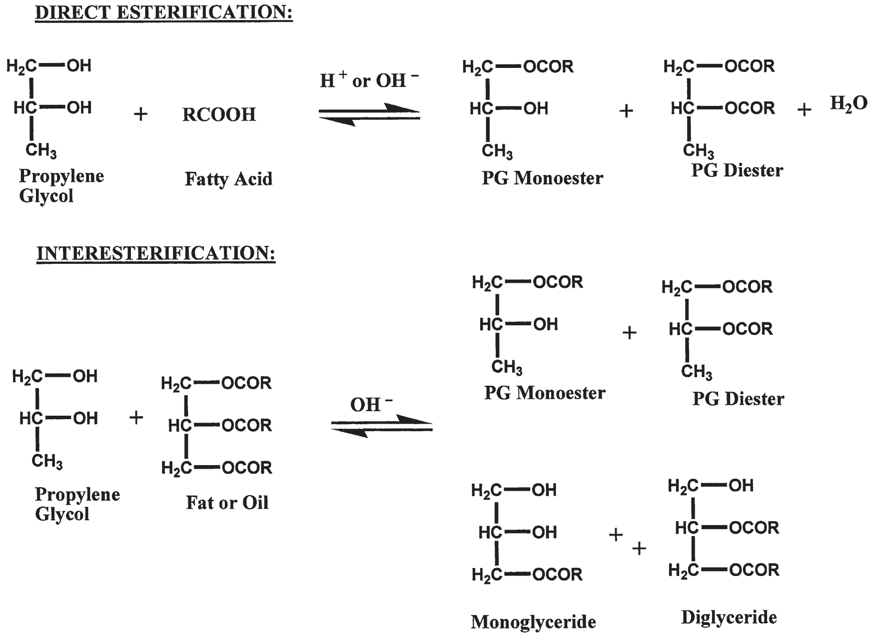

Fig. 2.5 Preparation of propylene glycol monoesters by direct esterification and interesterification

2.4 Polyglycerol Esters of Fatty Acids

Oligomerization and subsequent esterification with fatty acid allows the emulsifier designer to increase the size of the hydrophilic head group. The hydrophile–lipophile balance and mean molecular weight are controlled by the degree of glycerol polymerization and the fatty acid/polyglycerol ratio. These factors along with the nature of the fatty acid determine whether the product is solid, liquid, or semisolid.

In the first step of this synthesis, shown in Fig. 2.6, glycerol is heated to high temperatures in the presence of an acidic or alkaline catalyst under an inert atmosphere. Free hydroxyl groups condense to eliminate water and form ether linkages. Condensation may be intermolecular to produce linear oligomers, or intramolecular to give cyclic species. Lower reaction temperatures and lower pH favor cyclic isomers. When sodium hydroxide is used as the catalyst, pH declines as the reaction progresses. Side reactions occur at high temperatures to produce dark colors and off-flavors and objectionable odors. Recently, processes have been developed using mesoporous (Charles et al., 2003) and zeolite (Esbuis et al., 1994) catalysts under milder conditions. Progress of the reaction may be monitored by refractive index, near-infrared reflectance, or hydroxyl value (see Chap. 3). In addition, the reaction mixture increases in viscosity as the degree of polymerization increases. Polyglycerols for the food industry have an average degree of polymerization from diglycerol to decaglycerol. Polyol distribution may be measured by converting a sample to trimethylsilyl ethers followed by gas-liquid chromatography (Sahasrabuddhe, 1967; Schuetze,

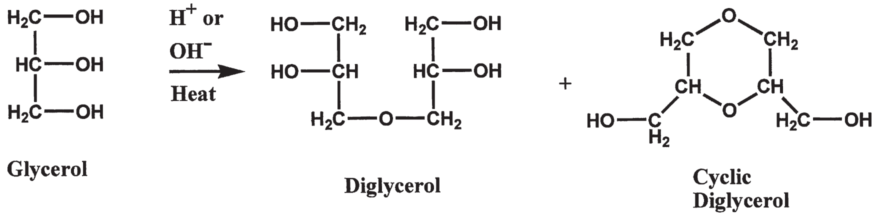

Fig. 2.6 Polymerization of glycerol

1977). Polyglycerol may be used as produced, or may be stripped of excess glycerol and cyclic diglycerol by steam distillation at reduced pressure (Aoi, 1995).

Either direct esterification with fatty acids or interesterification with fats or oils may be used to produce polyglycerol esters. For polyols with higher degrees of esterification, fatty acids are used to prevent introduction of glycerol into the distribution. Interesterification can be used for lower degrees of polymerization, which have been stripped of glycerol and cyclic diglycerol. The degree of esterification and HLB are controlled by the ratio of fatty acid to polyglycerol in the reaction mixture. Some selectivity in the esterification has been reported by control of reaction temperature (Kasori et al., 1995). High reaction temperatures are associated with undesirable side reactions. A lower temperature process using a solid catalyst has been described (Marquez-Alvarez et al., 2004). Monoesters may be prepared by using an isopropylidene protecting group (Jakobson et al., 1989) or by enzymatic transesterification with lipase (Charlemange and Legoy, 1995).

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

2.5 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% C-18:0, depending on its source. Cyclization/dehydration reactions produce a mixture of sorbitol, sorbitan, and isosorbide. The simultaneous esterification reaction yields a random distribution of monostearates through hexastearate. Sorbitan monostearate and tristearate are averages of their respective distributions.

A reaction mixture of stearic acid, sorbitol and a catalyst is heated under an inert atmosphere to cause simultaneous esterification and cyclization reactions as shown in Fig. 2.7. The ratio of stearic acid to sorbitol is chosen to produce either the mono- or the tristearate. 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 of the reaction mixture, caramelization side reactions occur which produce dark colored compounds. These side reactions may be reduced by inclusion of a reducing agent, such as sodium hypophosphite (Furuya et al., 1992). An alternative process has been described in which sorbitol is reacted with an acidic catalyst at lower temperatures to form Sorbitan and isosorbide (Stockburger, 1981). The mixture is purified and reacted with stearic acid to produce the emulsifier.

As with preparation of the monoacylglycerols, following the decrease in acid value may be used to monitor the progress of the reaction. Infrared or near infrared spectroscopy may be used to determine disappearance of the hydroxyl group. Although these tests are fairly rapid, they do not provide any information about the molecular distribution. Gas chromatography has been used to obtain such information (Sahasrabuddhe and Chadha, 1969) (Giacometi et al., 1995). The reaction mixture may also be analyzed by HPLC (Garti and Asarin, 1983) Unfortunately; these methods are more complex and time-consuming. The final product must meet tight values for hydroxyl value and saponification number (see Chap. 3). Sorbitan monostearate and monooleate are used as intermediates in the production of polysorbates, discussed in a later section.

2.6 Sucrose Esters

Fully esterified sucrose fatty acid esters have been widely investigated as synthetic fat replacements (Akoh and Swanson, 1994) and their synthesis has been reviewed (Swanson and Swanson, 1999). Partially esterified sucrose esters are versatile emulsifiers for food products. A typical reaction is displayed in Fig. 2.8. The distribution of mono- di- and triesters, and therefore the HLB, may be controlled by the ratio of fatty acid and sucrose in the reaction mixture. The degree of saturation and chain length of the fatty acid also influence the functional properties of the product.

As with other polyol starting materials, sucrose fatty acid esters are prepared by interesterification. However, sucrose undergoes caramelization reactions above 140 °C. High temperatures cannot be used to force homogeneity of the two-phase reaction

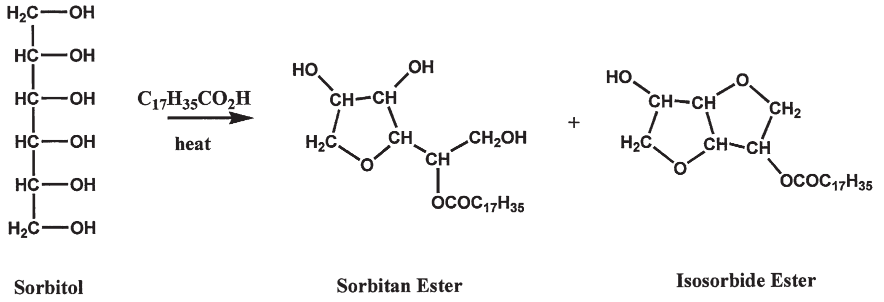

Fig. 2.7 Cyclization and esterification of sorbitol

mixture. One approach is to carry out a base-catalyzed interesterification with fatty acid methyl esters in a solvent, such as Dimethylformamide (DMF) (Wagner et al., 1990) or dimethyl sulfoxide (DMSO) (Kasori and Taktabagai, 1997). The major disadvantage of this method is the difficulty of completely removing the high-boiling, toxic solvent. A reaction has been reported in which hydrofluoric acid was used both as catalyst and solvent (Deger et al., 1988). In this case, hydrofluoric acid is extremely corrosive and hazardous to handle. Kinetics of the interesterification reaction have been described (Huang et al., 2000).

Another synthetic approach is the use of high levels of soap or other surfactants to promote miscibility of the phases (Meszaros et al., 1989). Excess soap may be removed by neutralization to the fatty acid, followed by short path distillation. Alternatively, solvent extraction, such as in an ethyl acetate/water mixture may be employed. Sucrose octaacetate, an oil soluble derivative of sucrose may be used as a starting material to promote a homogeneous reaction (Elsner et al., 1989). Reaction of sucrose with methyl esters can be performed with a high-shear, mixer to improve contact between the insoluble phases (Van Nispen and Olivier, 1989). A continuous process, where the reaction mixture is passed through an immobilized solid catalyst, has been described (Wilson, 1999). A two-component emulsifier system of sucrose esters and monoacylglycerols may be obtained by interesterification of sucrose and triacylglycerols (Nakamura et al., 1986). Enzyme catalyzed interesterification may be used to produce regioselective isomers of sucrose esters (Li et al., 2003).

Reaction of 2 moles of acetic acid and 6 moles of isobutyric acid with one mole of sucrose produces an oil analog with short alkyl chains and consequently higher specific gravity. The resulting food additive, sucrose acetate isobutyrate (SAIB) is used as a weighting agent in beverages (Reynolds and Chappel, 1998). Emulsions are stabilized by reduction of the water/oil density differential.

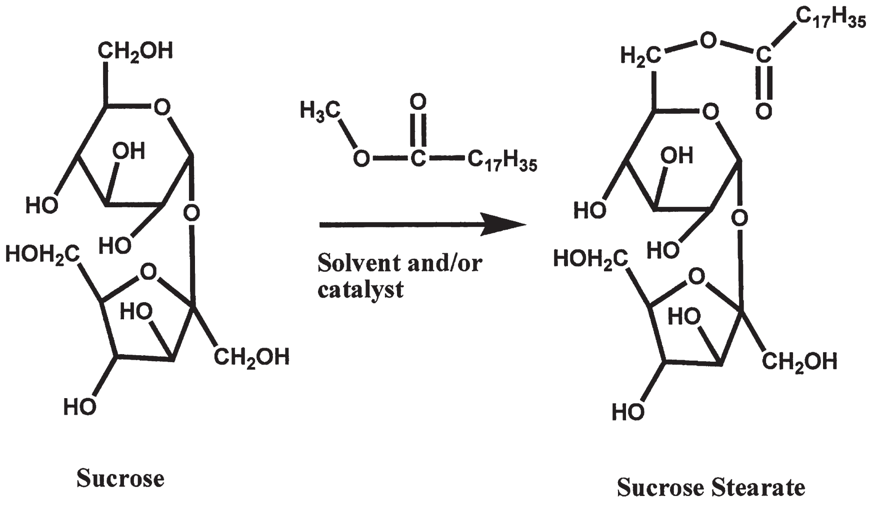

Fig. 2.8 Preparation of sucrose esters