

Preface

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

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

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

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

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Chapter 2

Synthesis and Commercial Preparation of Food Emulsifiers

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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 emulsifier, 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.

TYPES OF SURFACTANT STRUCTURES

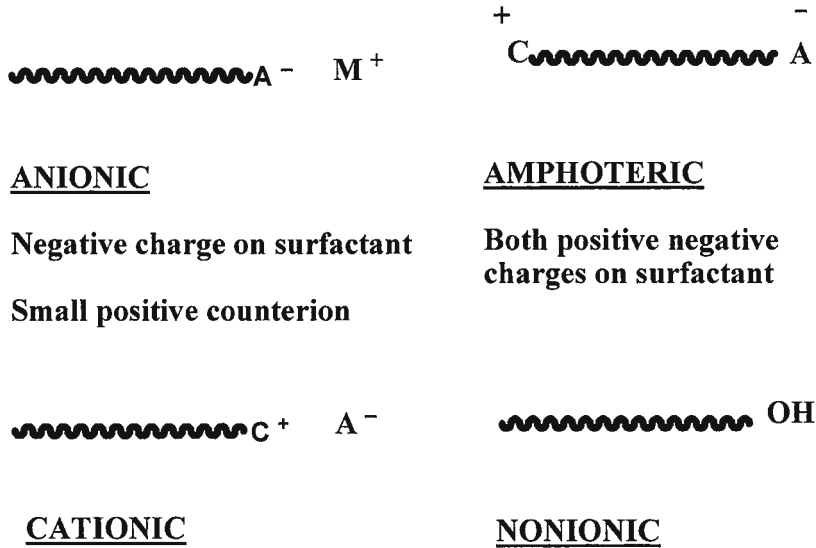


Fig. 2.1 Structures of anionic, cationic, amphoteric, and nonionic surfactants

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

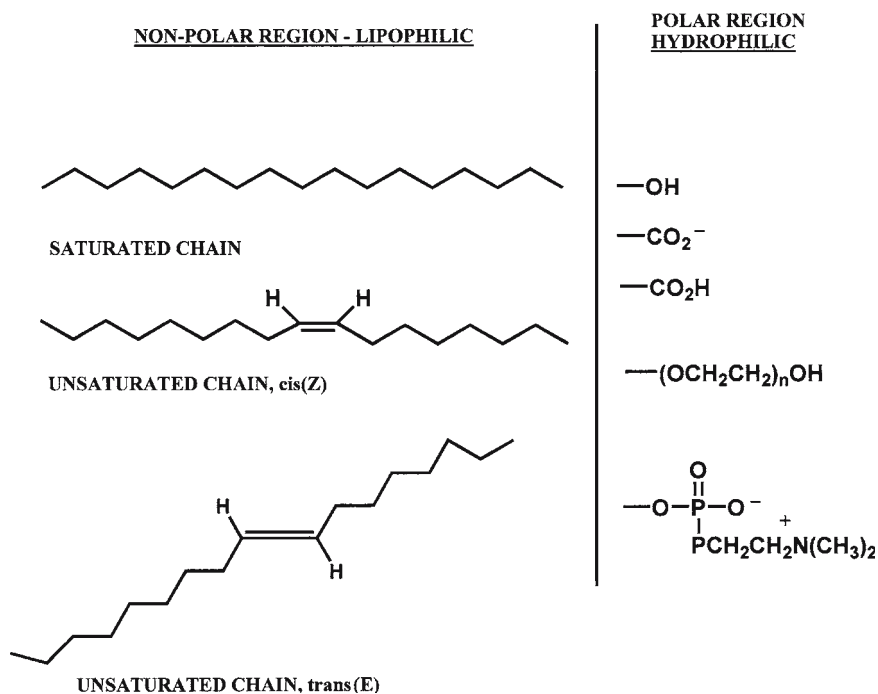


Fig. 2.2 Polar and nonpolar functional groups

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 diacetyltartrate 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)

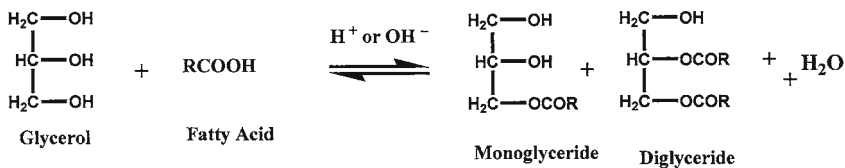
Mono- and diacylglycerols are the most widely used synthetic emulsifiers in the food industry. They are present in small quantities in natural fats and oils as a result of hydrolysis, which also releases fatty acids. Monoacylglycerols, which contain two free hydroxyl groups, exhibit stronger surface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

DIRECT ESTERIFICATION:



INTERESTERIFICATION:

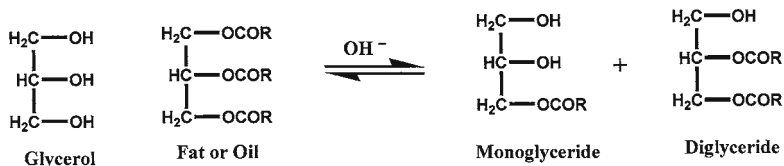


Fig. 2.3 Monoacylglycerol synthesis through direct esterification and interesterification

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,

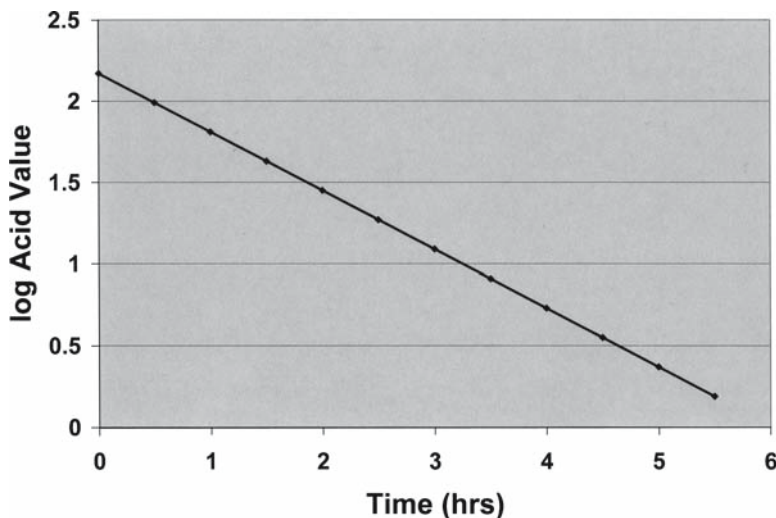


Fig. 2.4 Measurement of direct esterification using acid value

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.

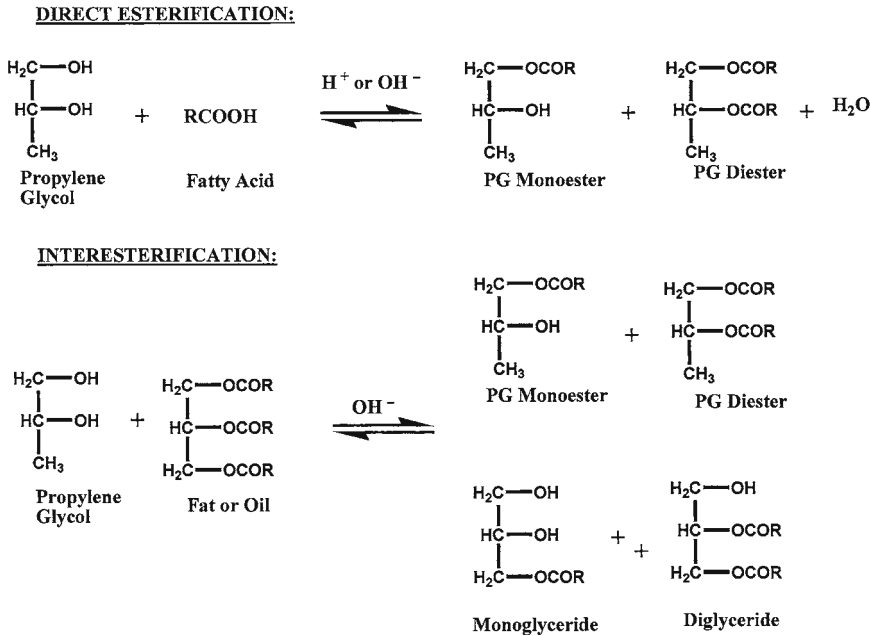


Fig. 2.5 Preparation of propylene glycol monoesters by direct esterification and interesterification

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 (Sahasrabudhe, 1967; Schuetze,

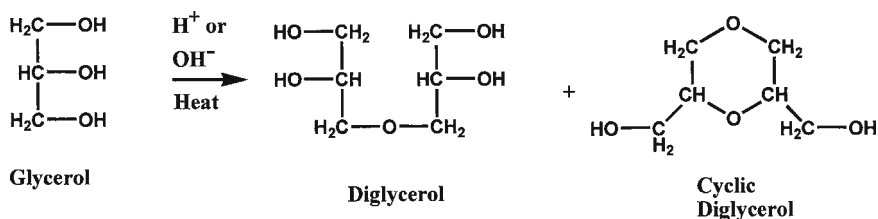


Fig. 2.6 Polymerization of glycerol

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.

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.

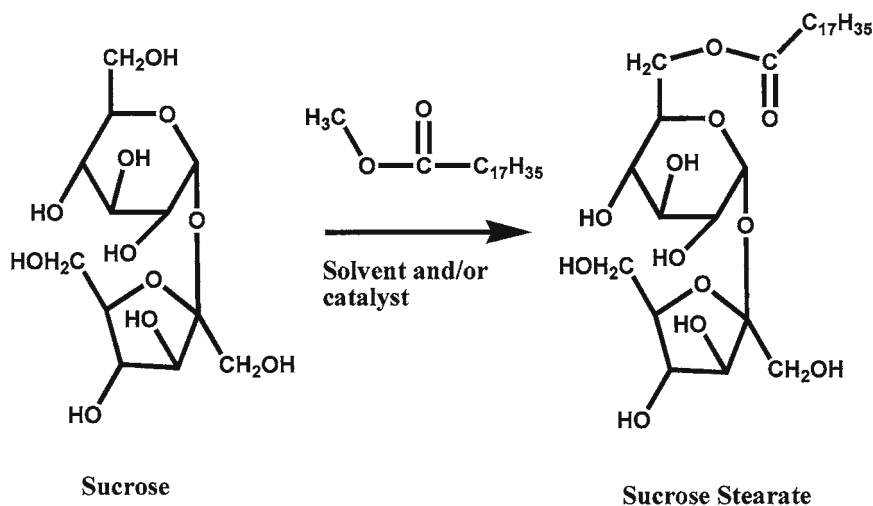


Fig. 2.8 Preparation of sucrose esters

Composition of the reaction product may be determined by thin layer chromatography (TLC) (Li, 2003) or reverse-Phase high performance liquid chromatography (RPHPLC) (Murakama et al., 1989) (Okumura et al., 2001). Esterification homologs can also be determined by electrospray mass spectrometry (Schuyt and Platerink, 1994).

2.7 Sodium and Calcium Stearoyl Lactylate

A surfactant with a carboxylic acid functional group may be nonionic, or if reacted with sodium or calcium hydroxide, converted into an anionic molecule. Lactic acid is a bifunctional molecule, which can self-condense to form an oligomer or react with a fatty acid to form stearoyl lactic acid (Eng, 1972). Reaction with sodium or calcium hydroxide forms sodium or calcium stearoyl lactylate. Figure 2.9 shows the dimeric homolog, known as sodium stearoyl 2-lactylate.

In a typical preparation, lactic acid is neutralized with sodium or calcium hydroxide and excess water is removed by distillation. Iron is highly detrimental to the quality of the product. Consequently, raw materials should have minimum iron content and the reactor should contribute no leachable iron. Stearic acid is added and esterification is carried out at 160–180 °C. Higher temperatures lead to side reactions, which produce dark colors and disagreeable odors and flavors. Water of reaction is removed by distillation and acid value is monitored until a minimum value is obtained.

Color of the final product may be improved by bleaching with 30% hydrogen peroxide (Anon, 1981) followed by heating to destroy excess peroxide. The final product is characterized by acid value, saponification number and total lactic acid (Franzke and Kroll, 1980).

2.8 Derivatives of Monoacylglycerols

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 varied by reacting monoacylglycerols with polar functional groups. The result is an increase in hydrophilicity for the emulsifier. Table 2.1 shows several derivatives of monoacylglycerols.

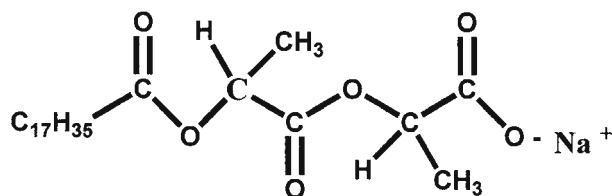


Fig. 2.9 Structure of sodium stearoyl lactylate

Table 2.1 Some monoacylglycerol derivatives

Acetate	$\text{~O}-\text{C}(=\text{O})-\text{CH}_3$
Lactate	$\text{~O}-\text{C}(=\text{O})-\text{C}(\text{OH})(\text{H})-\text{CH}_3$
Phosphate	$\text{~O}-\text{P}(=\text{O})(\text{OH})-\text{O}^-$
Succinate	$\text{~O}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(\text{H}_2)-\text{C}(=\text{O})-\text{O}^-$
Citrate	$\text{~O}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(\text{OH})(\text{COO}^-)-\text{CH}_2-\text{CO}_2\text{H}$
Diacetyltartarate	$\text{~O}-\text{C}(=\text{O})-\text{CH}(\text{H})-\text{CH}(\text{H})-\text{C}(=\text{O})-\text{O}^-$ $\text{H}_3\text{C}-\text{C}(=\text{O})-\text{O}-$ (on the left CH) $\text{O}-\text{C}(=\text{O})-\text{CH}_3$ (on the right CH)

2.8.1 Acetylated Monoacylglycerols

Addition of an acetyl group replaces a free hydroxyl group and, as a result, a less hydrophilic molecule is produced. Because of their alkyl chain diversity, acetylated monoacylglycerols are excellent film-formers (Guillard et al., 2004).

Two methods for preparation of these surfactants are commonly used. (1) Monoacylglycerols are reacted with acetic anhydride to produce the acetate ester and one equivalent of acetic acid. The reaction is catalyzed by strong mineral or organic acids. If the reaction vessel is suitably equipped, acetic acid may be removed by distillation and recycled to regenerate acetic anhydride. (2) Monoacylglycerols may also be reacted with glyceryl triacetate (triacetoin) using an alkaline catalyst. Although acetic acid is not formed as a by-product, glyceryl di- and triacetate is produced and must be removed by distillation at reduced pressures. The advantage of the latter process is that the reaction mixture is less corrosive and less flammable.

2.8.2 *Lactylated Monoacylglycerols*

As mentioned previously, lactic acid is a bifunctional molecule with both a free hydroxyl and free carboxyl group. When the carboxyl group is condensed with a hydroxyl group of a monoacylglycerol, a lactylated monoacylglycerol is formed. This has the effect of enlarging the hydrophilic group, while maintaining its nonionic character.

Synthesis of the surfactant is accomplished in two stages: (1) Preparation of the mono/diacylglycerol or distilled (90 +%) monoacylglycerol. (2) Reaction of this intermediate with lactic acid (Woods, 1961). Kinetics of the reaction are similar to direct esterification of glycerol with fatty acids. Water of reaction is generated and continuously removed and, the acid value decreases with time. Temperature of the reaction is limited to a maximum of 170–180 °C. Higher temperatures cause caramelization side-reactions of lactic acid. The degree of esterification (1–2) is controlled by the lactic acid/monoacylglycerol ratio in the reaction mixture (Shmidt et al., 1976b). After the reaction is complete, lactate esters of free glycerols must be removed because they contribute to strong off-flavors in finished food products. Steam distillation and aqueous extraction are commonly used for this purpose. The product may be characterized by acid value, saponification number, water-insoluble combined lactic acid (WICLA), and chromatography (Shmidt et al., 1976a).

2.8.3 *Succinylated Monoacylglycerols*

Succinic anhydride is similar to acetic anhydride in its reaction with monoacylglycerols. However, since a carbon chain tethers the two carboxyl groups, the second carboxyl group is retained in the surfactant molecule rather than expelled as an acid by-product. The hydrophilic group is enlarged and is 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 since it has been identified as a cancer suspect agent (Sax and Lewis, 1989). Although the reaction is exothermic, heat is added to raise the temperature to 150–165 °C in order to promote homogeneity of the reaction mixture. Since succinic acid is bifunctional, it may react with one or two monoacylglycerol molecules. The ratio of monoester/diester has been found to be ~6.5 (Hadeball et al., 1986). The product is characterized by acid value, melting temperature, free succinic acid, and chromatography (Shmidt et al., 1976).

2.8.4 *Citrate Esters of Monoacylglycerols (CITREM)*

Condensation of monoacylglycerol with citric acid or its anhydride produces a derivative with diverse functional groups. The hydrophilic head group is expanded in

size and polarity. In addition to their surface and interfacial activity, the citrate esters can chelate transition metals, which promote oxidation, such as iron and copper.

Preparation of the citrate esters is carried out by reacting acylglycerol with citric acid or its anhydride in the presence of an acid catalyst, e.g., acetic acid (Bade, 1978). The anhydride method can be carried out at lower temperatures. However, this process is more expensive because of the extra step necessary to synthesize of the anhydride. When citric acid is used, temperatures above 130 °C must be avoided to prevent decomposition of the acid.

2.8.5 Diacetyltartaric Acid Esters of Monoacylglycerols (DATEM)

Like succinylated and citrate derivatives, DATEM results from the condensation of a monoacylglycerol with a polycarboxylic acid. In this case, the acetate esters serve as protecting groups to prevent the self-condensation of tartaric acid. The resulting surfactant has an enlarged hydrophilic head group, which may exhibit anionic character at pH values above the pK_a .

Synthesis of this surfactant is accomplished in two or three stages: (1) Diacetyltartaric acid is produced by reacting tartaric acid with acetic anhydride, using sulfuric acid as a catalyst (Gladstone, 1960). (2) Optionally, the diacetyltartaric acid may be converted to its anhydride. (3) Diacetyltartaric acid or its anhydride is reacted with a monoacylglycerol. As with CITREM, the anhydride reaction proceeds under less stringent conditions but is more costly. Bound and free tartaric acid may be determined by extraction/saponification and UV spectrometry (Shmidt et al., 1979).

An interesting class of compounds has been produced by reaction of diacetyltartaric acid with fatty acids using a transacylase or lipase enzyme (Aracil Mira, 2000). In this reaction, fatty acids are esterified to the hydroxyl groups on tartaric acid. Surface properties and food applications of these compounds have not been extensively investigated.

2.8.6 Monoacylglycerol Phosphate

Conversion of a free hydroxyl group on monoacylglycerols with a phosphate ester introduces four (1P + 3O) additional electronegative heteroatoms into the molecule. The surfactant can become anionic at $pH > pK_a$.

Synthesis comprises reaction of a monoacylglycerol with phosphoric acid (Cawley and O'Grady, 1969), polyphosphoric acid (Kazyulima et al., 1986), or phosphorous pentoxide. As with other reactions described in this chapter, the mixtures are initially heterogeneous, but as the reactions proceed, the surfactant product coalesces into a single phase. Alternatively, a solvent may be used to obtain homogeneity under less stringent conditions. A synthesis directly from triacylglycerols has been reported (Ranny et al., 1989); in this process, the reactants are heated at

120 °C in the presence of P2O10 as a catalyst. The reaction is continued until triacylglycerols concentration reaches a minimum. Mono- and diacylglycerol phosphates may also be obtained by phospholipase modification of lecithin (see Sect. 2.10.1). The phosphoric acid esters from these reactions are neutralized with an alkaline sodium salt to yield an anionic surfactant.

2.9 Polyoxyethylene Derivatives

Ethylene oxide (oxirane) is a molecule with a three-membered, oxygen-containing ring. Since ring-strain is high, the molecule can readily undergo an exothermic SN-2 ring-opening reaction. The open ring nucleophile can then condense with a second molecule of ethylene oxide to initiate a polymerization chain reaction. Surfactants have been synthesized by using fatty acids or fatty alcohols as the initiating nucleophiles. The resulting polyoxyethylene chain is a large polar head group, which may also chelate cations to a small extent. In the food industry, sorbitan esters and monoacylglycerols have been ethoxylated to form higher HLB surfactants.

2.9.1 Polyoxyethylene Sorbitan Esters (Polysorbates)

The synthesis of sorbitan esters was previously discussed in Sect. 2.5. Although sorbitan monooleate is not approved for use in foods, its ethoxylated derivative is permitted. The nomenclature of sorbitan esters and polysorbates has evolved from the trade names of surfactants marketed by ICI Inc. The system is shown in Table 2.2

A number of challenges arise in the synthesis of ethoxylates. Ethylene oxide has a boiling point of 10.4 °C (Udajari, 1996a). Therefore ethylene oxide is a gas at ambient temperature. It is also a suspected carcinogen so reaction mixtures must be tightly contained to avoid exposures. Ethylene oxide may also dimerize to form dioxane, another carcinogen suspect. Great care must be taken to completely remove dioxane from the final product. Unlike other reactions in this chapter, ethoxylation is exothermic. Slow addition rate, efficient mixing and heat exchange are necessary to avoid explosions.

In a typical preparation (Fig. 2.10), a sorbitan ester is introduced into a pressure reactor, similar to that used for hydrogenation. Ethylene oxide is added while the reactor is cooled to remove the heat of reaction. Slow addition serves to moderate

Table 2.2 Nomenclature of sorbitans and polysorbates

Fatty acid (abbreviated)	Sorbitan ester	Ethoxylated derivative
Lauric (12:0)	Sorbitan monolaurate	Polysorbate 20
Palmitic (14:0)	Sorbitan monopalmitate	Polysorbate 40
Stearic (16:0)	Sorbitan monostearate	Polysorbate 60
Stearic (16:0)	Sorbitan tristearate	Polysorbate 65
Oleic (18:1)	Sorbitan monooleate	Polysorbate 80

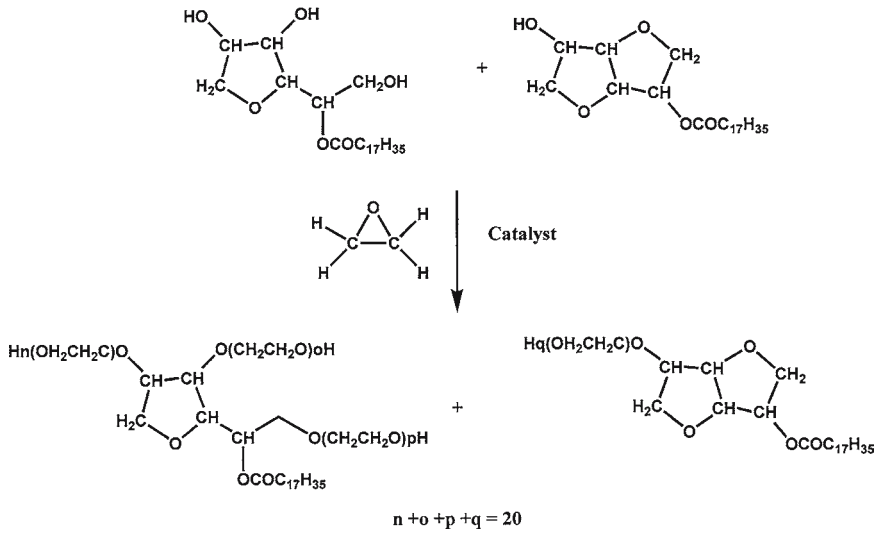


Fig. 2.10 Ethoxylation to convert sorbitan esters to polysorbates

the exotherm and to minimize the extent of dimerization. After the reaction has been completed, the product is steam distilled to remove any traces of dioxane. Saponification number, hydroxyl value and polyoxyethylene content characterize the product. Negative ion ionization mass spectrometry has also been used to determine the distribution in polymeric chains (Brumley et al., 1985). This technique may be valuable to sort out subtle differences in product functionality in foods.

2.9.2 Ethoxylated Mono- and Diacylglycerols

Preparation of this surfactant is carried out in two stages: (1) Mono- and diacylglycerols are prepared from saturated fats or fatty acids. However, in this case, the alkaline catalyst is not neutralized but carried over to the second reaction. (2) Ethoxylation is carried out in a fashion similar to sorbitan esters, but the temperature is raised to 170–180 °C. The product is steam or nitrogen deodorized to remove dioxane. Excess catalyst is removed by filtration.

2.10 Modification of Naturally Occurring Species

Many naturally occurring compounds have been used to impart functional properties to food products. For example, gums such as sodium alginate have been used to stabilize emulsions by thickening the aqueous phase. Lecithin has been used as

an emulsifier in margarine and for viscosity control in chocolate. These compounds may be physically, enzymatically, or chemically modified to improve their amphiphilic characteristics.

2.10.1 Modified Lecithins

Lecithins are found in animals and vegetables as essential components of membranes. Two major differences may be observed: (1) Animal sources have higher saturated fatty acids esterified at the sn-1 and sn-2 positions, while those from vegetables are unsaturated. (2) Animal and vegetable lecithins vary in the distribution of groups esterified to the terminus of the phosphate (mainly choline, ethanolamine and inositol). Egg yolk and soy lecithins are the most widely used in the food industry (Szuhaj, 2005).

Egg yolk is generally separated from whole egg and may be dried or frozen, if not used immediately. Egg lecithin may be further purified by extraction with ethanol (Sim, 1994). Soy lecithin is obtained by degumming crude soybean oil. Both these “raw” lecithins are complex mixtures, which contain significant quantities of triacylglycerols. Solvents may be used to separate lecithin from these triacylglycerols. For example soy lecithin may be precipitated (de-oiled) by acetone. Lecithin may also be fractionated into its constituents. For example, egg yolk lecithin can be purified and fractionated by sequential extraction with ethanol, hexane and acetone (Palacios and Wang, 2005). Soy lecithin may be enriched in phosphatidylcholine by extraction with ethanol (Gu, 2002; Belitz et al., 2004a).

Lecithin may also be chemically or enzymatically modified to obtain a wider variety of HLB values or surface properties. As shown in Fig. 2.11, phospholipase enzymes may be used to cleave selected ester bonds. In egg yolk or soy, phospholipase A2 cleaves the ester bond at sn-2 to produce lysolecithin, a single tailed surfactant (Hibino et al., 1991; Morgado et al., 1995). The reaction may be carried out in reverse to produce lysolecithin from glycerolphosphatidylcholine and a fatty acid (Hibino et al., 1989). These reactions are carried out in emulsions or organic solvents in the presence of calcium ions. Phospholipase A2 may be added to crude soybean oil to make lecithin more hydratable and therefore easier to separate. Phospholipase D cleaves the ester bond between the phosphate and the head group. Diacylglycerol [phosphate may be produced from lecithin using this enzymatic hydrolysis reaction (Wang et al., 1997). Head groups on lecithins may be interchanged (transphosphatidylation) by reaction with phospholipase D and a hydroxyl-containing molecule (Masashi et al., 2005). The method does not appear to require organic solvents or calcium.

A second polar head group may be introduced into the soy lecithin molecule by reaction with hydrogen peroxide (Sietze, 1982). A four-centered reaction adds two hydroxyl groups across a double bond in a fatty acid chain. Surface activity is increased and the molecule can adopt a looped “inchworm” structure at the interface.

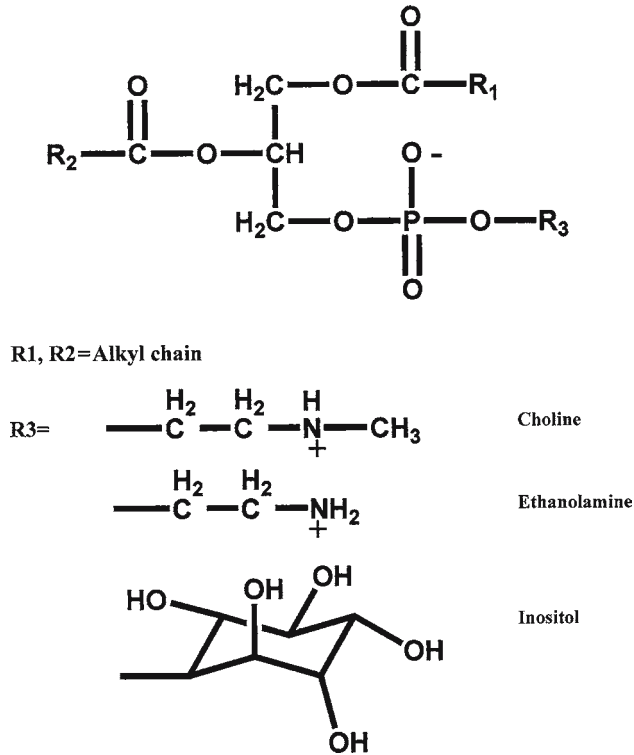


Fig. 2.11 Major phospholipids of lecithin

2.10.2 Propylene Glycol Alginate

Alginic acid is a polar hydrocolloid containing hydroxyl groups, derived from seaweed. It is a copolymer of mannuronic and guluronic acids. Sodium and calcium salts of this ingredient form gels and are used as thickeners in a number of food products. These ingredients do not display appreciable surface activity. Esterification of the free carboxyl groups with propylene glycol or propylene oxide reduces the hydrophilicity of the ingredient. Approximately 80% of the carboxyl groups can be esterified (McDowell, 1970; McDowell, 1975). Figure 2.12 shows a unit of the esterified alginate containing mannuronic and guluronic acids.

Propylene oxide is a volatile liquid with a boiling point of 34 °C (Udajari, 1996b). Like ethylene oxide, propylene oxide is extremely flammable and exposure can cause burns and blistering. In a typical procedure, a concentrated alginic acid is reacted with propylene oxide in a pressure reactor at 65–80 °C for 30–60 min (Nielsen et al., 1971). The degree of esterification can be improved by neutralization of the acid with sodium hydroxide (Noto and Pettitt, 1972; Strong, 1976; Ha et al., 1987).

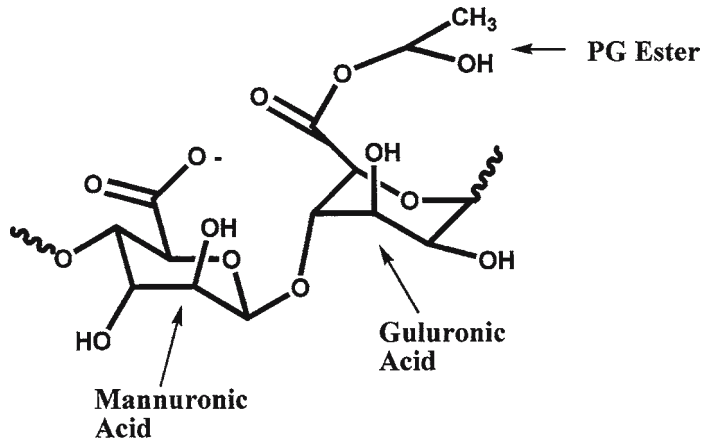


Fig. 2.12 Structure of propylene glycol alginate

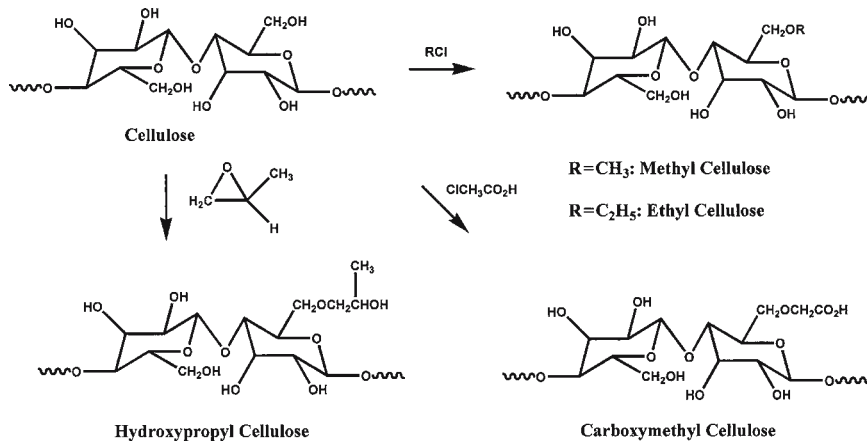


Fig. 2.13 Cellulose derivatives

2.10.3 Alkyl Esters of Cellulose

Cellulose is polymeric carbohydrate of glucose, which differs from starch in stereochemistry of the bond between monomers. It is a very tight structure and is used as a source of fiber in food products. Hydroxyl groups in the cellulose may react to form an interrupted structure, which results in greater water absorption and swelling. Lipophilic groups are also introduced to provide some surface activity. Methyl and ethyl chlorides are reacted to give methyl and ethyl ethers. Chloroacetic acid yields carboxymethyl cellulose. Analogous to the synthesis of propylene glycol alginate, propylene oxide reacts to form hydroxypropylcellulose, an ether-alcohol. Structures of these cellulose derivatives are shown in Fig. 2.13. The degree of substitution is determined by the ratio of reactants and the reaction conditions (Belitz et al., 2004b).

2.11 Commercial Preparation of Food Surfactants

Syntheses of surfactants in the laboratory and in commercial reactors are often different. On a small scale in glass equipment, corrosive and toxic materials can be handled and reaction products can be purified using chromatographic methods. Although glass lined reactors are available commercially, they are vulnerable to breakage and pinhole leaks. Chromatographic purification on a large scale is frequently uneconomical. The choice between batch or continuous process depends on product volumes and product mix. A continuous process is well suited to a few products produced in large volume. A large number of products, produced in smaller quantities are best prepared by a batch process. Direct esterifications with fatty acids need to be performed in a batch process because of their slower reaction rates.

2.11.1 Batch Esterification/Interesterification

Commercial batch reactors are generally constructed of carbon or stainless steel. High molybdenum stainless steel is required if strong acids are involved in the reaction, for example, in direct esterification with fatty acids at high temperatures. In a typical process, a polyol, fat or fatty acid and a catalyst are weighed or metered from storage tanks into the reactor. A nitrogen atmosphere is maintained and heat is applied through a jacket or heating coils. When the reaction is completed, a neutralizing agent is introduced and cooling is applied through the coils or jacket. Most often, heating and cooling coils are separate systems. A high boiling heat exchange fluid is used for heating and water is used for cooling. Excess polyol is removed by distillation, gravitational separation, or extraction. The product is filtered and pumped to storage.

Figure 2.14 shows a schematic of a typical batch reactor. Some critical design criteria for batch reactors are (1) The reactor, piping, and storage tanks must be constructed of corrosion-resistant materials. In addition to damage to equipment, iron or copper leached into products may act as pro-oxidants, which lead to quality problems. (2) Meters and/or scales used to measure reactants must be accurate and precise in order to maintain consistent product quality. (3) If excess polyols are to be recycled, fractionation efficiency must be sufficient to prevent cross-contamination of subsequent batches. (4) Sufficient heat capacity is essential to allow rapid heating and cooling of reaction mixtures. (5) Starting oil storage, the reactor, filtration apparatus, and product storage should be protected with an inert atmosphere to minimize degradation reactions caused by oxygen. (6) An adequate cleaning system is necessary to prevent cross-contamination between products. A waste treatment system is needed to avoid environmental contamination.

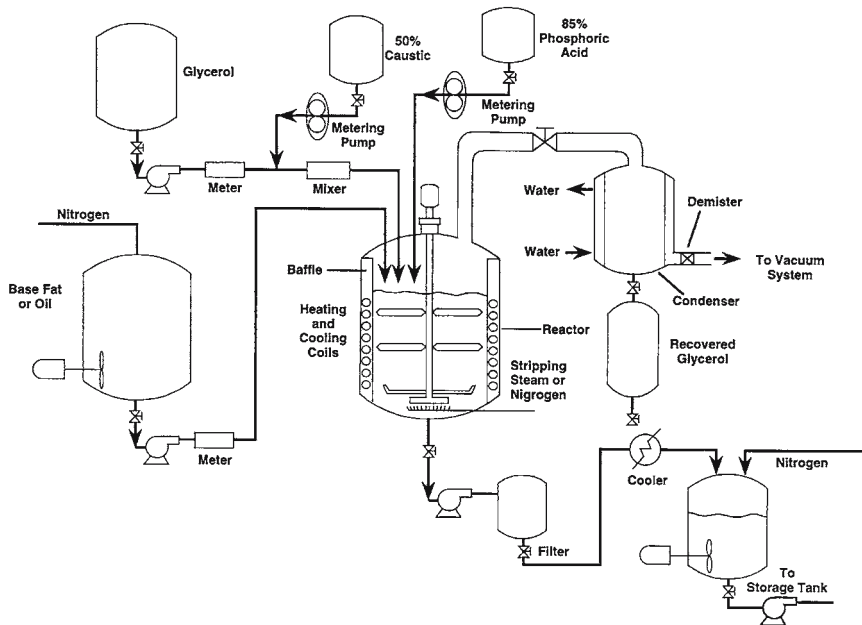


Fig. 2.14 Typical batch esterification reactor (Hasenhuettl, 1999a). Reproduced with permission of Elsevier Ltd

2.11.2 Continuous Interesterification Reactors

Continuous processes are generally economical, because once conditions are established; large volumes of product may be produced as long as the process is maintained under control. In a typical commercial reactor, as shown in Fig. 2.15 (Allen and Campbell, 1967), oil, polyol and catalyst are metered through a multiplex pump into a heated flow-through reactor. At high temperature, homogeneity is rapidly achieved. The product stream then exits to a falling-film evaporator, where excess polyol is removed at reduced pressure. Since the residence time in the evaporator is short, pre-neutralization is not necessary to prevent disproportionation. The product is neutralized, filtered, and sent to storage or packaging.

Some critical design factors for continuous reactors are (1) An inert atmosphere should be provided for reactants and products to prevent oxidative degradation. Since there is little or no headspace in the reactor, only dissolved gases can produce side reactions. (2) The metering pump must be accurate and stable in order to produce consistent product with minimal off-grade product. (3) Heat exchange capacity in the reactor must be sufficient to raise the temperature as high as 260° C while maintaining adequate product flow. (4) The falling film evaporator must be sufficient to consistently remove excess polyol. For two polyols, such as propylene glycol and glycerol, either two evaporators in series must be used or the polyol mixture must

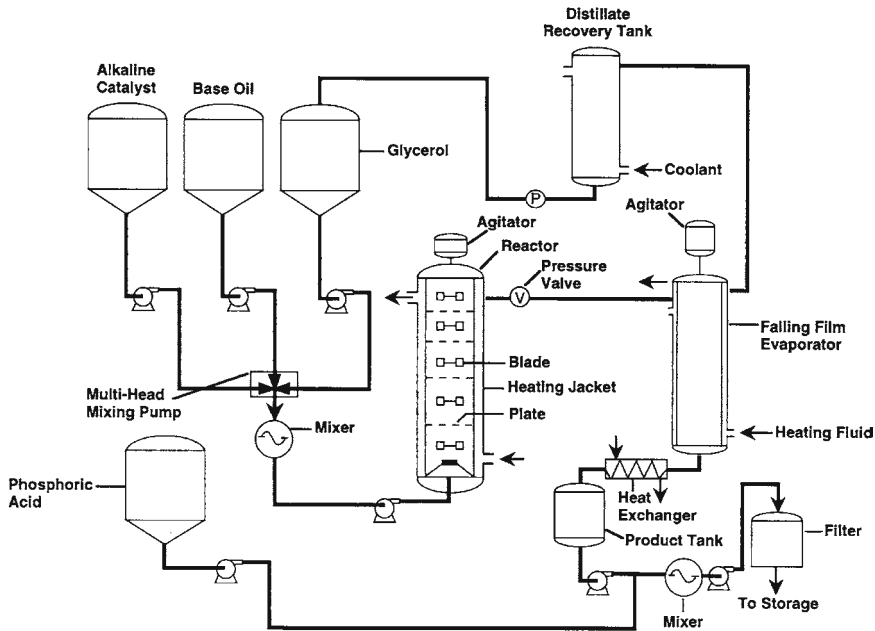


Fig. 2.15 Continuous esterification reactor (Allen and Campbell, 1967; Hasenhuettl, 1999b). Reproduced with permission of Elsevier Ltd

be separated in a subsequent process. (5) Neutralization and filtration should be sufficiently robust to produce a clear molten product.

2.11.3 Bioreactors for Esterification/Interesterification

Esterification and interesterification syntheses can be accomplished with intact microorganisms or purified lipase or esterase enzymes. The bioreactors may be either batch or continuous. Some advantages of bioreactors are (1) Operation at lower temperatures, lower energy costs and reduced undesirable side reactions. (2) Stereoselective reactions, where fatty acids combine with primary alcohols, can yield products with higher concentrations of hydrophilic surfactant molecules. For example, sucrose may be selectively esterified to yield mono and diesters (Li et al., 2003). (3) Materials of construction do not have to be as corrosion-resistant as vessels operating at higher temperatures. Because temperatures are low and less corrosive materials are used, the safety of operating personnel is improved.

Some disadvantages of bioreactors are (1) High cost and denaturation of the enzyme make the process expensive. (2) Heterogeneity must be overcome at relatively low temperature by using solvent or carrying out the reaction on large interfacial areas. (3) Reaction rates are slow. For direct esterifications, water must be

removed to shift the equilibrium. However, a small amount of water is necessary to maintain the activity of the enzyme

Stirred tank and fixed bed reactors were initially used to carry out reactions with enzymes and microorganisms (Patterson et al., 1984),(Arcos et al., 2000). Residence time, exposure to enzyme, and polyol/fatty acid ratio were the critical factors controlling the rate and selectivity of the reaction. A flow-through microporous membrane reactor, as shown in Fig. 2.16, has been used to produce surfactants (Yamane et al., 1984; Hoq et al., 1985). A fatty acid stream is passed along one side of the membrane

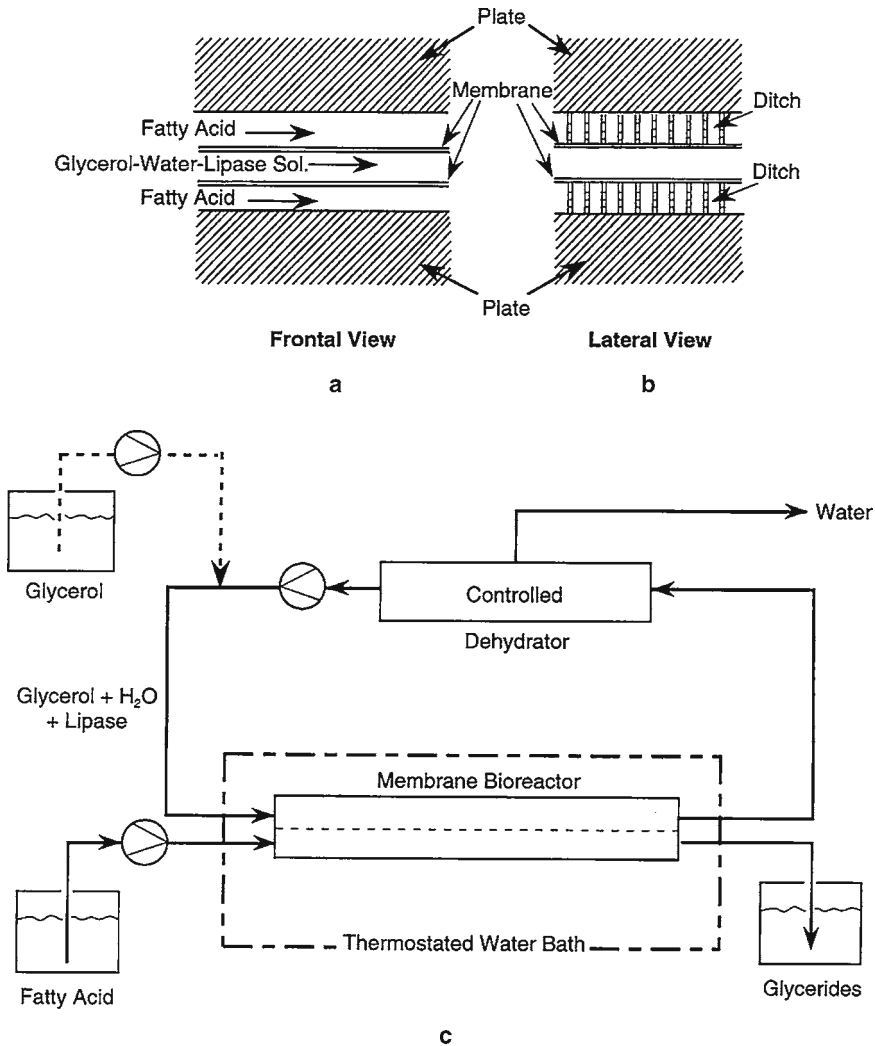


Fig. 2.16 An enzymatic esterification reactor (Hasenhuettl, 1999c). Reproduced with permission of Elsevier Ltd

while glycerol, an activating concentration of water, and lipase enzyme are passed along the other side. An improvement using a pervaporative membrane has been developed and design factors reviewed (Lim et al., 2002). This reactor system enables the evaporative separation of water, thus shifting the reaction equilibrium. In another recent improvement, protein, lipid, or chitosan may be deposited on the surface of a macroporous membrane. The film improves phase contact in the reactor. Design factors have been reviewed for this reactor type (Paolucci-Jeaniean, 2005).

2.11.4 Ethoxylation/Propoxylation Reactors

Reactions of ethylene or propylene oxide may be carried out in batch, continuous, or semi-continuous systems. Since the epoxides are generally in the gaseous state at reaction temperatures, liquid polyols may be sprayed through a tower containing these reactive compounds (Santacesaria, 1999). In designing ethoxylation reactors, careful consideration must be given to safety factors. Since the epoxides are cancer suspect agents, leakage must be prevented and exposure of workers strictly monitored. Ethoxylation reactions are exothermic and heat must be efficiently removed in order to avoid explosion or fire. Solubility of the epoxide in the reaction mixture is the most critical factor controlling the reaction rate (Santacesaria et al., 1995).

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