

MAXIMIZING THE USE OF FOOD EMULSIFIERS

by

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Abstract

Emulsifiers have been and remain highly functional ingredients in the food industry. Emulsifiers contain both hydrophilic and lipophilic parts, resulting in their ability to be useful in foods at very low levels. However, knowledge of why emulsifiers work and how to use them most effectively is reserved for the few scientists who specialize in the discipline. Therefore, a comparison of current emulsifier theory with known emulsifier usage in the industry is beneficial to all who use these ingredients. Current emulsifier theory effectively describes how emulsifiers behave in food systems. Emulsion theory details how emulsifiers facilitate the formation and stability of emulsions through study of the kinetics of food systems. Emulsion theory further relates the ability of emulsifiers to interact with other substances in a food system.

The main interactions concerning emulsifiers are their ability to form mesophases with water, to strengthen or weaken protein interactions, to form complexes with starches, and to promote or subdue fat crystallization. However, industrial applications of emulsifiers indicate areas where exceptions to theory exist. While emulsion theory has been found to effectively describe the individual interactions and functions in food, the simplicity of the models indicates that complex food system models are still needed to truly understand how to maximize the functionality of emulsifiers.

Key Words: Emulsifiers, functionality, monoglycerides, mesophases.

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CHAPTER 1 – Background Information

Emulsifier Market and History

Emulsifiers have become highly functional ingredients in the food industry. They are used at very low amounts in foods, many times at fractions of a percent, yet can greatly affect the final products' performance. For example, emulsifiers can aerate foams and batters, extend shelf-life, promote fat agglomeration, and improve texture in foods. The functionality of emulsifiers depends on the particular emulsifier used and the concentration, formulation, and processing the final food product has experienced. This range in functionality has resulted in 400 million pounds of emulsifiers being used in the food industry in 1996, with an estimated annual growth of 3% in the bakery division (Brandt, 1996) and a 6% annual growth throughout the entire industry (Turner, 2008).

Commercial emulsifiers were introduced to the food industry in the 1930s in the form of mono- and diglycerides (O'Brien, 2004). Before the introduction of commercial emulsifiers, the emulsification properties found within eggs were utilized. Egg yolks contain lecithin and other phospholipids that act as natural emulsifiers in foods (Pylar, 1988). Mono- and diglycerides were initially added to shortenings so that high-ratio cakes could be produced. A high-ratio cake contains a greater amount of sugar than flour. These cakes contain a softer and lighter crumb structure when compared to cakes without emulsified shortening. Around the same time lecithin was starting to be used in confectionery products and margarines (Szuhaj, 2005). Mono- and diglycerides were quickly utilized for shelf life extension in yeast-leavened baking products. Following the introduction of mono- and diglycerides in the baking industry, monoglyceride

derivatives were developed. These emulsifiers provided specialized functionality to the food industry. Some benefits of monoglyceride derivatives are protein interactions leading to dough strengthening and aeration abilities, carbohydrate interactions leading to starch complexing and gelation optimization, and fat interactions leading to customization of the crystal behavior of the fat. Recently, the development of novel food emulsifiers has been minimal. The reasons behind the lack of new emulsifiers are the costs and time of getting regulatory approval of new food ingredients (Karel, 1999) and the trend in the industry to move toward natural ingredients (Turner, 2008).

Fats and Oils

A strong background of fats and oils technology is essential to understanding how emulsifiers behave. Many of the defining characteristics of triglycerides also pertain to emulsifiers. Edible fats and oils or triglycerides consist of three fatty acid chains attached to the carbon atoms of glycerol. Figure 1.1 displays the molecular configuration of a triglyceride. The characteristics of triglycerides are dependent on the makeup of the three fatty acid chains. The three main factors that affect the characteristics of triglycerides are chain length, number and type of double bonds, and the position of the fatty acids chains on the glycerol molecule (O'Brien, 2004). The melting point of fatty acids increases as the chain length increases. For example, the melting point of an 18-carbon length chain is 69.6°C, while a 16-carbon length chain is 62.9°C (Strayer et al. 2006). Consequently, the presence of double bonds in a fatty acid chain depresses the melting point. The melting point depression is amplified as the number of double bonds increases. For example, an 18-carbon length fatty acid with one double bond has a

melting point of 16.3°C, whereas the presence of two double bonds results in a melting point of -6.5°C (Strayer et al. 2006). The type of double bond has an effect on the melting point of the fatty acid chain as well. Almost all double bonds are in the cis configuration without artificial intervention. However, if fatty acids have been hydrogenated, they can form double bonds in the trans configuration. Figure 1.2 displays the configuration of cis and trans bonds. Trans double bonds have a higher melting point than cis double bonds. The ability to create vegetable oils with a customized blend of cis and trans fatty acid chains through hydrogenation led to the proliferation of partially hydrogenated shortenings in the food industry. Table 1.1 displays some of the characteristics of popular fatty acid chains utilized in the food industry.

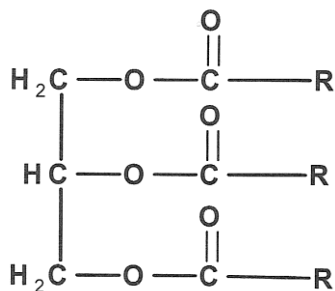


Figure 1.1 – Chemical structure of a triglyceride (Strayer et al. 2006)

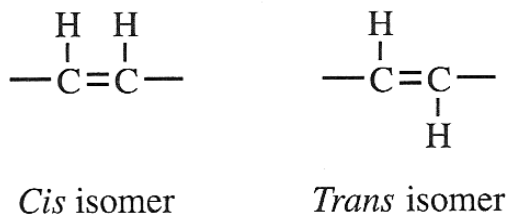


Figure 1.2 – Cis- and trans-isomers of unsaturated fatty acids (Gupta, 2005)

Table 1.1 – Fatty acid characteristics (O’Brien, 2004)

Fatty Acid	Carbon Atoms	Double Bonds	Melting Point	
			°F	°C
Butyric	4	0	17.6	-8.0
Caproic	6	0	25.9	-3.4
Caprylic	8	0	62.1	16.7
Capric	10	0	88.9	31.6
Lauric	12	0	111.6	44.2
Myristic	14	0	129.9	54.4
Myristoleic	14	1 cis	65.3	18.5
Palmitic	16	0	145.2	62.9
Palmioleic	16	1 cis	113.0	45.0
Margaric	17	0	142.3	61.3
Margaroleic	17	1 cis	135.5	57.5
Stearic	18	0	157.3	69.6
Oleic	18	1 cis	60.8	16.0
Petroselinic	18	1 positional	86.0	30.0
Elaidic	18	1 trans	110.7	43.7
Linoleic	18	2 cis, cis	19.4	-7.0
Linoleladic	18	2 trans, trans	132.8	56.0
Linolenic	18	3 cis, cis, cis	8.6	-13.0
α -Eleostearic	18	3 cis, trans, trans	120.2	49.0
β -Eleostearic	18	3 trans, trans, trans	159.8	71.0
Arachidic	20	0	167.5	75.3
Behenic	22	0	175.8	79.9
Erucic	22	1 cis	92.3	33.5
Lignoceric	24	0	183.6	84.2

The most common commercially available food emulsifiers are synthesized from edible fats and oils or specific fatty acids. The interesterification process randomly distributes the fatty acid chains from the source oil. Consequently, many of the attributes that distinguish fats and oils from each other also indicate how emulsifiers behave. Each type of edible oil has a specific fatty acid composition. Table 1.2 illustrates the fatty acid compositions for the most widely used

edible oils utilized in the food industry. Therefore, source oils that contain fatty acids that are longer in chain length, more saturated, or contain higher amounts of trans bonds will have higher melting points. These fats and fatty acids will produce emulsifiers that have high melting points as well. Mono- and diglycerides actually have elevated melting points when compared to a triglyceride of the same makeup (Krog and Sparso, 2004).

Table 1.2 – Typical fatty acid composition of vegetable and animal fats and oils in the United States¹ (% of total fatty acids) (Strayer et al. 2006)

	Butyric	Caproic	Caprylic	Capric	Lauric	Myristic	Pentadecanoic	Palmitic	Margaric	Stearic	Arachidic	Behenic	Lignoceric	Myristoleic	Palmitoleic	Oleic	Margaroleic	Gadoleic	Linoleic	Linolenic
	Saturated												Monounsaturated					Poly-unsaturated		
<i>Oil or Fat</i>	4:0	6:0	8:0	10:0	12:0	14:0	15:0	16:0	17:0	18:0	20:0	22:0	24:0	14:1	16:1	18:1	17:1	20:1	18:2	18:3
Beef Tallow						3	1	24	2	19				1	4	43	1		3	1
Butterfat	4	2	1	3	3	11	2	27	1	12					2	29			2	1
Canola								4		2						62			22	10
Cocoa butter								26		34	1					34			3	
Coconut		1	8	6	47	18		9		3						6			2	
Corn								11		2						28			58	1
Cottonseed						1		22		3					1	19			54	1
High oleic canola								4		2						75			17	2
High oleic safflower								7		2						78			13	
High oleic sunflower								4		5						79			11	
Lard						2		26		14					3	44		1	10	
Mid oleic sunflower								4		5						65			26	
Olive								13		3					1	71			10	1
Palm kernel			3	4	48	16		8		3	1					15			2	
Palm						1		45		4						40			10	
Peanut								11		2	1	3	2			48		2	32	
Safflower								7		2						13			78	
Soybean								11		4						24			54	7
Sunflower								7		5						19			68	1

¹Fatty acid composition data determined by gas-liquid chromatography and provided by member companies of the Institute of Shortening and Edible Oils.

Fatty acids (designated as number of carbon atoms: number of double bonds) occurring in trace amounts are excluded. Component fatty acids may not add to 100% due to rounding.

Commercial fats and oils can form into a number of different configurations when they crystallize. This ability to form into different configurations with the same chemical makeup is known as polymorphism. The configuration or crystalline microstructure of fats and oils can affect the textural and physical characteristics of the fat. Consequently, the configuration also affects the properties of the final product. The configuration into which fats and oils stabilize into depends on the makeup, the presence or absence of impurities, the amount of shear, the temperature, and the speed of the crystallization (Metin and Hartel, 2005). Commercial food emulsifiers also display polymorphism dependent on the same factors.

The three major crystalline forms are alpha (α), beta prime (β'), and beta (β). The alpha form has the lowest melting point. This formation contains a loosely packed arrangement of molecules. These molecules form crystals that are five microns in size and are very fragile (O'Brien, 2004). The alpha polymorph contains a hexagonal subcell structure (Metin and Hartel, 2005). The subcell structure indicates the way the hydrocarbon chains are laterally packed. Figure 1.3 displays the alpha polymorph and hexagonal subcell structure. Alpha crystals readily convert to more stable and higher melting polymorphs in solid fats and oils products (O'Brien, 2004).

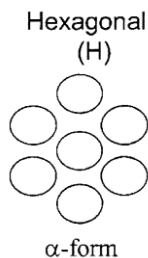


Figure 1.3 – Alpha polymorph and hexagonal subcell structure (Sato and Ueno, 2005)

Fats that do not have a great degree of variability in their fatty acid compositions tend to transform rapidly into the beta formation (O'Brien, 2004). The beta formation has very high melting temperatures with relatively large and stable crystals. These crystals are between 25 and 50 microns in size (O'Brien, 2004). Close packing of the molecules give the beta formation its high melting temperature and stability. Having a low amount of variability in the fatty acid composition allows the molecules to form a very closely-packed crystalline network. The beta formation contains a triclinic parallel subcell structure (Metin and Hartel, 2005). Figure 1.4 displays the beta polymorph and parallel subcell structure. Since all of the molecules are facing the same direction, the formation is closely packed and stable. However, the coarse crystals do not trap great amounts of liquid oil. This can lead to a grainy appearance and eventual oil migration out of the product (O'Brien, 2004). If the food application requires a grainy texture, as in pie crusts, or heats the crystals so they are completely melted, as in frying applications, then fats and oils in the beta formation are recommended (O'Brien, 2004).

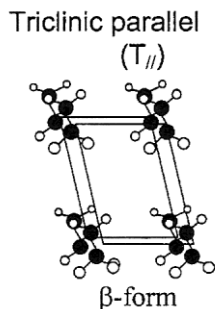


Figure 1.4 – Beta polymorph and parallel subcell structure (Sato and Ueno, 2005)

Fats that have greater amounts of variability in their fatty acid compositions tend to transform slowly into beta prime formations (O'Brien, 2004). This formation has very small,

needle-like crystals. These crystals are able to trap a large amount of liquid oil, making them desirable in many food applications. The beta prime formation has an orthorhombic perpendicular subcell structure (Metin and Hartel, 2005). Figure 1.5 displays the beta prime polymorph and orthorhombic perpendicular subcell structure. Fats and oils that have variability in their fatty acid compositions impede their ability to pack closely and move toward the beta formation (O'Brien, 2004). This allows the beta prime formation to be highly stable. In many bakery applications the beta prime formation is the most desirable. Fats and oils in this formation have the greatest aeration capabilities and produce the smoothest icings (O'Brien, 2004).

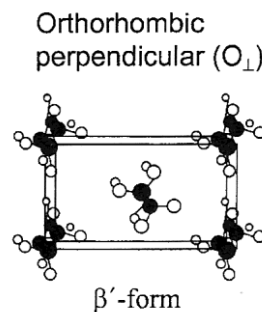


Figure 1.5 – Beta prime polymorph and orthorhombic perpendicular subcell structure (Sato and Ueno, 2005)

The source fat or oil has a great amount of influence on the final crystal configuration. This is due to the different fatty acid compositions inherent to each fat or oil source. Table 1.3 displays the most likely crystal configuration for most hydrogenated edible oils used in the food industry. As expected, the fats and oils that have large amounts of similar fatty acids prefer the beta configuration and the fats and oils that contain a mixture of fatty acids prefer the beta prime configuration. However, the preferred crystal formation can be altered by manipulating the

palmitic fatty acid content, randomizing the fatty acids on the glycerol molecule, or hydrogenating the fat and oil (O'Brien, 2004).

Table 1.3 – Crystal configuration of hydrogenated oils (O'Brien, 2005)

β	β'
Canola oil	Cottonseed oil
Cocoa butter	Butter oil
Coconut oil	Herring oil
Corn oil	Menhaden oil
Olive oil	Modified lard
Lard	Palm oil
Palm kernel	Rapeseed oil
Peanut oil	Tallow
Safflower oil	Whale oil
Sesame oil	
Soybean oil	
Sunflower oil	

Emulsion Theory

Emulsifiers are substances that can promote and stabilize the dispersion of one material into another immiscible material. Immiscible materials are incapable of mixing together without assistance. These immiscible materials in food can be a solid dispersed into a liquid, a liquid dispersed into another immiscible liquid, a gas dispersed into a liquid, and a gas dispersed into a solid. Food emulsifiers are able to promote and stabilize dispersion due to their amphiphilic properties. Amphiphilic means containing both water loving (hydrophilic) and fat loving (lipophilic) parts. Figure 1.6 displays the structure of a simple emulsifier.

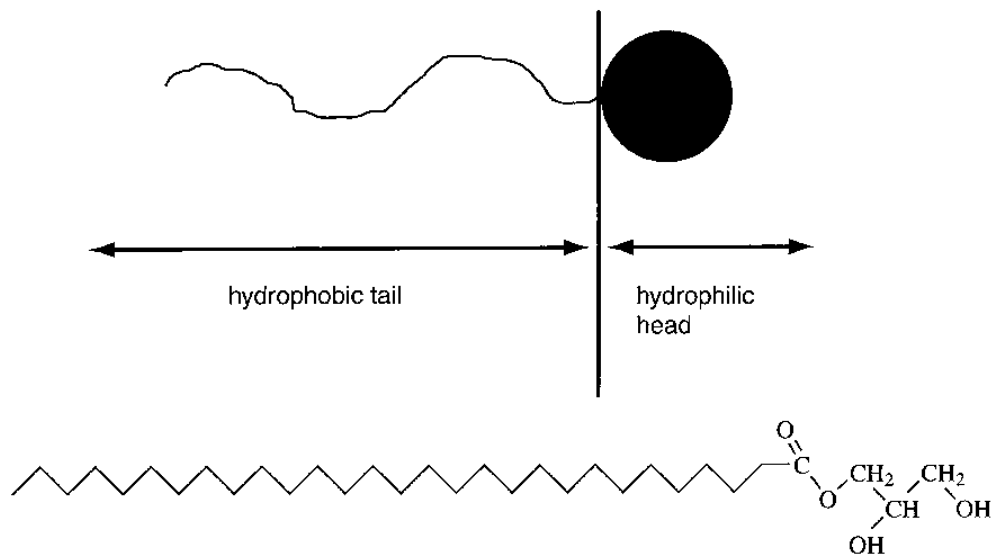


Figure 1.6 – Structure of a simple emulsifier (McClements and Weiss, 2005)

A fatty acid chain usually makes up the lipophilic section in food emulsifiers, while the hydrophilic section can be from different molecules. The hydrophilic section could simply be glycerol, as is the case with monoglycerides, or it could have a much larger structure through the reactions of monoglyceride derivatives. The amphiphilic character of emulsifiers allows them to concentrate and adsorb at the interface of two immiscible substances. Figure 1.7 displays an oil-soluble emulsifier concentrating at the interface between oil and water.

When an emulsifier is introduced in a solution, it will be soluble in the phase that it most associates with. An emulsifier that has a large lipophilic section in comparison will be soluble in oil, while more hydrophilic emulsifiers will be soluble in water. Emulsifiers go into solution by association, meaning they keep their structure while in solution (Morrison and Ross, 2002). The emulsifiers will adsorb at the interface between two immiscible substances at low concentrations.

As the concentration of emulsifier is increased, it will form into micelles within the substance in which it is soluble (Morrison and Ross, 2002).

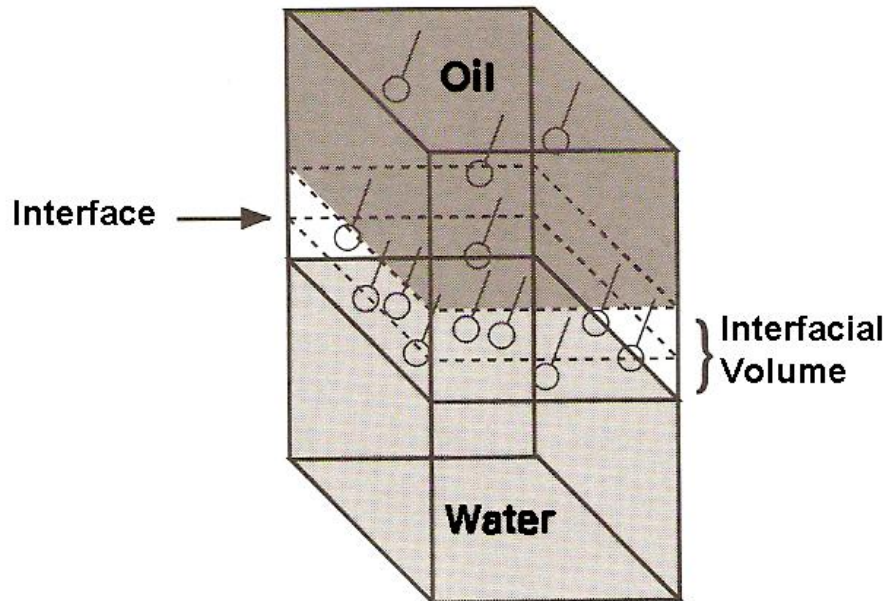


Figure 1.7 – Illustration of an oil soluble emulsifier concentrating at the interface (Stauffer, 1999)

An emulsion is described as the dispersion of one liquid into another immiscible liquid. When two materials that show a dislike for each are put in the same vicinity, they orient themselves in two separate phases. The phases will contain all of one material on one side of the area and all of the other material on the other side. The area where these two materials meet is called the interface. When two materials that dislike each other interact, they will seek this arrangement which minimizes the interfacial area. This is because this orientation has the lowest free energy. Food systems prefer to carry as little free energy as possible.

Adequate energy is needed to create emulsions. A stable emulsion will have a dispersed phase that is broken up into tiny droplets in the continuous phase. Figure 1.8 illustrates an emulsion with this type of configuration. The dispersed phase needs adequate energy to turn it into dispersed droplets of 1-100 micro meters in diameter for a stable emulsion to be reached (Stauffer, 1999). When shear is put on a liquid droplet, it will first elongate into a cylinder. Once the length of the liquid cylinder is one-and-a-half times the width, the cylinder will break up into smaller droplets. These droplets continue to be broken up into smaller droplets until shearing forces are no longer greater than interfacial tension forces (Stauffer, 1999). Figure 1.9 displays the creation of smaller droplets through shear. An emulsifier's ability to decrease interfacial tension allows smaller droplets to be created with lower shear forces. Having the dispersed phase in smaller droplets has a great effect on emulsion stability. Smaller droplets will slow down its sedimentation from gravitational forces. The rate of sedimentation of droplets is determined by the square root of its size (McClements and Weiss, 2005).

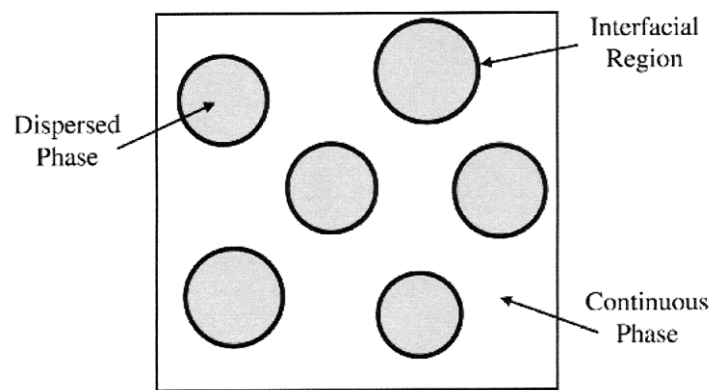


Figure 1.8 – Illustration of an emulsion (McClements and Weiss, 2005)

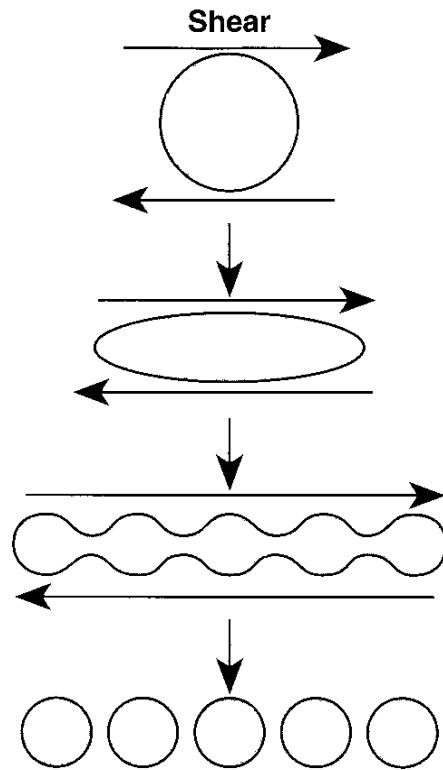


Figure 1.9 – Creation of smaller droplets in a dispersion through shear forces (Stauffer, 1999)

The two major types of food emulsions are oil-in-water and water-in-oil. Oil-in-water emulsions are where oil is dispersed as micelles in a continuous water phase. This type of emulsion is the most common in food applications. Some examples of oil-in-water emulsions are non-dairy creamers, cake batters, and mayonnaise. Water-in-oil emulsions are where micelles of water are dispersed in oil. Some food product examples of water-in-oil emulsions are margarine and butter (Stauffer, 1999).

Emulsions created between immiscible substances are thermodynamically unstable. The instability is due to the hydrophobic effect (McClements and Weiss, 2005). The hydrophobic effect explains that dispersed droplets tend to combine or coalesce when they come in contact

with each other. An emulsion needs to prevent the coalescence of the dispersed phase if it is to remain stable. Coalescence of the dispersed phase is prevented by having repulsive forces greater than attractive forces. Repulsive forces can range from building stronger, thicker, or more organized interfacial regions to creating an electrical charge on the surface of the dispersed substance or interacting with protein and fat molecules so they will form a network to stabilize the emulsion. Increasing the viscosity of the continuous phase through the addition of thickening agents can stabilize emulsions as well.

Creating a mechanically strong interfacial surface prevents coalescence of dispersed droplets in an emulsion. There are many ways to create strong interfaces. Interfaces that are condensed and organized contribute to stable emulsions. Emulsifiers that are balanced between being water-loving and fat-loving form condensed monolayers at the interface. Therefore, these emulsifiers form the most stable emulsions. The condensed monolayers resist coalescence of dispersed droplets due to hydrophobic interactions (Krog, 1977).

Steric hindrance can also increase emulsion stability. Steric hindrance is where the interfacial area forms a layer that prevents coalescence of the dispersed phase. Alpha-tending emulsifiers can form a protective fat layer on oil droplets. This protective layer increases emulsion stability (Stauffer, 1999). Proteins, gums, and polyoxyethelene derivatives can form a water layer on the dispersed phase which will prevent coalescence as well.

Electrical repulsion can help stabilize emulsions. This is where the micelles contain an electrical charge. The electrical charge prevents coalescence because positive charges repel other

positive charges and vice versa. Electrical charges are diminished with increasing ion or salt content (Stauffer, 1999). This will need to be considered when determining emulsion stability.

Increasing the viscosity of the continuous phase can help stabilize emulsions. By adding thickening agents, the mobility of the dispersed droplets can be reduced so that they do not come into contact with each other throughout the desired shelf life of the emulsion. Hydrocolloids are the most common thickening agents utilized in the food industry. The most common thickening agents are xanthan gum, alginate, carageenan, and guar gum (Carr et. al. 1995).

Repulsive forces are very important in stabilizing emulsions because attractive forces are ever-present. Van der Waals forces are referred to as the total attractive force that contributes to emulsions. Technically, Van der Waals forces can be attractive and repulsive, but in food emulsions this relatively weak force is almost always attractive (Walstra and Vliet, 2008). Dispersed droplets in an emulsion generally have a lower energy when they are in contact with each other than when in contact with water. Therefore, dispersed molecules show a constant attraction to each other. This constant attraction of dispersed molecules requires repulsive forces strong enough to prevent coalescence and destabilization of the emulsion. The food industry applies all of the preceding emulsion principles to create stable food emulsions. The application of various stabilizers ensures that the repulsive forces remain greater than attractive forces during the shelf life of the food product.

CHAPTER 2 – Characterizing Food Emulsifiers

Foods emulsifiers can be created through a number of different components. Each of these components alters the properties of the emulsifier. Therefore, food emulsifiers can perform different functions in the food industry through its composition. The most common food emulsifiers are monoglycerides, monoglyceride derivatives, fatty acid derivatives, and lecithin.

Monoglycerides

The oldest and most commonly used food emulsifiers are mono- and diglycerides and their purified form, distilled monoglycerides. These emulsifiers make up approximately 75% of the total annual production of commercial emulsifiers (Stauffer, 1999). Most commercial mono- and diglycerides contain 40-60% alpha monoglyceride content, with a free glycerol content of less than 2%. Alpha monoglycerides pertain to the configuration of the monoglyceride. Commercial monoglycerides contain a fatty acid chain connected to a glycerol molecule.

Glycerol is an alcohol containing three carbon atoms. If the fatty acid chain is connected to the first or third carbon atom, which is also considered the 1- or 3- carbon atom, it is considered an alpha monoglyceride. If the fatty acid chain is connected to the middle or 2- carbon atom, the molecule is considered a beta monoglyceride. Figure 2.1 displays monoglycerides in the alpha and beta configuration. Historically commercial monoglycerides have been measured by their alpha monoglyceride content. This is primarily due to the chemical method used to measure monoglyceride content. This wet chemical method only detects alpha monoglycerides and does not measure monoglycerides in the 2- configuration. The wet chemical method can only isolate the alpha monoglycerides because this method tests for periodic

oxidation (Lauridsen, 1976). Monoglycerides in the 2- configuration do not show up in this test. Measuring only the alpha monoglyceride content is not detrimental to the quality and reproducibility of commercial product because the ratio of 1-monoglycerides to 2-monoglycerides is measurable depending on the storage temperature. Table 2.1 displays the percentage of 1- to 2-monoglycerides at different storage temperatures. Today chromatography methods exist to measure both the 1- and 2-monoglycerides. These are reported as total monoglycerides. However, alpha monoglycerides have become recognizable in the food industry. Therefore, alpha monoglyceride remains the main specification in determining monoglyceride content.

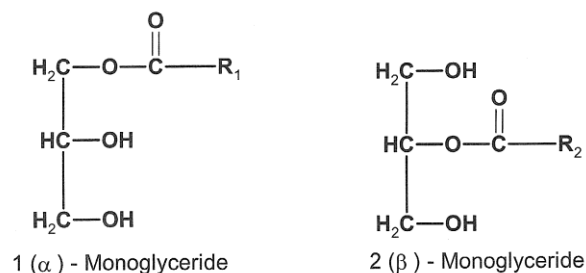


Figure 2.1 – The alpha and beta configuration of monoglycerides (Strayer et al. 2006)

Table 2.1 – Percentage of 1- and 2- monoglycerides dependent on storage temperature (Krog and Sparso, 2004)

Temperature (°C)	1-Monoglycerides (%)	2-Monoglycerides (%)
20	95	5
80	91	9
200	82	18

Commercial mono- and diglycerides are most commonly synthesized through glycerolysis. Glycerolysis is an interesterification process between an alcohol and an ester. In commercial products, the ester is a triglyceride from edible fats or oils, such as soybean, cottonseed, palm, or canola oil from vegetable sources or lard or tallow from animal sources. The alcohol in mono- and diglycerides comes from glycerol. When the triglyceride and excess glycerol are heated to elevated temperatures of 200-260°C, with the addition of an alkaline catalyst such as sodium or calcium hydroxide, the acyl residues or fatty acid chains from the triglyceride separate from the triglyceride and randomly form mono-, di-, and triglycerides and free glycerol (Senanayake and Shahidi, 2005; O'Brien, 2004; Krog and Sparso, 2004; Zielinski, 1997). Figure 2.2 displays the glycerolysis reaction. This figure effectively displays how triglycerides and glycerol form mono- and diglycerides. The glycerolysis reaction is an equilibrium process and the concentration of the mono- and diglycerides produced is dependent upon the ratio of triglycerides to edible fats and oils. Table 2.2 indicates the concentration of mono- and diglycerides produced through the glycerolysis reaction depending on the amount of glycerol added. Once equilibrium is reached, the catalyst is neutralized through the addition of a food grade catalyst. To make the product commercial quality, the neutralized catalyst is removed through filtration and the excess free glycerol is stripped off by vacuum distillation (Senanayake and Shahidi, 2005).

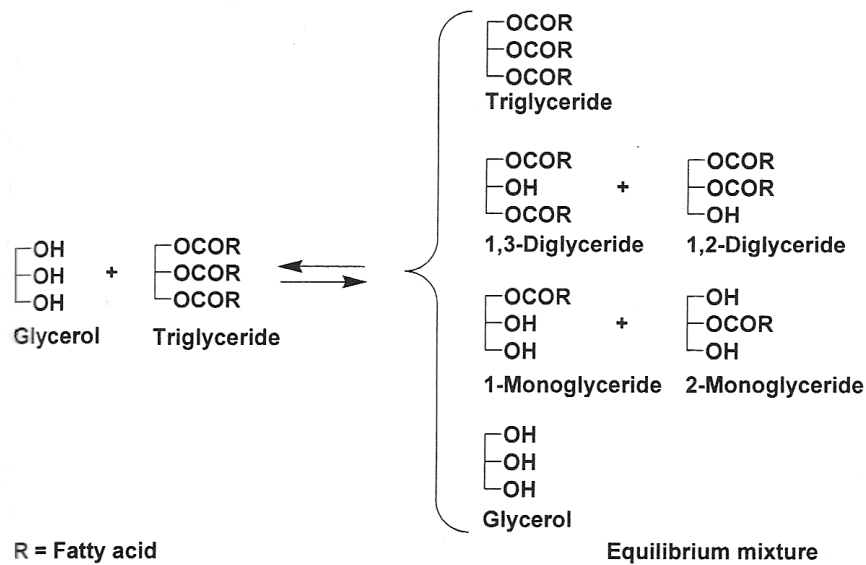


Figure 2.2 – Starting components and end products produced through the glycerolysis reaction (Krog and Sparso, 2004)

Table 2.2 – Mono-, di-, and triglyceride composition of commercial mono- and diglycerides according to the amount of glycerol added (Krog and Sparso, 2004)

Amount of glycerol added to triglyceride (% w/w)	Equilibrium mixture		
	Triglycerides (% w/w)	Diglycerides (% w/w)	Monoglycerides (% w/w)
0	100	-	-
7	35	50	15
14	15	45	40
16	11	43	46
20	8	39	53
24	5	35	60

Mono- and diglycerides can also be synthesized through the reaction of a fatty acid chain and an alcohol. This process is an acidolysis reaction. Figure 2.3 displays the acidolysis reaction. The higher cost of fatty acids when compared to edible fats and oils make this type of synthesis

not as prevalent in the industry (Senanayake and Shahidi, 2005). Generally mono- and diglycerides are only commercially produced in this manner when triglyceride-based products do not perform well.

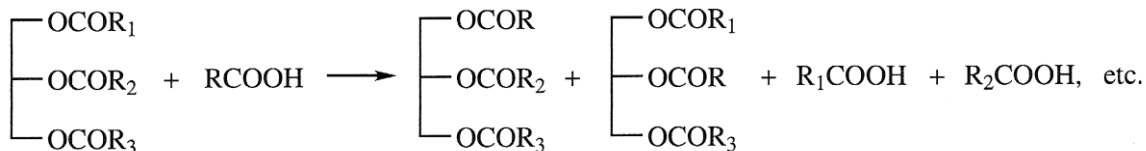


Figure 2.3 – Starting components and end products of the acidolysis reaction (Senanayake and Shahidi, 2005)

The production of mono- and diglycerides through an enzymatic process has been reportedly achieved (Krog and Sparso, 2004). However, the process to date is not efficient enough to be considered for commercial production. With the food industry trending towards natural products, an enzymatic process to producing mono- and diglycerides remains a topic of interest (Fisher and Carvajal, 2008).

The monoglyceride content can be raised to over 90% through molecular distillation. Figure 2.4 is a representation of a molecular still. The still is heated on the outside and has a condenser in the center. The 40-50% mono- and diglycerides product is run through a column at very low pressures. The low pressures are achieved through the use of a vacuum. The monoglycerides will evaporate and move towards the center of the still, where they will return to a liquid state once they come in contact with the condenser (Lauridsen, 1976). This material

contains over 90% monoglycerides and is collected for sale. The residue can either be recycled to maximize the monoglyceride yield or discarded.

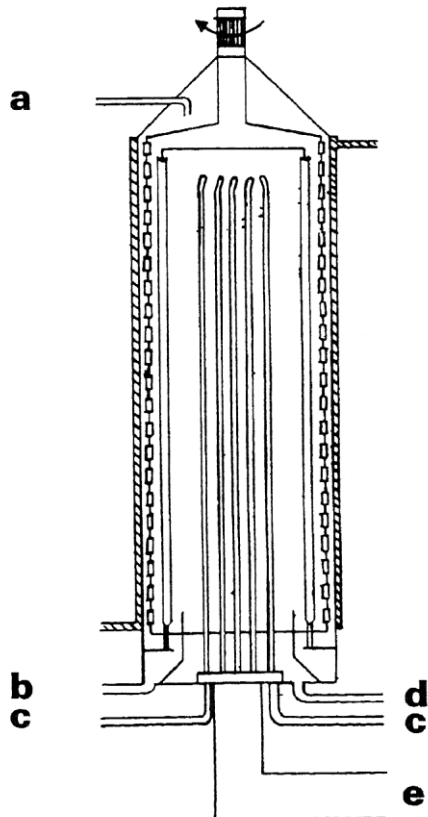


Figure 2.4 – Illustration of a molecular still used to produce distilled monoglycerides from mono- and diglycerides: (a) glycerolysis product inlet, (b) residue removal, (c) cooling medium in and out, (d) distillate removal, and (e) to vacuum pumps (Lauridsen, 1976).

Monoglyceride Derivatives

The combination of other molecules with monoglycerides creates emulsifiers that can have specialized functionalities. These emulsifiers can be categorized as monoglyceride derivatives. Figure 2.5 displays the many possible monoglyceride derivatives and their

components. In most cases the primary hydroxyl or 3- position in the monoglyceride contains the derivative of these reactions. This is because the primary hydroxyl is more chemically active than the secondary hydroxyl or 2- position (Stauffer, 1999). Some monoglyceride derivatives have been specially categorized as alpha-tending emulsifiers. These emulsifiers are named because they are stable in the alpha crystalline formation (Lauridsen, 1976). The alpha crystalline formation is very flexible and has been found to be very effective in whippable foams by facilitating fat agglomeration.

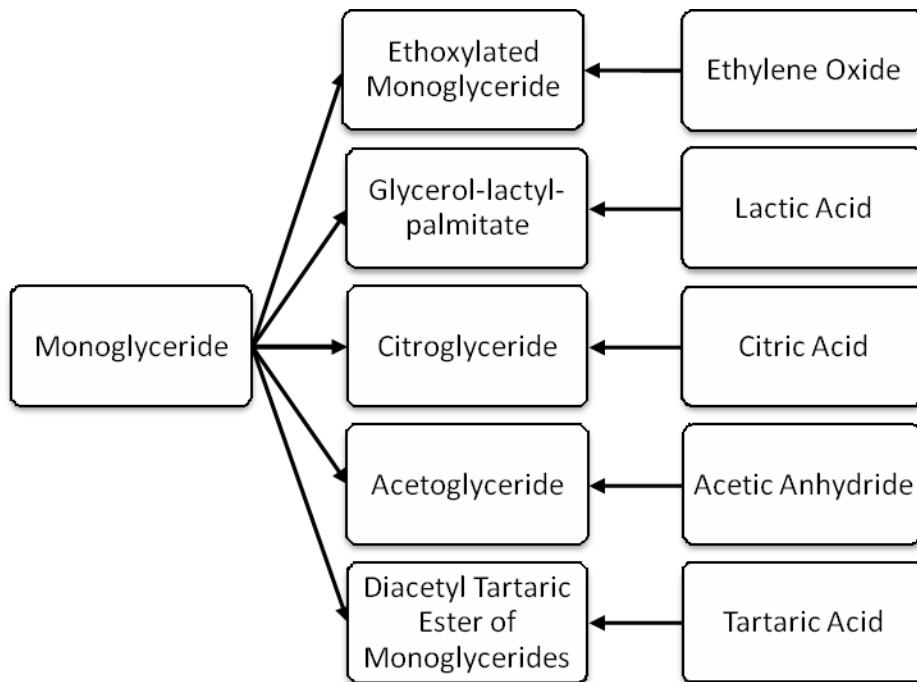


Figure 2.5 – The origin of some monoglyceride derivatives (adapted from Lauridsen, 1976)

Ethoxylated monoglycerides are created by reacting monoglycerides with ethylene oxide. Ethylene oxide can be highly explosive and the ethoxylation process is a highly exothermic

reaction (Zielinski, 1997). Therefore, safety measures and processing controls need to be closely monitored during production of these emulsifiers. The makeup of the monoglyceride determines the functionality of ethoxylated monoglycerides. More saturated ethoxylated monoglycerides work well as dough conditioners in yeast-leavened products and unsaturated ethoxylated monoglycerides work well in aeration of cakes and icings (O'Brien, 2004). Figure 2.6 displays the chemical structure of ethoxylated monoglycerides.

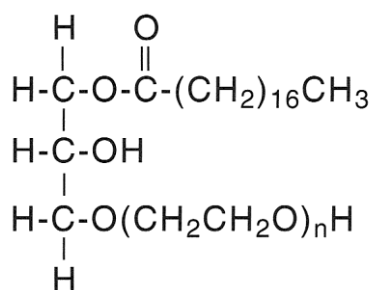


Figure 2.6 – Chemical structure of ethoxylated monoglycerides (Stauffer, 1999)

Glycerollactylpalmitates are created by reacting monoglycerides with lactic acid. Lactylated monoglycerides are more soluble in oil and have a lower melting point than similar monoglycerides (Zielinski, 1997). Glycerollactylpalmitates have been found to have excellent aeration ability and have been used in whipped toppings and cakes (O'Brien, 2004). Figure 2.7 displays the chemical structure of lactylated monoglycerides.

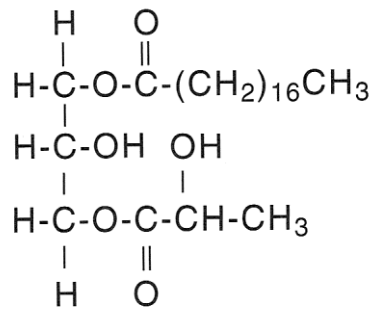


Figure 2.7 – Chemical structure of lactylated monoglycerides (Stauffer, 1999)

Citroglycerides or citric acid esters are created by esterifying monoglycerides with citric acid. The esterification of glycerol monooleate with citric acid produces monoglyceride citrate and the reaction of monoglyceride, stearyl alcohol, and citric acid produces stearyl monoglyceride citrate (Zielinski, 1997). These emulsifiers are not used commonly in the United States.

Acetoglycerides or acetic acids esters are created by reacting monoglycerides with acetic anhydride or by reesterifying monoglycerides with triacetin (Lauridsen, 1976). The properties of acetylated monoglycerides depend on the makeup of the monoglyceride and the degree of acetylation (O'Brien, 2004). Acetylated monoglycerides are alpha-tending emulsifiers. Therefore, they are effective in promoting fat agglomeration and corresponding aeration in whipped toppings. Figure 2.8 displays the chemical structure of acetylated monoglycerides.

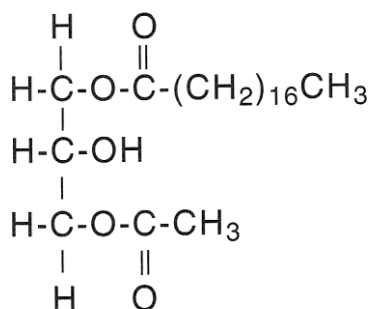


Figure 2.8 – Chemical structure of acetylated monoglycerides (Stauffer, 1999)

Diacetyl tartaric esters of monoglycerides or DATEM are created when monoglycerides are combined with diacetyl tartaric acid anhydride. DATEM is an anionic emulsifier, meaning that it carries a negative charge. This property allows DATEM to interact with proteins readily. Consequently, DATEM has been found to be an excellent dough strengthener when used in breads and other baked products. Figure 2.9 displays the chemical structure of DATEM.

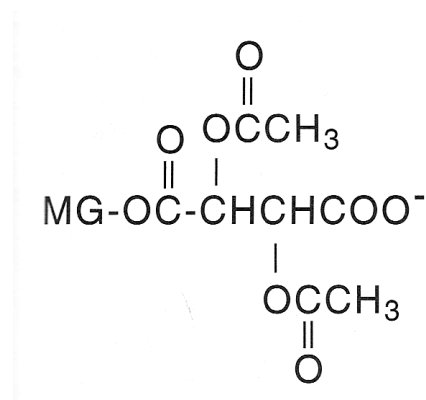


Figure 2.9 – Chemical structure of diacetyl esters of monoglycerides (Stauffer, 1999)

Fatty Acid Derivatives

Food emulsifiers can also be synthesized by direct esterification of fatty acids with other compounds. These emulsifiers are categorized as fatty acid derivatives. These emulsifiers also possess specialized functionalities similar to monoglyceride derivatives. Figure 2.10 displays some of the most popular fatty acid derivatives and their components.

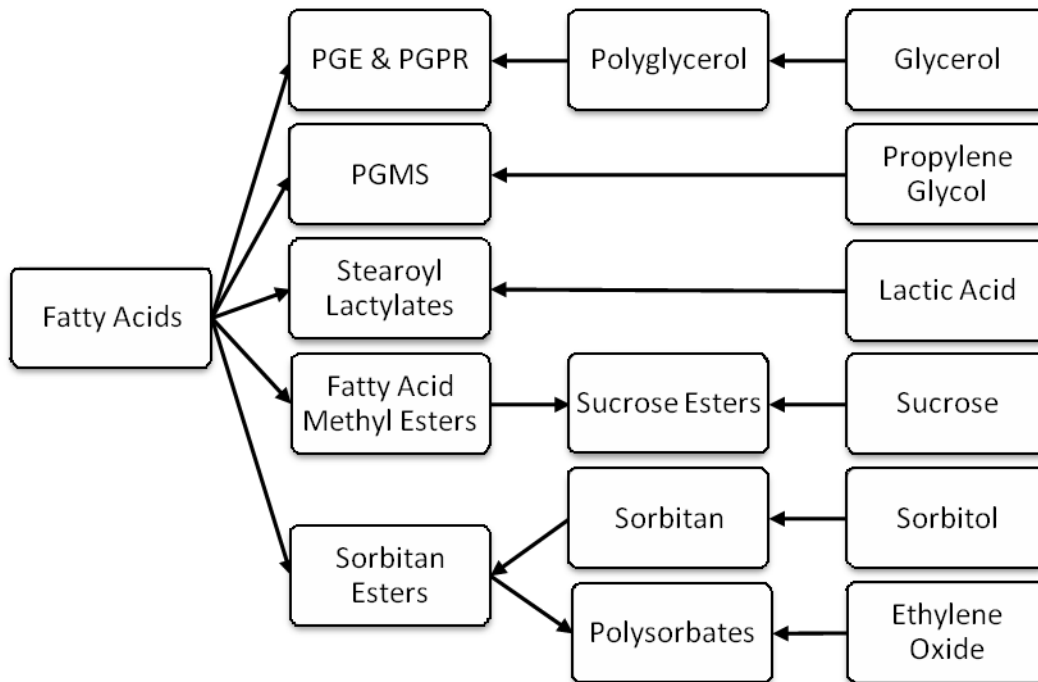


Figure 2.10 – The origin of some fatty acid derivatives (adapted from Lauridsen, 1976)

Polyglycerol esters are also known as PGE. They are created by first creating a polyglycerol. Then fatty acids are reacted with this polyglycerol to make the final product. The amount of polymerization depends on the functionality of the final product. During production,

the glycerine is put through the polymerization process until the desired refractive index or hydroxyl value is reached (Zielinski, 1997). Polyglycerol esters have a large range of applications. This is due to the large variation in final composition dependent on the amount of polymerization of the glycerol. Some of these applications are aeration in cakes and icings, antispattering agents in margarine, and crystal inhibition in salad oils (O'Brien, 2004). Figure 2.11 displays the chemical structure of polyglycerol esters.

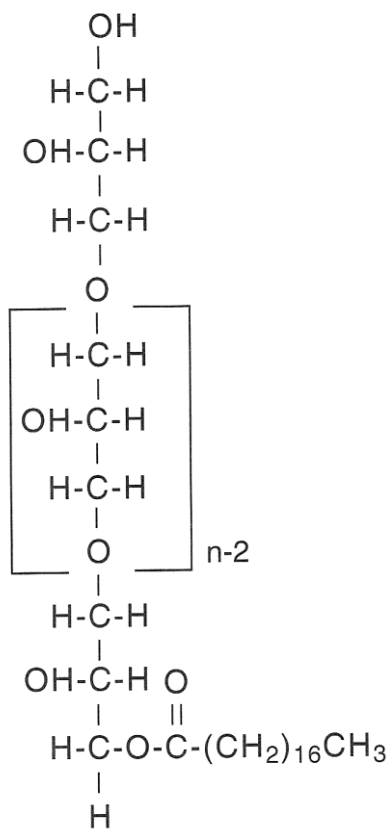


Figure 2.11 – Chemical structure of polyglycerol esters (Stauffer, 1999)

Propylene glycol esters are also commonly referred to as PGMS or PGME. These emulsifiers are created through either interesterification of propylene glycol with triglycerides or

by direct esterification with fatty acids. The two processes create somewhat different products. The interesterified product will produce mono- and diglycerides as well as propylene glycol esters (Zielinski, 1997). The direct esterification product contains only propylene glycol esters. Propylene glycol esters do not display very good emulsion stability attributes, however they are excellent aerators when liquid oil is in the formulation (O'Brien, 2004). That is because propylene glycol esters are alpha-tending emulsifiers. These emulsifiers have also been found to promote fat agglomeration and have extensive use in whippable toppings and other non-dairy whipped products (O'Brien, 2004). Figure 2.12 displays the chemical structure of propylene glycol monoesters.

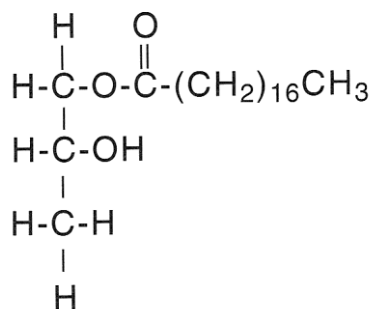


Figure 2.12 – Chemical structure of propylene glycol monoesters (Stauffer, 1999)

Stearoyl lactylates are created by reacting lactic acid with a fatty acid. The two most common stearoyl lactylates are sodium stearoyl lactylate and calcium stearoyl lactylate. The metallic salt used in the reaction will determine which product is produced (Zielinski, 1997). The use of calcium salts will produce calcium stearoyl lactylate and the use of sodium salts will produce sodium stearoyl lactylate. Stearoyl lactylates are anionic emulsifiers, meaning they carry a negative charge (Stauffer, 2005). These emulsifiers have been found to be excellent dough

strengtheners and conditioners in breads. Figure 2.13 displays the chemical structure of sodium stearoyl lactylate.

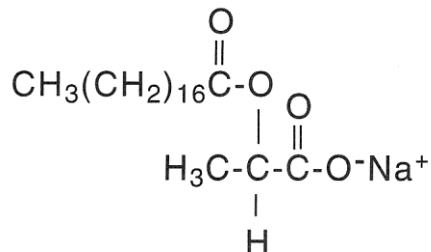


Figure 2.13 – Chemical structure of sodium stearoyl lactylate (Stauffer, 1999)

Sucrose esters are created by reacting sucrose with fatty acid methyl esters. Sucrose is insoluble in fatty acids. This insolubility requires the use of solvents in the synthesis of sucrose esters (Macdonald, 1968). The purification process of these esters utilizes either ethyl acetate, methyl ethyl ketone, or isobutyl alcohol as solvents (Zielinski, 1997). The production of sucrose esters is somewhat more complicated than the production of other commercial emulsifiers. Therefore, they are not used as frequently as other emulsifiers in the food industry. Figure 2.14 displays the chemical structure of a sucrose diester.

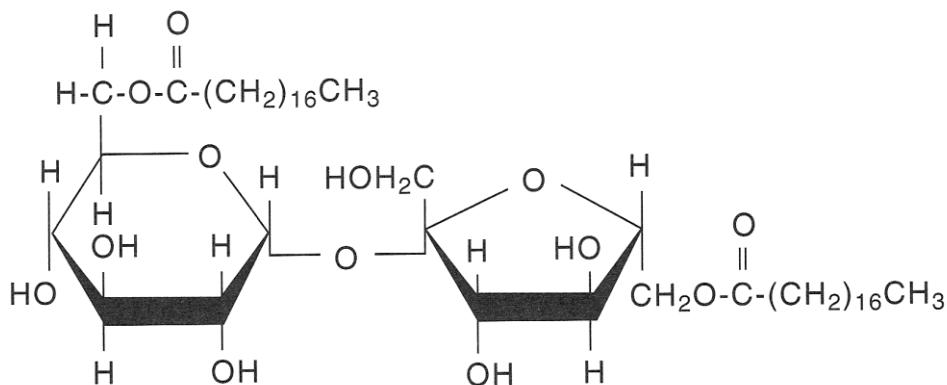


Figure 2.14 – Chemical structure of a sucrose diester (Stauffer, 1999)

Sorbitan esters are created by reacting sorbitan with fatty acids. These esters are slightly more water soluble than mono- and diglycerides (O'Brien, 2004). Sorbitan monostearate has commonly been used for aeration in cakes and icings (Wetterau et al. 1964; Stauffer, 1999). Sorbitan tristearate has been noted for its ability to inhibit crystallization in fats (Miskandar et al. 2007). Figure 2.15 displays the chemical structures of two sorbitan esters.

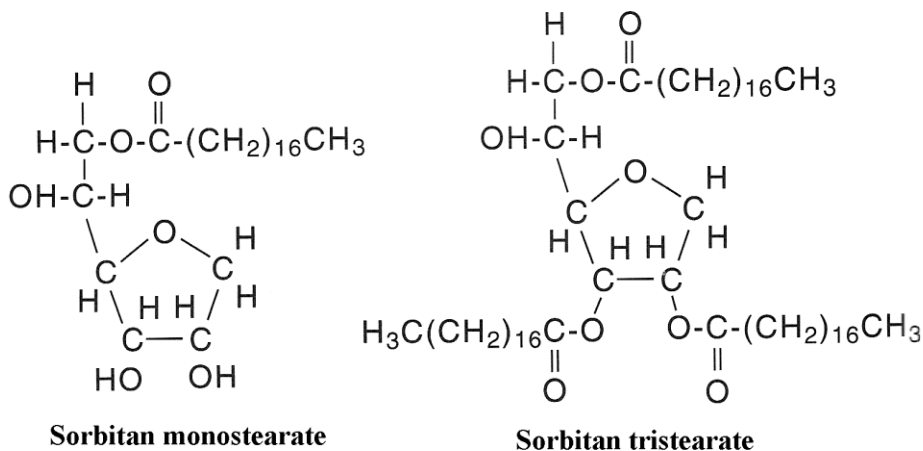


Figure 2.15 – Chemical structure of sorbitan esters (Stauffer, 1999)

Polysorbates are created by reacting sorbitan esters with ethylene oxide. The ethoxylation process is highly exothermic and care must be taken when producing these products. The final product is determined by the starting fatty acid. The ethoxylation of sorbitan monostearate creates polysorbate 60, sorbitan monooleate creates polysorbate 80, and sorbitan tristearate creates polysorbate 65 (Zielinski, 1997). These emulsifiers are highly hydrophilic and are used in cakes, breads, icings, and whipped topping applications. Figure 2.16 displays the chemical structures of two polysorbate esters.

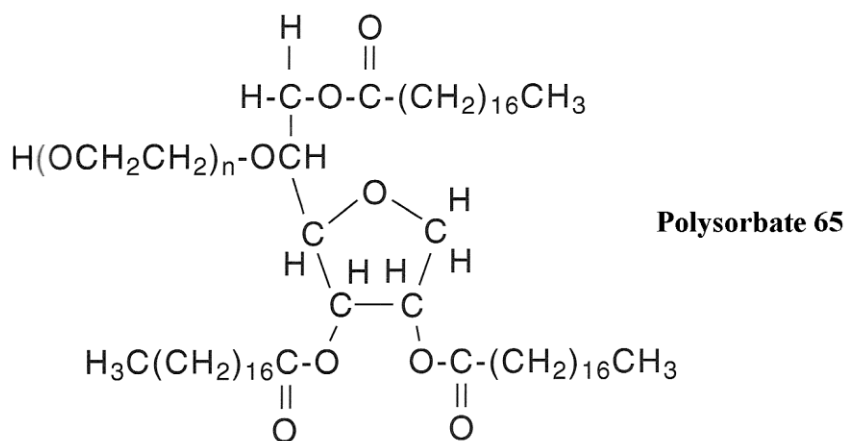
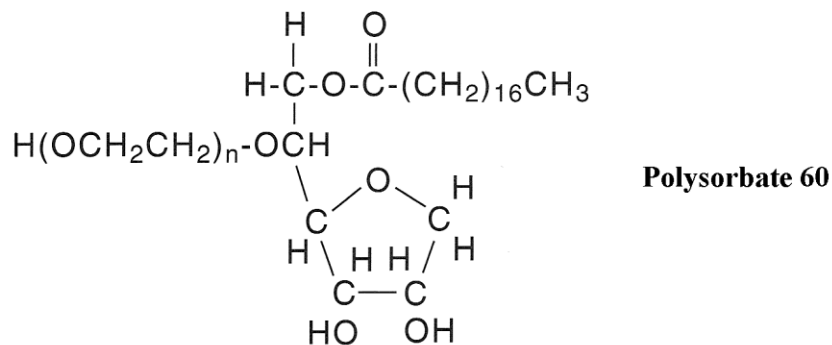


Figure 2.16 – Chemical structures of polysorbate esters (Stauffer, 1999)

Lecithin

Lecithin has been used in the food industry since the 1930s. Lecithin is a mixture of polar lipids. These lipids are extracted from the degumming process of crude vegetable oils (Szuhaj, 2005). Figure 2.17 displays the three principal components of soybean lecithin. The first food industry applications of lecithin were antispattering in margarines and viscosity reduction in confectionery products (Szuhaj, 2005). These applications of lecithin are still in use today. Lecithins have been known to be excellent wetting agents in food.

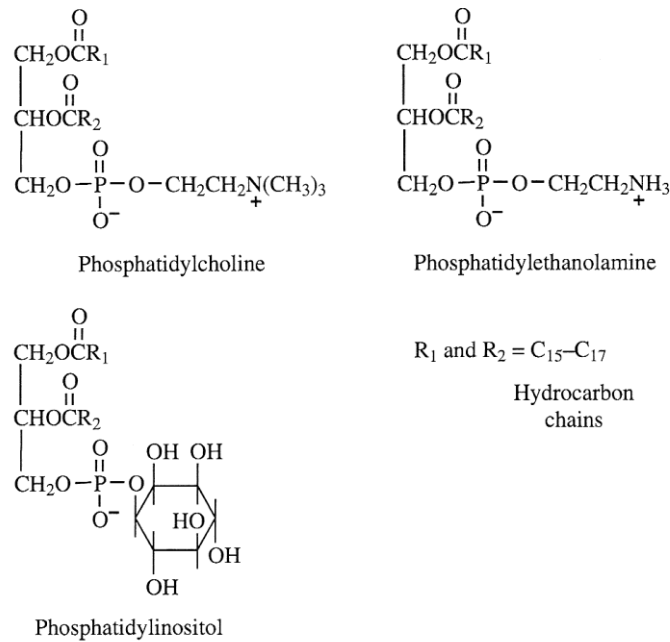


Figure 2.17 – Principle components of lecithin (Szuhaj, 2005)

Hydrophilic/Lipophilic Balance Scale

The HLB or hydrophilic/lipophilic balance is very popular in characterizing emulsifiers. The concept was introduced by Griffin in 1949 which explained that the balance between

hydrophilic and lipophilic parts of molecules determine which type of emulsions are formed. Emulsifiers are assigned a numerical value dependent on its components (Stauffer, 1999). Hydrophilic groups of an emulsifier contribute positive values while lipophilic groups contribute negative values (Walstra and Vliet, 2008). Table 2.3 illustrates some of the values that functional groups of an emulsifier contribute to the final HLB value. The sum of these values are added or subtracted from 7 to determine the HLB value of an emulsifier (Walstra and Vliet, 2008; Stauffer, 1999). From this HLB value, various properties of emulsifiers can be assumed. For example, emulsifiers with HLB values below 6 indicate good water-in-oil emulsifiers, between 7 and 9 indicate good wetting agents, and above 10 indicate good oil-in-water emulsifiers (Stauffer, 1999). Furthermore, the HLB value indicates whether the emulsifier is water or oil soluble. Emulsifiers with low HLB values are soluble in oil while high values are soluble in water (Walstra and Vliet, 2008). Consequently, HLB values are helpful when determining which emulsifiers will perform the best in a given application. For example, margarines are a water-in-oil emulsion. Low HLB emulsifiers, such as glycerol monostearate, are an excellent place to start testing an emulsifier in this type of system. If the application contains a oil-in-water emulsion, such as a beverage, then polysorbates would be an excellent selection due to their high HLB values. Often when formulating, the most stable emulsions are created with a combination of a high and low HLB value emulsifiers (O'Brien, 2004). Table 2.4 lists the HLB values of some common food emulsifiers.

The HLB scale receives some criticism because it is determined on a pure system of oil and water. Food systems contain many different ingredients, such as sugar, starch, and salt that can affect which emulsifier is optimal (Stauffer, 2005). However, the HLB scale remains a

valuable tool for recognizing emulsifiers with the same attributes and how they may function in a given application.

Table 2.3 – Functional group contribution to the hydrophilic/lipophilic balance of an emulsifier (Stauffer, 1999)

Group	Value
-COOK ^{3 3}	21.1
-N(CH ₃) ₃	9.4
Sorbitan ring ester	6.8
-COOH	1.9
-OH (sorbitan ring)	0.5
-OH ₂ (other)	1.9
-CH ₂ -	-0.475

Table 2.4 – Hydrophilic/Lipophilic Balance values of common food emulsifiers (Stauffer, 2005)

Surfactant	HLB
Sodium stearyl lactylate	21.0
Polysorbate 80 PE(20) sorbitan monooleate	15.4
Polysorbate 60 PE(20) sorbitan monostearate	14.4
Sucrose monostearate	12.0
Polysorbate 65 PE(20) sorbitan tristearate	10.5
Diacetyl tartaric ester of monoglyceride	9.2
Sucrose distearate	8.9
Triglycerol monostearate	7.2
Sorbitan monostearate	5.9
Succinylated monoglyceride	5.3
Glycerol monostearate	3.7
Propylene glycol monostearate	1.8

CHAPTER 3 – Emulsifier Interactions

The functionality of emulsifiers is highly dependent on their interaction with other substances in food products. Emulsifiers are able to interact with water, fats and oils, proteins, and carbohydrates. Emulsifiers perform different functions in foods depending on the substances they interact with.

Emulsifier/Water Interactions

The interaction between emulsifiers and water has been highly studied and is the most complex of all emulsifier interactions. This complexity is due to the ability of emulsifiers to form mesophases with water. However, the phases formed are dependent on many factors. Each type of emulsifier will be unique in which mesophases they form with water. These mesophases are temperature and concentration dependent. Even altering the lipophilic section of the emulsifier will greatly alter how emulsifiers interact with water. For example, mono- and diglycerides made from a fully hydrogenated source compared with mono- and diglycerides that are from an unsaturated source do not interact similarly with water.

Monoglycerides, diglycerides, and triglycerides in crystalline form have a hydrophobic surface (Birnbaum, 1971). The lipophilic fatty acid chain protects the hydrophilic glycerol section. This prevents water from interacting with the hydrophilic section of the emulsifier. Hydrated emulsifiers have a modified configuration with their hydrophilic sections exposed to the surface. This configuration enables them to interact with water and become functional ingredients in food systems. The study of emulsifier interactions with water is important because

it explains at what conditions emulsifiers become hydrated. These conditions can then determine how to maximize emulsifier functionality.

The way monoglycerides interact with water depends on the concentration and the temperature of the solution. Emulsifiers demonstrate mesomorphism with water at different concentrations and temperatures. Phase diagrams have been created that illustrate the many configurations emulsifiers form with water. Phase diagrams of emulsifier systems have been constructed using X-ray diffraction technology. X-ray diffraction easily differentiates the mesophases that are created when emulsifiers interact with water. Sharp diffraction lines will appear indicating long spacings in the structure whereas no diffraction lines in the small-angle region indicate disordered chains (Larsson, 2004). The pattern of the diffraction lines can classify which liquid-crystal phase the emulsifier and water are in. The lamellar liquid crystalline phase is recognized by long spacings in the ratio of 1:2:3 and so on (Larsson, 2004). The thickness of the water layer can be estimated from these spacings. Conversely, the hexagonal liquid crystalline phase diffraction pattern contains long spacings where the square roots are in the ratio of 1:3:4:7:12 and so on (Larsson, 2004). Finally, the cubic liquid crystalline phase reveals a pattern where the square root of the long spacings are at ratios of 1:2:3:4 and so on (Larsson, 2004). Identification of the various mesophases of emulsifiers with water helps determine the efficacy of emulsifiers in food systems.

Monoglycerides can form into three mesophases with water. These phases only form at temperatures above the solid-crystalline state of the monoglyceride (Zetzi et al. 2009). This temperature is referred to as the Krafft temperature. The mesophases consist of the lamellar,

hexagonal, and cubic liquid crystalline phase. Figure 3.1 illustrates the three mesophases formed by emulsifiers. The lamellar phase has been found to be the most functional. In this phase the lipid liquid crystals form a bilayer with a water layer in between (Larsson, 2004). The lamellar liquid-crystalline phase converts to an alpha-gel once the liquid crystals are cooled. This alpha-gel configuration allows easier distribution of the emulsifier to the interface resulting in maximum functionality (Richardson et al. 2002). If the temperature and water concentration is raised from the lamellar phase, the emulsifier can form into a cubic liquid crystalline phase. This phase contains spheres of water surrounded by monoglycerides (Stauffer, 1999). The switch toward the cubic phase is accompanied by an increase in viscosity. The third mesophase is the hexagonal phase. This phase contains cylinders of monoglyceride surrounded by water (Stauffer, 1999). The reverse of this, or cylinders of water surrounded by monoglyceride, is called the hexagonal II phase. Figure 3.1 displays this configuration.

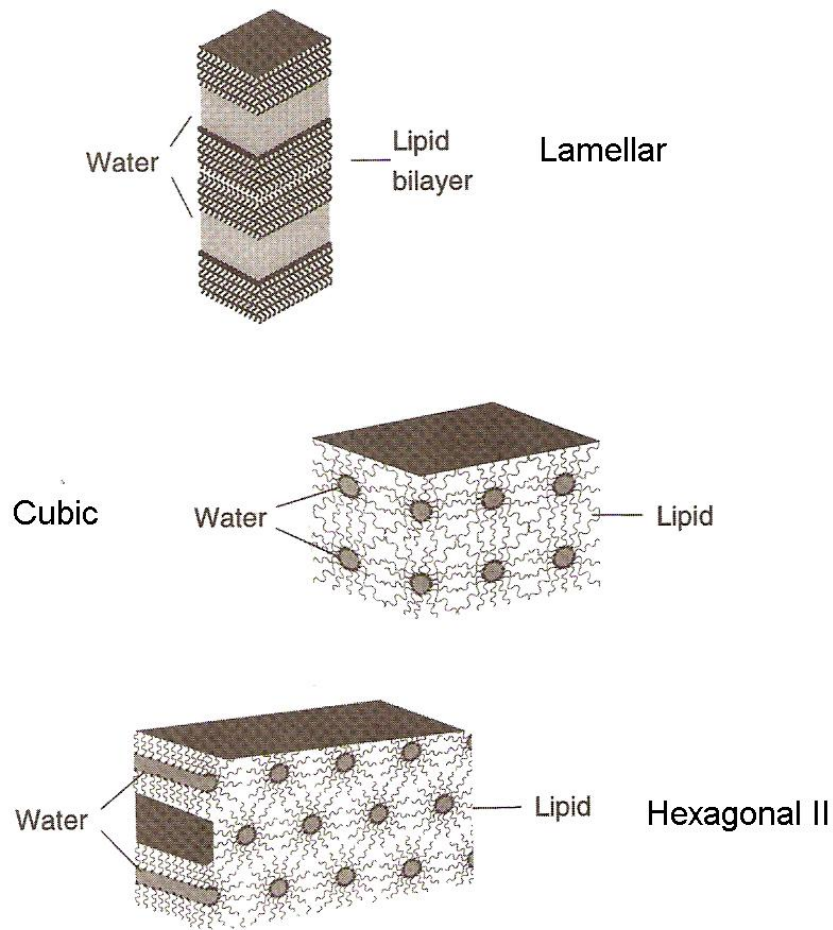
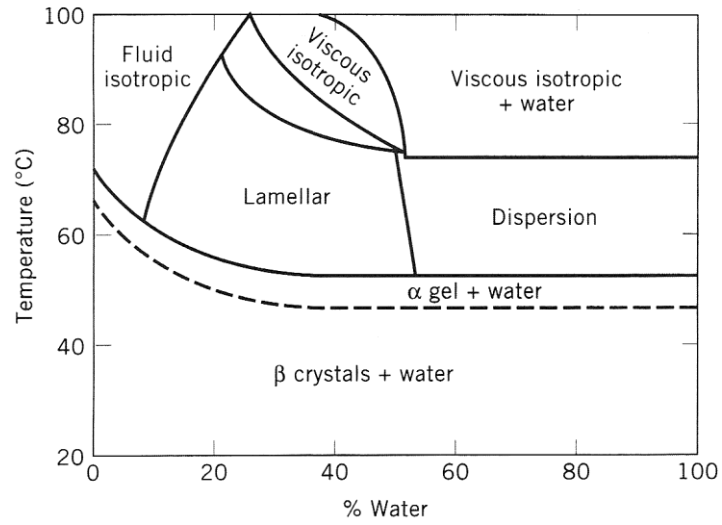


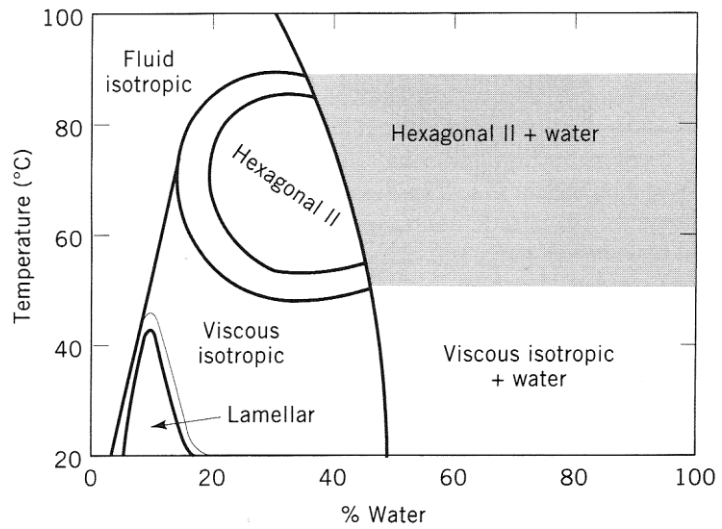
Figure 3.1 – The lamellar, cubic, and hexagonal configuration of monoglycerides and water (Stauffer, 1999)

Phase diagrams have been created on various emulsifiers. X-ray diffraction identifies the mesophase at various temperatures and concentrations of the water and emulsifier solution. Figure 3.2 illustrates the phase diagrams for a fully saturated and unsaturated monoglyceride. These phase diagrams are a valuable tool in explaining why certain emulsifiers are more functional than others in certain applications. As mentioned previously, emulsifiers in the

lamellar configuration have been found to be more functional than the hexagonal and cubic phases. If the emulsifier never leaves the beta crystals and water section, then little functionality can be expected. Alpha-tending emulsifiers do not form the standard mesophases with water (Krog, 1977). However, they are dispersible in water. Figure 3.3 illustrates a phase diagram of diacetyl tartaric esters of monoglycerides. Its functionality in cakes, whipped toppings, and breads demonstrates that achieving the desired mesophase is not the only factor that should be considered. Many other interactions determine how an emulsifier system functions in foods.



(a)



(b)

Figure 3.2 – Phase diagrams of monoglycerides in water. (a) Refers to a distilled monoglyceride from fully saturated lard and (b) refers to a distilled monoglyceride from sunflower oil (Stauffer, 2005)

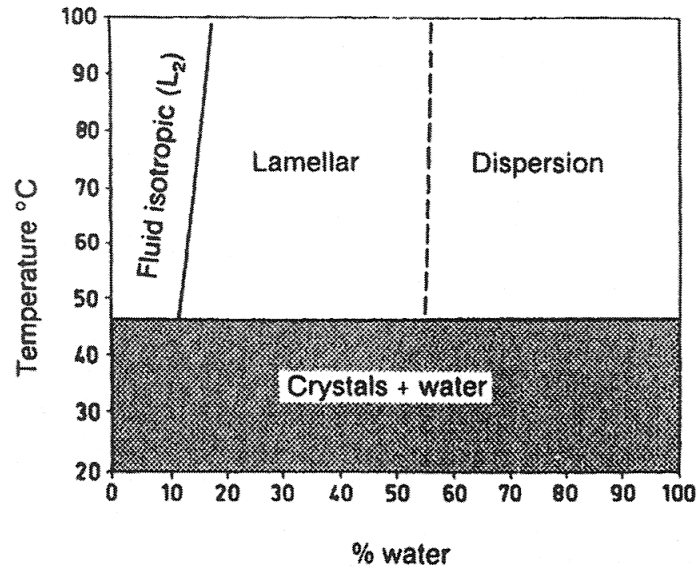


Figure 3.3 – Phase diagram of diacetyl tartaric esters of monoglycerides in water at a pH of 5 (Krog and Sparso, 2004)

Setting the correct liquid crystal formation at higher temperatures can bring optimum functionality to the emulsifier once it is cooled to its solid crystal form (Birnbaum, 1971). This type of procedure is utilized in emulsified shortenings and commercial hydrated emulsifiers. During the production of commercial hydrates, water and emulsifier are added at the right temperatures so that they are in the lamellar configuration. Then the solution is cooled. Upon cooling, the lamellar structure transforms into an alpha gel (Krog and Sparso, 2004). Alpha gels have the same structure as the lamellar phase, except the liquid crystals are now solid. This alpha gel converts to a coagel of these crystals and free water during storage. The coagel remains a highly functional form for emulsifiers (Krog and Sparso, 2004). Setting the lamellar configuration can also be done in the processing of a final product. For example, Moncrieff (1970) describes a process in which polyglycerol esters are used to create a very low density

icing. To achieve this, hot water was used for aeration to take place. This illustrates how this particular polyglycerol ester most likely moves into the lamellar phase at hot water temperatures.

Emulsifier/Fat Interactions

Emulsifiers affect fat in many ways. They can promote or inhibit crystallization, determine which crystal configuration the fat crystallizes into, and increase fat's dispersion throughout a product. Emulsifiers interact with fats and oils mainly through their hydrophobic groups (Miskandar et al. 2007). The most widely used application of emulsifiers with fat is emulsified shortenings. The use of emulsified shortenings allows the fat to be more finely distributed in food systems. The increased dispersion is implemented by the emulsifier's ability to reduce the interfacial tension between the fat and water during production (Miskandar et al. 2007).

Emulsifiers act with shortenings to help disperse ingredients in icings and cakes. This dispersion creates a greater and finer distribution of the shortening. The shortening traps air bubbles inside itself during the mixing process in cake production. With the help of emulsifiers, shortening is more evenly and finely divided within the batter. This dispersion results in air bubbles that are greater in number and more consistent in size. Water vaporizes inside these air bubbles during baking, contributing to increased volume in the finished cake (Painter, 1981). Another mechanism for increasing the volume in cakes occurs when gas is produced from chemical leavening agents. This gas combines with air cells during baking also contributing to increases in volume. The finer distribution of air cells results in a finer and more even crumb

and a texture with increased tenderness. The finer distribution of air cells also creates thinner cell wall structures, leading to a softer eating sensation (Painter, 1981).

Because emulsifiers affect fat crystallization, they can be used to either promote or inhibit crystallization depending on the emulsifier (Moncrieff, 1970). Miskandar et al. (2007) has performed research testing the theory that emulsifiers with similar acyl groups to the fat phase will promote crystallization and dissimilar groups will inhibit crystallization. This same principle can be used to explain how emulsifiers can affect the final crystal structure of a food product.

Emulsifiers are able to influence which crystalline phase the fat stabilizes into. For example, margarines sometimes incorporate sorbitan monostearate to prevent the fat phase from converting to the beta polymorph from the beta prime polymorph (Stauffer, 2005). Over time, fat in the beta prime configuration can convert to the more stable beta form. While the beta configuration is more stable, it is usually less favorable to the food industry. Fat stabilized in the beta configuration does not aerate as well and displays a grainier texture and appearance. By the addition of some emulsifiers, this conversion from the beta prime to beta configuration can be delayed (Stauffer, 1999). Since the emulsifier is slightly different in structure than triglycerides, it interferes with tight packing of fat crystals. Tight crystal packing is characteristic of the beta configuration. This interference by emulsifiers ultimately extends the stability of the beta prime configuration (Stauffer, 1999).

Emulsifier/Protein Interactions

The ability of proteins to perform multiple functions in foods makes them similar to emulsifiers. Proteins can act as stabilizers since they contain both hydrophobic and hydrophilic

parts. They also are able to give structure to foods. Emulsifiers interact with proteins to help strengthen the gluten network in baked goods, as well as compete with proteins for distribution onto the interfacial region.

The formation of a gluten network in dough is considered a large contributor to the strength and volume in baked goods. Gluten is made up of two main groups of proteins. These proteins are gliadin and glutenin. The gluten proteins align themselves into a network throughout the mixing and fermentation process (Hoseney, 1998). This gluten network is responsible for the volume and eating quality in baked goods. Figure 3.4 illustrates the gluten fibril network in well-mixed dough. Many commercial emulsifiers promote the formation of the gluten network. These emulsifiers are commonly known as dough strengtheners or conditioners. The most common dough strengtheners or conditioners are sodium stearoyl lactylate, ethoxylated monoglycerides, calcium stearoyl lactylate, polysorbates 60, and diacetyl tartaric acid esters of mono- and diglycerides (Hoseney, 1998; Stauffer, 2005). Dough strengtheners or conditioners result in baked products that are greater in volume and more tolerant to abuse during processing (Hoseney, 1998).

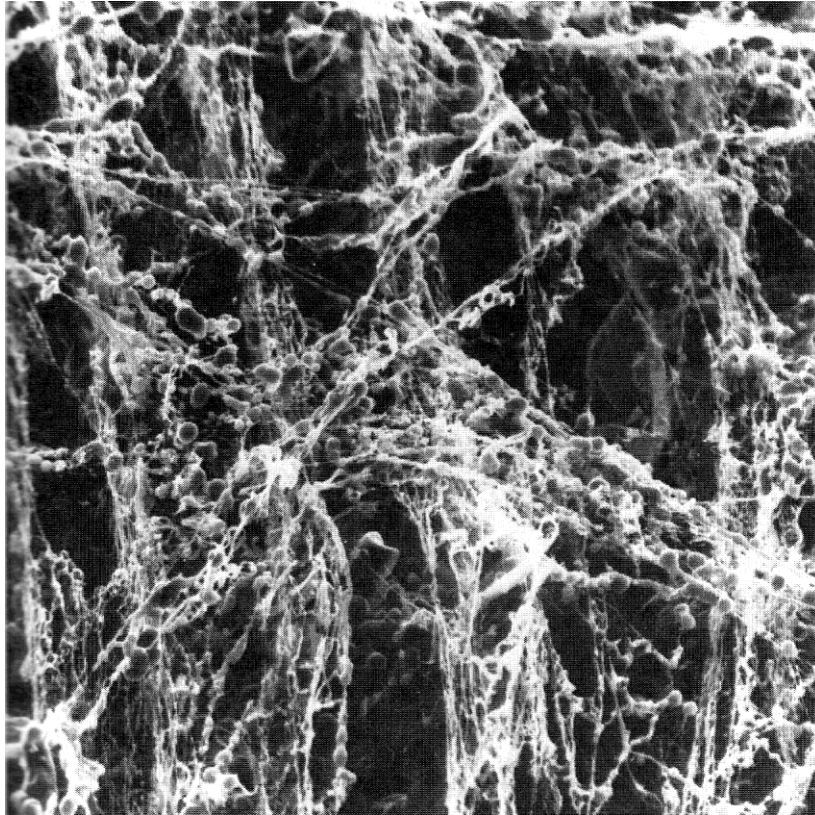


Figure 3.4 – Scanning electron microgram of dough demonstrating a strong gluten network (Hoseney, 1998)

Proteins often compete with emulsifiers for attachment to the interfacial surface. Proteins usually have their hydrophobic sections oriented toward the center of the protein molecule. Sometimes proteins have exposed hydrophobic sections as well. These sections allow proteins to adsorb to the interface. Figure 3.5 displays how hydrophobic patches allow proteins to adsorb on the interface of an emulsion. Emulsifiers interact with proteins affecting how they behave with the interface. Emulsifiers can either denature or displace proteins through interactions (Stauffer, 2005). The displacement of proteins sometimes only affects sections of a protein molecule. This can greatly affect the stability of emulsions. Emulsifiers will generally displace the loosely-

bounded protein first. By selectively displacing proteins, the emulsifier can increase the stability of emulsions (Stauffer, 1999). Once proteins become denatured, they will uncoil and allow the hydrophobic sections to interact with other molecules. Displaced proteins by emulsifiers have been linked to increased foam stability with egg whites (Stauffer, 2005). Therefore, emulsifiers are able to affect the stability of emulsions through both denaturing and partial displacement of proteins.

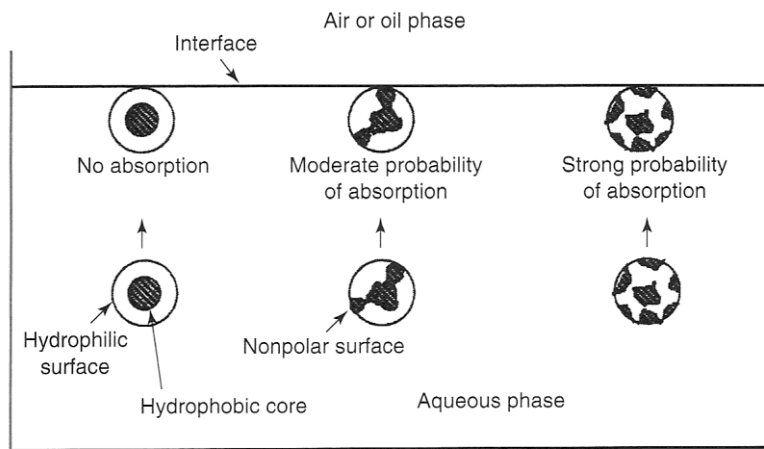


Figure 3.5 – Protein adsorption at the interface of an aqueous and air or oil phase through hydrophobic patches (Damodaran, 2008)

Emulsifiers also can be used to promote fat agglomeration in whipped toppings and ice cream. Fat agglomeration is responsible for much of the structure and texture in these food systems. Proteins migrate to the fat globular surface in these systems. These proteins will create a film over the fat globule surface that inhibits fat agglomeration. The film is difficult to remove since the proteins are held together through hydrophobic interactions. Emulsifiers interact with the proteins. This interaction only allows proteins to interact with each other through hydrogen

bonds rather than strong hydrophobic interactions. This will allow the protein film to be easily removed, resulting in fat agglomeration (Krog, 1977). Then the agglomerated fat crystallizes. The crystallized, agglomerated fat provides the structure and stability in whippable emulsions.

Emulsifier/Carbohydrate Interactions

Emulsifiers are able to interact with carbohydrates. The most noticeable emulsifier interaction with carbohydrates is with starch. Emulsifiers are able to affect the way starch behaves when it is heated and cooled in the presence of water.

Starch at ambient temperatures exists as highly ordered granules. This order allows the starch granule to display birefringence. Birefringence is the ability to split light into two beams. This allows highly ordered starch granules to be easily identified. Birefringence in starch granules displays a “maltese cross” formation under a polarized microscope. Figure 3.6 shows starch granules with the maltese cross. This configuration makes starch granules mostly insoluble in water at lower temperatures.

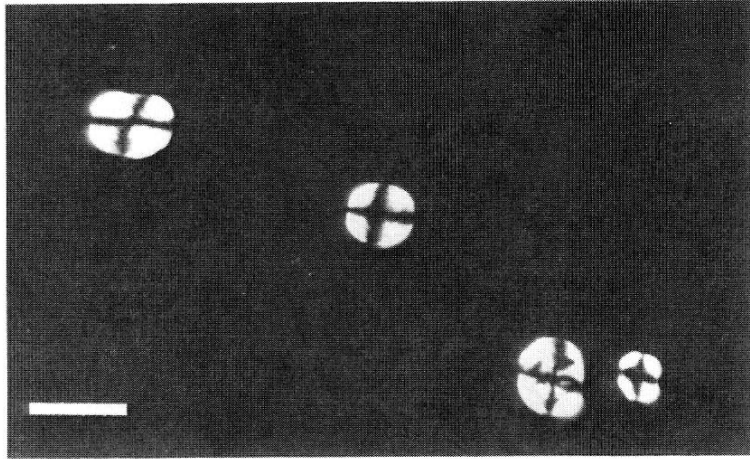


Figure 3.6 – Polarized microscopy illustrating wheat starch granules displaying the maltese cross configuration (Hoseney, 1998)

Starch is composed of long chains of glucose units. These glucose units form into two distinct types of polymers, amylose and amylopectin. Amylose has a long, linear structure that contains an average of 1,500 anhydroglucose units and a molecular weight that varies from 250,000 to 1.9 million (Hoseney, 1998; Pylar, 1988). The glucose units in amylose are linked through α -1,4 bonds. Amylopectin possesses a branched structure. While the majority of glucose units in amylopectin are linked through α -1,4 bonds, 4-5% of the bonds are α -1,6 bonds (Hoseney, 1998). These bonds allow amylopectin to assume a branched structure. The average chain length of amylopectin is only 20-30 glucose units, but the molecular weight of amylopectin can be up to 100 million (Pylar, 1988; Hoseney, 1998).

The two distinct polymers of starch, amylose and amylopectin, are important because each polymer behaves differently throughout gelatinization and retrogradation. Consequently, emulsifiers interact with each starch polymer differently. Therefore, the ratio of amylose to

amylopectin in different starches determines how effective emulsifiers are on the system. Many changes occur to starch granules when they are in the presence of water. The starch granules will swell if the water is at ambient temperatures. They will maintain their highly ordered structure and birefringent character. The granules will return to their original state if the water is removed. However, if the water and starch are heated to high enough temperatures, the starch granule goes through irreversible changes. These changes affect amylose and amylopectin differently, so the amounts of each polymer are important determining the nature of these changes.

As mentioned previously, starch granules swell with water at lower temperatures. However, as the temperature increases to around 140°F, the starch granule starts to lose its birefringence (Pylar, 1988). This is due to the breakage of the weaker bonds in the starch granule. This allows water to penetrate deeper into the amorphous areas of the granule, leading to gelatinization. Gelatinization of starch occurs when the crystalline organization of the starch granule is destroyed. This is accompanied by a loss of birefringence. The temperature of gelatinization is dependent of the composition of amylose and amylopectin in the starch granule.

Cultivars of grains and vegetables differ in their amylose content, amylopectin content, and proportions of amylopectin chain lengths. These differences have been shown to affect gelatinization characteristics. It is generally found that amylose content is negatively correlated with onset and peak temperatures of gelatinization (Varavinit et al. 2003). This can be explained by starch granules containing greater amounts of amylose and having more amorphous and less crystalline regions, allowing quicker and lower temperature gelatinization (Varavinit et al. 2003). Therefore, a high-amylose starch would gelatinize much quicker than a low-amylose or waxy

starch. Rice starch has been found to have the opposite relationship. Non-waxy or high-amylose rice varieties have been found to have higher gelatinization temperatures than waxy varieties. This is explained by the non-waxy varieties containing less crystalline regions from amylopectin. The crystalline regions are thought to restrict hydration of the amorphous regions, leading to a delay in gelatinization (Park et al. 2007).

Amylopectin chain length also alters the gelatinization of starch. Higher proportions of long chain length amylopectin result in more crystalline granules. The greater crystallinity provides more structural stability and makes the granules more resistant to gelatinization, ultimately leading to higher gelatinization temperatures (Singh et al. 2008). New variants of starches are continuously discovered and created with differing gelatinization properties. The genetics of these new starches can greatly affect how they behave during processing and are important in the control of starch gelatinization.

Emulsifiers differ on their effect on the gelatinization of starch. This difference is dependent on the type of emulsifier. Emulsifiers can inhibit the swelling of starch granules by preventing amylose from leaching out of the granule and also by forming a film around the granule (Siswoyo and Morita, 2001; Richardson et al. 2003). Both complexing and inhibition of granular swelling increase the gelatinization temperature of starch. The gelatinization temperatures of starch tend to increase when amylose forms complexes with emulsifiers of longer chain length (Siswoyo and Morita, 2001). However, some emulsifiers do not increase the gelatinization temperature of starch. Sodium dodecyl sulfate and polysorbate 60 do not complex with starch and do not increase the gelatinization temperature (Ghani et al. 1999; Richardson et

al. 2003). It is even theorized that sodium dodecyl sulfate may increase the swelling of starch, which potentially can decrease the gelatinization temperature.

Gelatinized starch will either form a gel or precipitate into insoluble particles upon cooling (Schoch, 1965). This phenomenon is known as retrogradation. Retrogradation has historically been linked to amylose. Amylose leaches out of the starch granule throughout gelatinization. These linear molecules readily crystallize out of solution. This crystallization has been recognized as the cause of staling in bread products and stickiness in pasta and potato products (O'Brien, 2004). However, if amylose forms complexes with organic acids, then it cannot crystallize with itself (Hoseney, 1998). Amylose possesses a helical arrangement with a hydrophobic inner surface (Stauffer, 1999). This arrangement allows emulsifiers or other organic acids to insert themselves into the helix and form a complex. Figure 3.7 illustrates amylose complexing with an emulsifier. Emulsifiers that effectively form complexes with starch can extend the shelf life of food products. The shelf life of baked products can be measured through the force it takes to compact a baked product a set distance. Figure 3.8 demonstrates the effect of shortening and monoglycerides on softness. The bread sample that contained shortening with monoglycerides remained the softest and therefore has the longest shelf life.

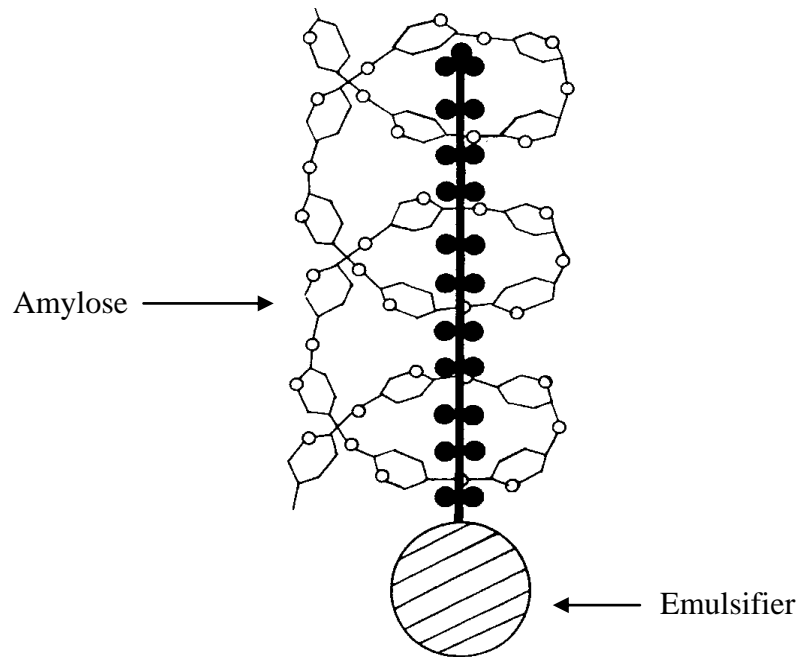


Figure 3.7 – Illustration of amylose complexing with an emulsifier (Hoseney, 1998)

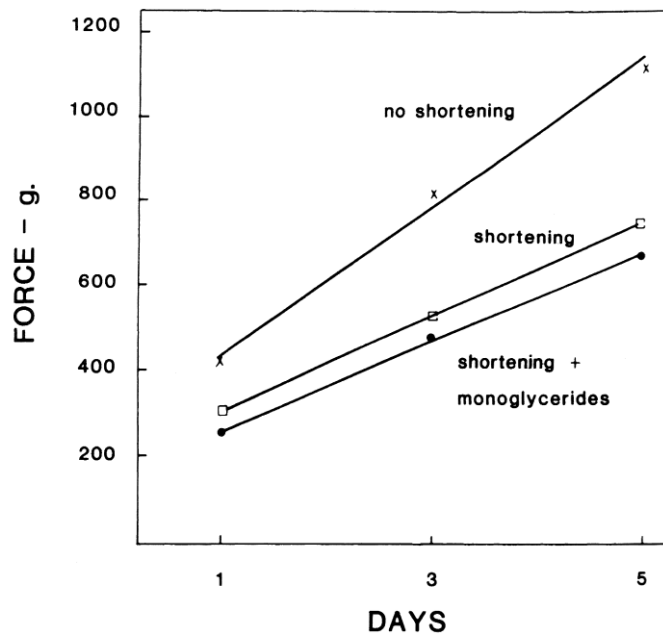


Figure 3.8 – Effect of shortening and monoglycerides on the firming rate of bread (Hoseney, 1998)

The makeup of the emulsifier has a great influence on its ability to complex with starch. Emulsifiers that most easily form insoluble complexes with amylose demonstrate the greatest antifirming and shelf-extension effects. Saturated monoglycerides have been found to form helical inclusion complexes with amylose (Jang and Pyun, 1996; Ghani et al. 1999). Monoglycerides with greater amounts of saturated fatty acids lack steric hindrance allowing efficient complexing with amylose. Unsaturated monoglycerides contain a tilt in the case of a trans-isomer bond and a bend in the case of a cis-isomer bond in their spatial configuration. These tilts and bends hinder their insertion into the amylose helix because cis bonds require twice the space as trans bonds (Birnbaum, 1971).

CHAPTER 4 – Maximizing Emulsifier Functionality

Emulsifier theory has effectively described how emulsifiers interact with the various main ingredients used in the food industry. To effectively select the optimal emulsifier or emulsifiers, many factors need consideration. Emulsifier theory and various research studies have indicated which emulsifiers are the most effective at each task. However, these studies have generally been performed on simple systems consisting of a minimal number of components. Commercial food products are very complex systems composed of a great number of components. Consequently, some of the findings concerning simple systems are negated by the presence of these unaccounted-for components (O'Brien, 2004). Furthermore, the food industry has many restrictions on which emulsifiers are available to them for each particular product and application. Some of the restrictions to the food industry include the physical form, processing conditions, formulation, costs, and regulations the food product is expected to achieve.

Function

To achieve maximum functionality of emulsifiers, the desired function of the emulsifier needs to be identified. Emulsifier theory and research has extensively studied various emulsifier's efficacy of performing food functions. Table 4.1 illustrates the most popular food emulsifiers and how proficient they are at performing various tasks in food. Once the desired function has been identified, the emulsifiers that are most proficient at performing that task should be chosen for evaluation. For example, if the shelf life of a baked product has been an issue and the goal is to increase the shelf life, then saturated mono- and diglycerides should be evaluated first. This is because they possess the greatest starch complexing ability. Furthermore,

if increasing emulsion stability is the goal, then lactylated monoglycerides, mono- and diglycerides, or certain polyglycerol esters should be evaluated. However, commercial emulsifiers that are specialized for certain applications almost always contain a combination of various emulsifiers. This shows the limitations of choosing emulsifiers solely on its functionality from emulsifier theory.

Table 4.1 – Common emulsifier functionality according to application (O’Brien, 2004)

Emulsifier	Emulsion Stability	Starch Complexing	Dough Conditioner	Crystal Modifier	Aeration
Mono- and diglycerides					
Hard or saturated	2	1	4	3	1
Soft or unsaturated	2	3	4	3	2
Propylene glycol esters					
Propylene glycol mono- and diesters	5	2	5	1	1
Propylene glycol mono- and diesters and mono- and diglycerides	3	1	4	1	1
Sorbitan esters					
Sorbitan monostearate	2	5	5	1	3
Polyoxyethylene sorbitan esters					
Polysorbate 60	3	2	1	3	1
Polysorbate 65	3	3	3	3	2
Polyglycerol esters					
Triglycerol monostearate	3	3	3	3	1
Hexaglycerol distearate	1	3	3	1	2
Lactylated esters					
Stearoyl-2-lactylates	1	2	1	5	2
Lecithin					
Standard fluid grade	3	3	3	1	4

Note: Emulsifier functionality evaluation: 1 = excellent, 2 = good, 3 = slight, 4 = poor, 5 = none

Past studies determined that combining different emulsifiers results in greater functionality (Richardson et al. 2002). For example, cakes, icings, and breads are improved

when a combination of emulsifiers is used. Knightly (1968), proposed that combinations of emulsifiers create stronger interfacial films with tighter packing and fewer voids. The stronger interfacial film can lead to increased resistance to coalescence, leading to greater emulsion stability. The use of two emulsifiers also lowers interfacial tension more than a single emulsifier in simple oil and water system. The lower interfacial tension allows emulsions to be created with less shear force. These considerations should be considered when optimizing the performance of emulsifiers.

Form

Emulsifier theory has shown that emulsifiers need to be hydrated to become functional in food products. The various emulsifier phase diagrams indicate that emulsifiers in the beta configuration have little or no functionality. Various research experiments (Richardson et al. 2002; Lauridsen, 1976) have supported this argument. Consequently, emulsifiers in the lamellar or corresponding alpha gel configuration have the greatest functionality. For example, hydrated emulsifiers result in cake batters with superior aeration capabilities that contribute to higher finished cake volumes (Painter, 1981) and bread products with the greatest volume and finest crumb structure (Birnbaum, 1971). However, there are many situations that prevent the usage of hydrated emulsifiers in the food industry.

Hydrated emulsifiers have superior functionality when added in the process of making the final product. However, in many cases the food industry is preparing products that are finished by the consumer. If these products are to be made in the household, then hydrated emulsifiers cannot be used because they are not common ingredients in the kitchen. Therefore,

the majority of emulsifiers are either incorporated into emulsified shortenings or dry blends. These shortenings and dry blends are used as ingredients to make the final product. The physical form of the emulsifier becomes very important in these products. Table 4.2 illustrates the functionality of mono- and diglycerides dependent on its physical form. The differences in functionality according to physical form are not limited to mono- and diglycerides. They apply to all emulsifiers. For example, fully hydrogenated propylene glycol esters reduce foams in icings and fillings. However, plastic propylene glycol esters aerate these products (O'Brien, 2004).

Table 4.2 – Mono- and diglycerides functionality based on physical form (O'Brien, 2004)

Emulsifier Form	Functionality	Food Products
Hard	Moisture retention	All baked products
	Crumb softener	All baked products
	Anti-staling	All baked products
	Volume improver	All baked products
	Tenderness improver	All baked products
	Grain and texture improver	Cakes
	Batter aeration	Cakes
	Palatability improver	Bread and rolls
	Stickiness retardant	Chewing gum and candy
	Anti-sticking	Pasta
	Oil Stabilization	Peanut butter
	Rehydration	Dehydrated potatoes
	Tight emulsion	Margarine
	Freeze/thaw stability	Frozen desserts
Dispersant	Coffee whiteners	
Plastic-like	Compromise of hard and soft forms	All products
Soft	Aeration	Icings and Fillings
	Water absorption	Icings and Fillings
	Texture improvement	Gravies and sauces
	Loose emulsion	Margarine
	Fat dispersant	Pet foods
	Fat dispersant	Cake donuts

Dry blends utilize emulsifiers in a powder or paste form. If a hydrated emulsifier were put in such a system, the water would evaporate. This evaporation would transform the emulsifier back to the beta configuration, rendering it minimally functional. Also, water is detrimental to the shelf life of dry blends. Powdered or granulated emulsifiers are the most convenient for this type of application. However, this form can be less functional than the paste or hydrate form. Since powdered or granulated emulsifiers need to be higher melting to assume this form, they also need higher processing temperatures to become functional in the application. If a powdered or granular monoglyceride has the ability to become hydrated during makeup of the final product, then these emulsifiers can be used (Stauffer, 2005). This characteristic also applies to emulsifiers in plastic or paste form. Temperatures are not as critical for plastic or paste emulsifiers because they do not need as high of temperatures to become functional. The phase diagrams comparing saturated to unsaturated emulsifiers display this relationship on temperature.

Emulsifier theory explains functionality by physical form very well. Both monoglyceride and non-monoglyceride emulsifiers follow the principles of the phase diagrams discussed in the emulsifier interactions with water section. As predicted by the phase diagrams, hydrated emulsifiers, which are set in the lamellar mesophase, outperform non-hydrated emulsifiers. These findings have been confirmed by Lauridsen (1976). Table 4.3 displays how the mesomorph of an emulsifier affects the volume of cakes. However, if emulsifiers are able to move into the lamellar mesophase during the makeup of the final product, then they are also functional in the application. Most importantly, emulsifier theory highlighted that emulsifiers are not very functional when in the beta crystalline configuration. Once emulsifiers were heated past the Krafft temperature, they were able to transform into liquid crystals and become functional

(Zetzl et al. 2009). This shows that the processing conditions of the food product are instrumental in the functionality of emulsifiers.

Table 4.3 – Effect of distilled, saturated monoglyceride mesomorph on cake and cake batter volume (Lauridsen, 1976)

Type of mesophase	Water contents of preparations (%)	Specific volume of cake batter (mL/kg)	Specific volume of cake (mL/kg)
Lamellar	40	1,140	3,400
Cubic	40	1,112	3,320
Cubic + water	90	1,560	5,060
Dispersion (lamellar)	90	2,970	6,900
Gel (α -crystalline)	90	2,700	6,000
Coagel (β -crystalline)	90	1,020	2,400

Processing Conditions

The way food products are prepared greatly affects which emulsifiers have the greatest functionality. The most important factors in processing conditions are the temperature, the amount of mixing or shear, and possibly the order of addition of ingredients.

Temperature is very important in determining which emulsifiers are suitable for an application. Emulsifiers need to be heated up to their Krafft temperature for them to be functional in food products. If the processing conditions do not bring emulsifiers to their Krafft temperature, then they need to be in a functional state before they are incorporated in the system. Emulsified shortenings and hydrated emulsifiers are in highly functional forms and can be used in applications at lower temperatures. There are many applications where processing temperatures are higher than the Krafft temperatures of commercial emulsifiers. These

applications include dehydrated potatoes, non-dairy creamers, and margarine. These applications can freely use high-melting emulsifiers without worry that they will not function from too low a temperature. However, they still may not function optimally without proper mixing or agitation.

The mixing procedure is very important in determining the optimal emulsifier.

Emulsifiers are able to concentrate at the interface between two immiscible phases. However, if they cannot come into contact with this interface through agitation or mixing, they will not function as well. It is very difficult to quantify exactly how much mixing is needed for an application. All mixers and mixing equipment are unique. Therefore, mixing procedures may need to be altered for every processing line. Cake production is a very good example of how mixing procedures can greatly affect emulsifier functionality.

Cakes with nice volume and fine and tender crumb structures can be attained from simple emulsified shortenings. These shortenings with 3-4% alpha-monoglyceride content have been used since the 1930s (Painter, 1981). However, to get a superior product the cakes needed to undergo a three-stage mixing process. The three-stage mixing process requires an initial creaming process to incorporate air bubbles in the shortening. To get superior quality cakes with a less complicated mixing process, more specialized emulsifiers needed to be implemented. Lactylated monoglycerides and propylene glycol esters allow cake batters to outperform monoglycerides. These specialized emulsifiers retain more liquid and increase the distribution of the fat phase when compared to monoglycerides (Painter, 1981). These emulsifiers allow superior quality cakes to be produced with a one-stage mixing process. When the fat phase is not distributed as finely as possible, the final product will display an open, thick-walled structure.

This is in comparison to a fine crumb structure that is very consistent in cakes with a finely distributed fat phase (Painter, 1981).

Formulation

The presence or absence of certain ingredients also determines which emulsifiers are best suited for a given product. Even the use of ingredients at slightly different levels can have a great effect on the final appearance and quality of the product. Sometimes certain ingredients are ineffective when used separately, but have excellent functionality when used in combination. Food systems are complex and unexpected interactions can greatly affect the final product. Consequently, the formulation of a food product can have a large effect on final product quality. Emulsifiers follow these same basic principles.

Sometimes the absence or presence of a single ingredient can determine if a formulation succeeds or fails. The aeration properties of emulsifiers in cakes and icings are an excellent example. The main difference between cake and icing formulations is the presence of flour. Lactylated monoglycerides, propylene glycol monoesters, and saturated monoglycerides are excellent aerators of cake batters (Moncrieff, 1970). However, lactylated monoglycerides and propylene glycol monoesters will not aerate icing formulations that do not contain flour. For these types of formulations, unsaturated monoglycerides and polysorbates have been found to work well (Moncrieff, 1970). It appears that lactylated monoglycerides and propylene glycol esters need the presence of flour to have aeration properties.

The selection of a suitable emulsifier for baked goods also depends on whether the fat phase is plastic shortening or liquid oil. Mono- and diglycerides have been found to work

adequately in cake formulations that utilize shortening. However, these emulsifiers cannot achieve the desired finished volumes when liquid oil is used. In these cases alpha-tending emulsifiers are needed. Alpha-tending emulsifiers will form a crystalline barrier on the liquid oil droplets. This allows aeration to take place and results in excellent cake volumes.

The usage level of emulsifiers can greatly affect its functionality in finished food products. In cake applications, mono- and diglycerides generally have a level at which their functionality is at its highest. At lower or higher concentrations or usage levels, they will display volume loss and inconsistency of the crumb structure (Birnbaum, 1971). This functionality agrees with the concept of the critical micelle concentration.

Critical micelle concentration refers to the level of emulsifier where the entire interfacial surface is covered. The interfacial tension of an emulsion will be at its lowest at this level (Stauffer, 1999). At concentrations above this level, the interfacial tension will be the same or even diminished. A correlation between functionality and the concentration of emulsifier below the critical micelle concentration is generally accepted (Richardson et al. 2002). Many of the dough strengtheners or dough conditioners do not function by the same principles. They generally will continue to show improvement in strengthening or starch complexing ability in bread as their levels are increased. Therefore, they have limits on the maximum level allowed in various applications (Birnbaum, 1971). Table 4.4 displays a table of regulations by country. Some emulsifiers will perform different functions in a food application when used at different levels. For example, polysorbate 80 at 0.03-0.10% aerates food systems. However, when used at levels of 0.005%, it defoams these same systems (Nash and Brickman, 1972).

Emulsifiers display maximum functionality when they are combined in food applications. Knightly (1968) proposed that combinations of emulsifiers are able to form a more compact interface, leading to an increased resistance to coalescence and therefore greater functionality. For example, combinations of ethoxylated monoglycerides with mono- and diglycerides and polysorbate 60 with mono- and diglycerides are commonly used as dough conditioners in bread (Nash and Brickman, 1972). Another example is with cake emulsifier systems, which commonly combine alpha-tending emulsifiers with other emulsifiers. These cake emulsifier systems also commonly combine a highly lipophilic emulsifier, such as monoglycerides, with a highly hydrophilic emulsifier, such as polysorbate 60 (O'Brien, 2004). Benerito and Singleton (1956) demonstrated that combining lipophilic emulsifiers with lipophilic emulsifiers result in emulsions of greater stability when compared to using only a single emulsifier. Currently only through experimentation can these synergistic systems be identified. Future research on complex systems would be very useful in better understanding emulsifiers.

Costs

The food industry is similar to most private businesses in that its success is determined by economics. Therefore, the cost and availability of emulsifiers are important factors to consider when choosing an emulsifier for a potential product. The specifications that are required also determine the cost of materials. Products that have more unusual or demanding specifications usually cost more than less demanding products (Fuller, 2005). Furthermore, emulsifiers that are composed of expensive raw materials or undergo multiple processing techniques demand a premium on price when compared to the simpler, more common emulsifiers. Monoglycerides

and lecithin were the first emulsifiers to enter the food industry and are relatively inexpensive. While the price of these ingredients rise and fall with the commodity markets for their raw ingredients, they generally will be less than \$1.50 per pound at current market prices. Many of the monoglyceride derivatives are also commonly used and have low prices. For example, the use of 0.5% sodium stearoyl lactylate based on flour weight will add less than half a cent to the cost of a one-pound loaf of bread at current commercial prices. However, the production of hydrated emulsifiers is fairly complex and has increased costs associated with it. Furthermore, the specialized emulsifier blends demand a premium on price. This premium is due to the extra research conducted on the product to optimize functionality.

Regulations

The Codex Alimentarius, or food code has been created to regulate the specifications of ingredients used in the food industry (FAO/WHO, 2006). Each ingredient is assigned an international numbering system number, which provides specifications and methods to test for these specifications. However, each country has its own set of regulations on what food ingredients are allowed and at what usage levels (Stauffer, 1999). If a product has the possibility of being used in multiple countries, then it is prudent to formulate the product so that it will pass regulations for all intended areas of consumption. Table 4.4 summarizes many of the emulsifiers used in the food industry with their regulatory codes for the United States, Canada, and European Union.

Table 4.4 – Regulatory codes of common commercial food emulsifiers dependent on the country of consumption (Stauffer, 1999)

Emulsifier	United States¹	Canada²	European Union³
Mono- and diglycerides (GRAS)	182.4505	M.4, M.5	E 471
Acetylated monoglyceride	172.828	A.2	E 472a
Lactylated monoglyceride	172.852	L.1	E 472b
Monoglyceride citrate	172.832	–	E 472c
Diacetyl tartrate ester of monoglycerides (GRAS)	182.4101	A.3	E 472e
Propylene glycol monoester	172.854	P.14	E 477
Sorbitan monostearate	172.842	S.18	E 491
Sorbitan tristearate	–	S.18B	E 492
Polysorbate 60	172.836	P.3	E 435
Polysorbate 65	172.838	P.4	E 436
Polysorbate 80	172.840	P.2	E 433
Calcium stearoyl lactylate	172.844	–	E 482
Sodium stearoyl lactylate	172.846	S.15A	E 481
Polyglycerol fatty acid esters	172.854	P.1A	E 475
Sucrose fatty acid esters	172.859	S.20	E 473
Lecithin (GRAS)	184.1400	L.2	E 322
Hydroxylated lecithin	172.814	H.1	E 322

¹ *Code of Food Regulations*, Title 21.

² *Canadian Food and Drug Regulations*, Table IV, Division 16.

³ European Parliament and Council Directive 95/2/EC, 20 February 1995.

Generally recognized as safe.

CHAPTER 5 – Summary

A great deal about emulsifiers is currently known. Scientists have discovered that emulsifiers need to be hydrated to become active and have constructed molecular models demonstrating the process. They have also discovered that some emulsifiers undergo mesomorphism as their concentration in water and temperature is changed. The many interactions that emulsifiers have with the most popular components of foods have been documented and studied in great detail. However, most of the research on emulsifiers has been performed on simple systems, using a single emulsifier and other component. Future research needs to investigate how multiple emulsifiers function in complex systems. The knowledge gained from studying complex systems will truly allow the food industry to maximize the functionality of emulsifiers.

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