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Food Emulsifiers: Their Chemical and Physical Properties

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I. INTRODUCTION

Foods are very complex colloidal systems and modern industrial production requires surface-active lipids such as emulsifiers as processing aids and to secure a uniform quality, improved texture, and long shelf life.

An emulsifier is defined as a substance that reduce surface tension between oil–water or air–water, thus enhancing emulsification and increasing emulsion stability. Many native polar lipids and proteins comply with this definition. Food emulsifiers, on the other hand, do not affect the emulsification process significantly, but have other functions which are related to interfacial properties and affect emulsion stability or destabilization of whippable emulsions. In addition, food emulsifiers have other functions in foods, such as the modification of fat crystallization, interactions with carbohydrate components, or act as film forming substances, controlling oxygen or humidity transport, and such applications are not related to the classical definition of an emulsifier.

The main goal of this chapter is to describe the relationship between the chemical structure and composition of the emulsifiers and their function in foods. The crystalline properties, interfacial adsorption, and interactions with food ingredients, such as fats, proteins, carbohydrates, and water, are playing important roles in the function of emulsifiers in food products.

II. CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES

A. Monoglycerides

An overview of food emulsifiers and their identification numbers is presented in Table 1. The use of mono-diglycerides dates back to the 1930s, when they were first used in margarine production.

Table 1 Food Emulsifiers and Their Legal Status

Chemical name	Abbreviation	ADI value[a]	EU No.	US FDA 21 CFR
Lecithin	—	Not limited	E322	§184.1400[b]
Mono-diglycerides (distilled monoglycerides)	MAG	Not limited	E471	§184.1505[b]
Acetic acid esters of monoglycerides	ACETEM	Not limited	E472a	§172.828
Lactic acid esters of mono-diglycerides	LACTEM	Not limited	E472b	§172.852
Citric acid esters of mono-diglyceries	CITREM	Not limited	E472c	§172.832
Diacetyl tartaric acid esters of monoglycerides	DATEM	0–50	E472e	§184.1101[b]
Succinic acid esters of monoglycerides	SMG	—	—	§172.830
Salts of fatty acids (Na, K, Ca)	—	Not limited	E470a	§172.863
Polyglycerol esters of fatty acids	PGE	0–25	E475	§172.854
Polyglycerol polyricinoleate	PGPR	0–7.5	E476	—
Propylene gycol esters of fatty acids	PGMS	0–25[c]	E477	§172.856
Sodium stearoyl-lactylate	SSL	0–20	E482	§172.844
Calcium stearoyl-lactylate	CSL	0–20	E481	§172.846
Sucrose esters of fatty acids	—	0–10	E473	§172.859
Sorbitan monostearate	SMS	0–25	E491	§172.842
Sorbitan tristearate	STS	0–15	E492	—[d]
Polysorbate 60	PS 60	0–25	E435	§172.836
Polysorbate 65	PS 65	0–25	E436	§172.838
Polysorbate 80	PS 80	0–25	E433	§172.840

[a] Acceptable daily intake in mg/kg body weight per day.

[b] Generally recognized as safe (GRAS).

[c] Calculated as propylene glycol.

[d] Petition filed and accepted.

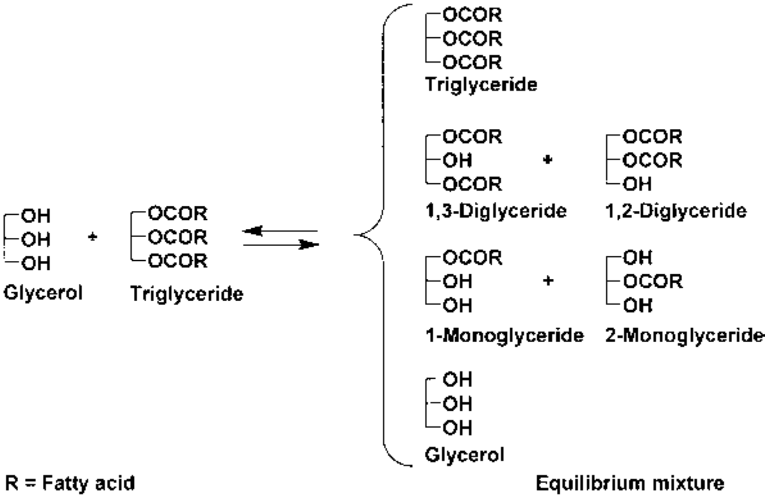

Figure 1 Reaction scheme of interesterification (glycerolosis) of triglycerides and glycerol. R_1, R_2, and R_3 are fatty acids.

Table 2 Composition of Glycerolysis Equilibrium Mixtures

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

Source: Adapted from Ref. 1.

Monoglycerides are produced industrially by interesterification (glycerolosis) of edible fats or oils with glycerol, the reaction of the components takes place at high temperature (200–260°C) under alkaline catalysis. The reaction scheme is shown in Fig. 1, and has been described in detail by Feuge and Bailey (1) and Sonntag (2). Table 2 shows the calculated composition of the fat-phase mixture from the glycerolosis of fat with different concentrations of glycerol. The so-called monodiglycerides produced by

Table 3 Equilibrium Reaction Mixtures of 1- and 2-Monoglycerides

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

glycerolysis contain from 40% to a maximum of 60% monoglycerides with the balance being diglycerides and triglycerides. High-diglyceride-containing products can also be made by glycerolysis using 6 to 8 parts of glycerol to 100 parts of fat. This ratio yields a blend containing 15% monoglycerides, 50% diglycerides, and 35% triglycerides.

Concentrated monoglycerides are produced by a high-vacuum thinfilm molecular distillation process yielding products containing typically 95% monoglycerides, 3–4% diglycerides, 0.5–1% free glycerol, and 0.5–1% free fatty acids.

Freshly distilled monoglycerides contain an equilibrium of 1-monoglycerides and 2-monoglycerides. The ratio between the two isomers at different temperatures is shown in Table 3. The composition varies considerably with temperature. The rate constant of the equilibrium reaction is very low at room temperature and depends on fatty acid composition, crystal form, and traces of basic catalysts present (3). The content of 1-monoglycerides in commercial distilled monoglycerides is usually from 90% to about 95%.

Enzymatic synthesis of monoglycerides and other emulsifiers bas been reported (7–9) as a method to produce stereospecific emulsifiers. However, isolation of the desired products from the reaction mixture is a problem for large-scale production, and commercial production of emulsifiers by biochemical methods is not commonly used.

Because the 1-monoglyceride isomer content can vary according to the temperature history of the product, the most reliable method for the determination of the monoglyceride content in commercial products is using gas–liquid chromatography (GLC) combined with a derivatization of the monoglycerides with, for example, trimethyl silylether (4). Figure 2 shows a gas chromatogram of distilled monoglycerides based on fully hydrogenated tallow fat.

Monoglycerides are polymorphic like triglycerides and can exist in different crystal forms depending on temperature conditions. Furthermore, as shown in Fig. 3, monoglycerides and diglycerides have a higher melting point than the corresponding triglycerides. For saturated

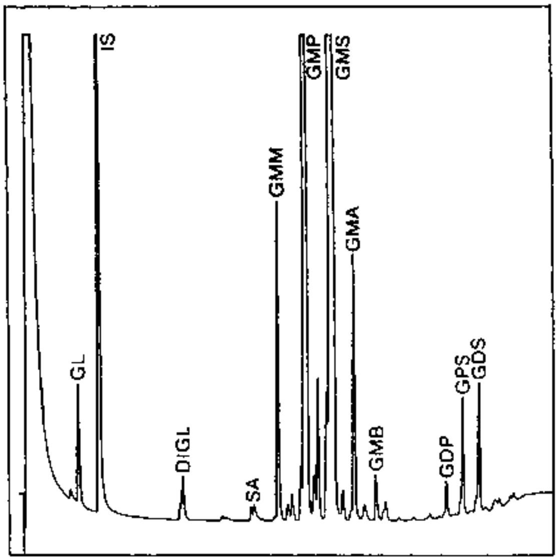

Figure 2 Gas–liquid chromatogram of trimethyl-silylether derivatives of distilled monoglycerides. GL = glycerol, IS = internal standard, DIGL = diglycerol, SA = stearic acid, GMM = glycerol monomyristate, GMP = glycerol monopalmitate, GMS = glycerol monostearate, GMA = glycerol monoarachidate, GMB = glycerol monobehenate, GDP = glycerol dipalmitate, GPS = glycerol palmitate-stearate, GDS = glycerol distearate.

monoglycerides of palmitic and stearic acid, the increase in melting point compared to the corresponding triglycerides is 10–12°C. For unsaturated glycerides, like mono-olein and triolein, the difference is as high as about 30°C.

The melting points of the polymorphs of pure monoglycerides with fatty acid chain length from C_{10} to C_{18} are shown in Fig. 4.

When cooled from melt, monoglycerides crystallize in a metastable α-form. On further cooling, a solid-state transition from an α-form to a sub-α-form takes place at a lower temperature. When stored at ambient temperature, transition to the stable β crystal form will take place. The polymorphism of monoglycerides thus follows the pattern of triglycerides that has been reviewed by Larsson (5).

All lipids form crystal structures with the hydrocarbon chains arranged in layers with a parallel chain axis. In lipids with polar head groups, such as surfactants, the molecule is always arranged in layers, with the polar head group in discrete layers separated by the fatty acid hydrocarbon chains, forming a lipid bilayer, which is an important feature

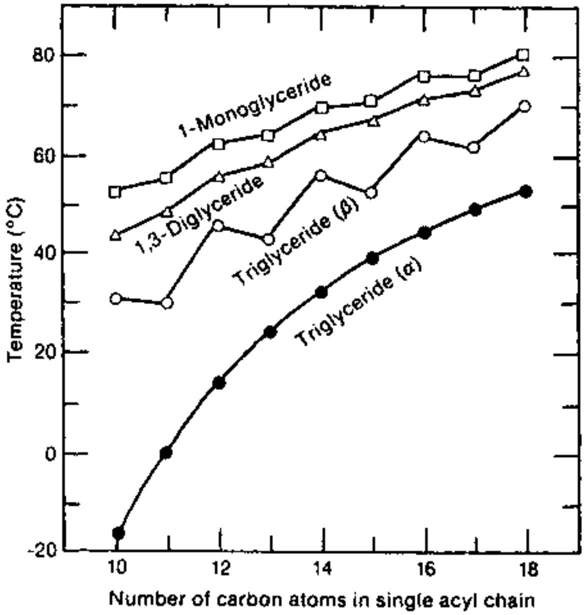

Figure 3 Melting points of monoglycerides and diglycerides compared to corresponding triglycerides with fatty acid chain length from C_{10} to C_{18}. (From Ref. 2.)

of polar lipids. Figure 5 shows the molecular orientation in crystals of polar lipids with double-chain-length packing (DCL) and single-chain-length packing mode (SCL) schematically, where the hydrocarbon chains of two adjacent layers penetrate each other. The crystal forms of monoglycerides and diglycerides as well as of distilled monoglycerides are the same as those in triglycerides except that the β′-form is not usually found in commercial monoglycerides.

X-ray diffraction patterns of commercial monoglycerides show a strong short spacing at 4.2 Å for the α-form (hexagonal subcell), as seen in Table 4 showing crystallographic data and melting points of distilled monoglycerides based on single fatty acids with minimum 90% purity or hydrogenated vegetable fats.

When the α-form is cooled, it transforms into a sub-α crystal form at approximately 35°C; the sub-α-form is characterized by a strong spacing near 4.3 Å, and several spacings from 3.9 to 3.7 Å, with medium intensity.

The stable, high-melting β-form is characterized by a strong short spacing at 4.6 Å, combined with several spacings in the region 3.9–3.6 Å or lower, with medium intensity.

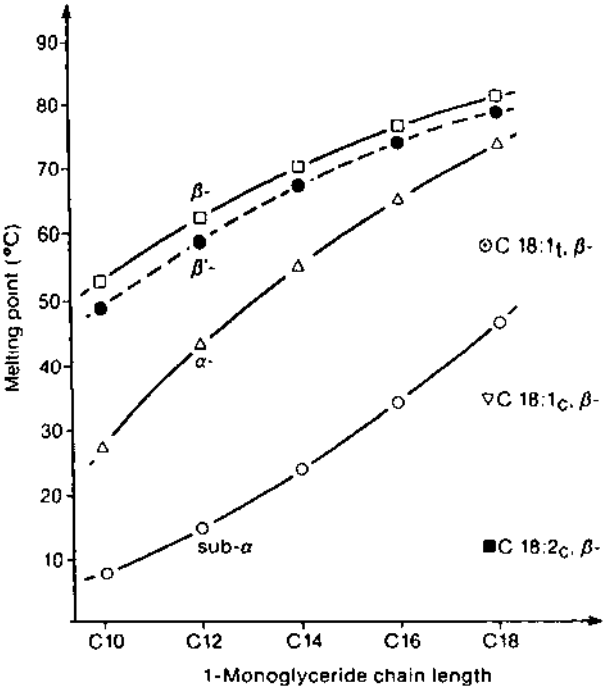

Figure 4 Melting points of crystal polymorphs of pure monoglycerides with chain length from C_{10} to C_{18}. $C_{18}:1_t$ = 1-monoelaidin, $C_{18}:1_c$ = 1-mono-olein, $C_{18}:2_c$ = 1-monolinolein.

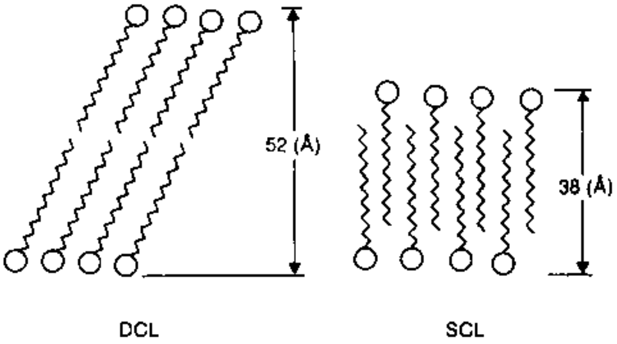

Figure 5 Schematic models of the molecular packing of polar lipids. DCL = double-chain-length structure, SCL = single-chain-length structure. Typical x-ray diffraction long spacings of the lipid bilayers are shown.

Table 4 Melting Points and X-Ray Diffraction Data of Mixed Fatty Acid Distilled Monoglycerides

	Melting points[a] (°C)			Long spacings (Å)		Main short spacings (Å)	
Monoglyceride	Sub-α	α	β	α	β	α	β
Monolaurin, 90% C_{12}	16	45	61	—	37.3	4.15	4.57-4.32-4.00-3.84-3.71-2.44
Monomyristin, 90% C_{14}	25	56	67	41.0	40.6	4.15	4.55-4.33-3.91-3.81-3.71-2.44
Monopalmitin, 90% C_{16}	35	66	73	47.0	44.7	4.15	4.51-3.91-3.84-3.67-2.43
Mono-olein, 90% $C_{18:1}$	—	30	34	—	48.5	—	4.60-4.38-4.31-4.04
Monobehenin, 90% C_{22}	56	82	85	57.3	57.5	4.15	4.50-3.94-3.84-3.74-2.43
Saturated monoglycerides[b,1] (hydrogenated soybean oil)	37	71	75	54.0	51.4	4.13	4.55-3.94-3.86-3.78-2.43
Saturated monoglycerides[b,2] (from hydrogenated lard)	20	66	72	53.2	49.8	4.15	4.52-4.35-3.93-3.84-2.43
Saturated monoglycerides[b,3] (hydrogenated palm oil)	16	68	72	51.6	47.0	4.15	4.55-4.33-3.89-2.43
Unsaturated monoglycerides[b,4] (palm oil)	8	(48)	60	—	46.5	—	4.55-4.31-4.03-3.86

[a] Differential scanning calorimetry (DSC) peak temperatures.

[b] Danisco ingredients products: [1]DIMODAN® HS, [2]DIMODAN® HL, [3]DIMODAN®HP, [4]DIMODAN®P/M.

Long spacings of $C_{16/18}$ saturated monoglycerides are in the order of 50 Å, corresponding to the DCL packing mode. Above the melting point, monoglycerides show a diffuse x-ray diffraction line in the long spacing region corresponding to 30 Å. This means that monoglycerides maintain an ordered structure in the melt due to hydrogen-bonding between the polar groups.

Diglycerides are usually only present in monodiglycerides in minor quantities and are not considered to be the main components. However, it is possible to produce a high-diglyceride product containing 50–60% diglycerides by glycerolysis. Such products have found some applications due to the specific crystallization properties of 1,2-diglycerides. Diglycerides exist in two isomeric forms: 1,2-and 1,3-diglycerides (see Fig. 1) in a relative ratio of 40 : 60. The 1,2-diglycerides crystallize from melt in a metastable α-form, which transforms to a stable β′-form. They can, therefore, be used to stabilize β′ crystals in fat blends, which otherwise show a tendency of growing β crystals, giving rise to textural problems (e.g., in margarine or low-calorie spreads).

B. Organic Acid Esters of Monoglycerides

The free hydroxyl groups in monoglycerides can be esterified with organic acids such as acetic, lactic, diacetyltartaric, citric, and succinic acids, and thus from more lipophilic or hydrophilic derivatives of monoglycerides. The esters are normally produced by reacting monoglycerides with the organic acid directly or with its anhydride.

The crystalline behavior, melting point, and polar properties of the organic acid esters are very different from that of the corresponding monoglycerides. Acetic and lactic acid esters are low-polar, lipophilic emulsifiers, whereas diacetyl tartaric acid esters or citric acid esters are anionic, hydrophilic emulsifiers. Therefore, such organic acid esters have different functional properties than monoglycerides and are used in many new applications in foods.

A common feature of the monoglyceride derivatives is that they are all monomorphic and crystallize from melt in an α-crystal form. The melting points and crystallographic data of organic acid esters are shown in Table 5. Some of the monoacyl esters crystallize with SCL packing mode, and these emulsifiers have the strongest decrease in melting point compared to monoglycerides (see Table 4).

The melting points shown in Table 5 are typical for monoglyceride derivatives based on blends of saturated palmitic and stearic acids. It should be noted that among commercial products, some variation in melting points

Table 5 Melting Points and X-Ray Diffraction Data of Organic Acid Esters of Monoglycerides (C_{16}/C_{18} ratio, 35 : 65)

Organic acid esters of monoglycerides	Melting point (°C)	Long spacings (Å)	Chain packing mode	Short spacings (Å)	Crystal form
Acetic acid esters (monoacetylated)	39	32.9	SCL	4.10	α
Lactic acid esters (LACTEM)	42	39.5	SCL	4.13	α
Diacetyl-tartaric acid esters (DATEM)	43	41.0	SCL	4.11	α
1.2-Dipalmitin-DATE[a] (synthetic)	—	54.6	DCL	4.21–3.76	—
Citric acid esters (CITREM)	60	60.3	DCL	4.11	α

[a] Diacetyl-tartaric acid ester of pure 1.2-dipalmitin.

could occur. This is due to variations in chemical composition and fatty acid profile.

C. Acetic Acid Esters (ACETEM)

By reacting one or both of the free hydroxyl groups in distilled monoglycerides with acetic acid anhydrid and removing the surplus of free acetic acid by distillation, a more lipophilic product is formed. Acetylation may be partial or complete depending on the ratio of the acetic acid anhydrid and monoglyceride used. Normally, products with 50%, 70%, or 90% acetylation of free hydroxyl groups are used in foods, depending on application.

The melting point of ACETEM is about 20–30°C lower than that of the monoglycerides used in production and varies from 35°C to 40°C depending on the degree of acetylation and type of monoglyceride. Acetylation of unsaturated monoglycerides with iodine values higher than 40 yields a product that is liquid at room temperature (melting point approximately 10°C).

The crystallization behavior of monoglycerides is changed considerably by acetylation, as ACETEM is monomorphic and stable in its α crystal form. Chemically pure 1-aceto-3-stearin shows the following polymorphic transitions when chilled from melt to below 0°C: sub-$\alpha_1 \rightarrow 3.5°\text{C} \rightarrow$ sub-$\alpha_2 \rightarrow 12.5°\text{C} \rightarrow \alpha \rightarrow 45°\text{C} \rightarrow \beta' \rightarrow 48.5°\text{C} \rightarrow$ melt (6).

Acetylated, saturated monoglycerides of C_{16}/C_{18} fatty acids form flexible films that can be stretched up to eight times their length before they break, and they are therefore used as coatings on fruits, nuts, and meat products (7). Due to its α-tending properties, ACETEM is also used in fats (shortenings) in aerated foods such as cakes and toppings.

D. Lactic Acid Esters (LACTEM)

Production of LACTEM is normally based on a reaction between lactic acid and monoglycerides based on fully hydrogenated vegetable or animal fats. An alternative production method is esterification of glycerol, lactic acid, and fatty acids in a mole-to-mole ratio. Lactic acid esters may contain from 15% to 35% esterified lactic acid distributed on a number of isomeric compounds. Some of the most typical components are shown in Fig. 6.

For LACTEM based on a C_{16}–C_{18} chain length, saturated monoglycerides has a melting point of about 45°C. From melt, it crystallizes into a stable α crystal form. X-ray diffraction of LACTEM often shows two long spacings at 38 Å and about 55 Å, indicating that some of the LACTEM components crystallize in a SCL form (long spacing 38 Å) and other components crystallize in a DCL form (long spacing 55 Å).

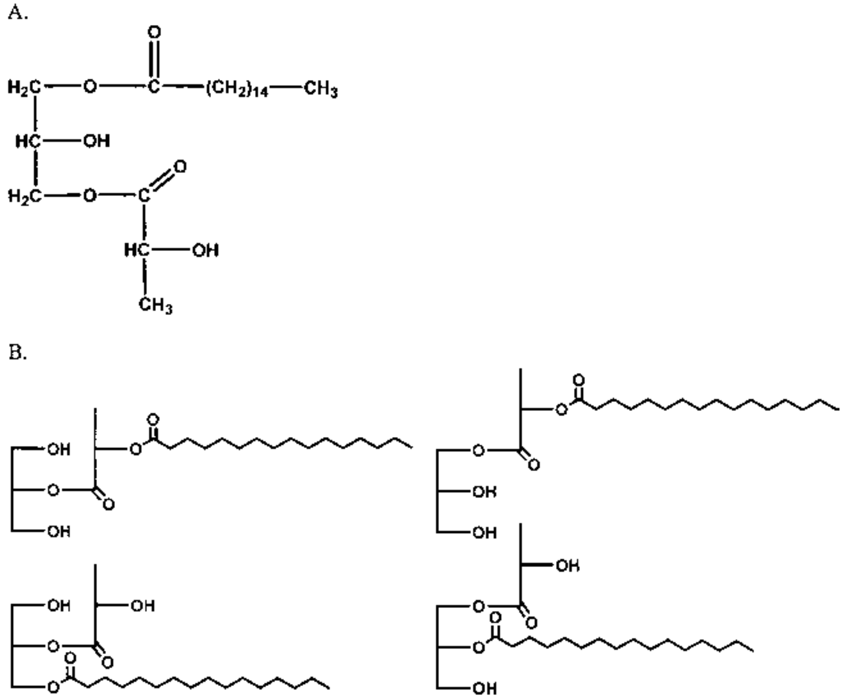

Figure 6 Chemical formulas of (A) lactic acid ester of monoglycerides (LACTEM) and (B) possible positional isomers of esters of lactic acid, palmitic acid, and glycerol.

Generally speaking, LACTEMs are nonionic emulsifiers, soluble in oils and fats, and only slightly water dispersable. LACTEMs are often less surface active than their corresponding monoglycerides, depending on the composition.

The LACTEMs are used mainly in foods such as cake shortenings and fats for toppings or imitation creams and often in combinations with saturated monoglycerides in order to make a product that is stable in the α crystalline form.

E. Diacetyl Tartaric Acid Esters (DATEM)

The anion-active and very hydrophilic DATEM products are produced by reacting diacetylated tartaric acid anhydride with monoglycerides. The diacetylated tartaric acid anhydride is produced from refined, natural tartaric acid from the wine industry by reaction with acetic acid anhydride. The chemistry of DATEM production is described in detail by Schuster and

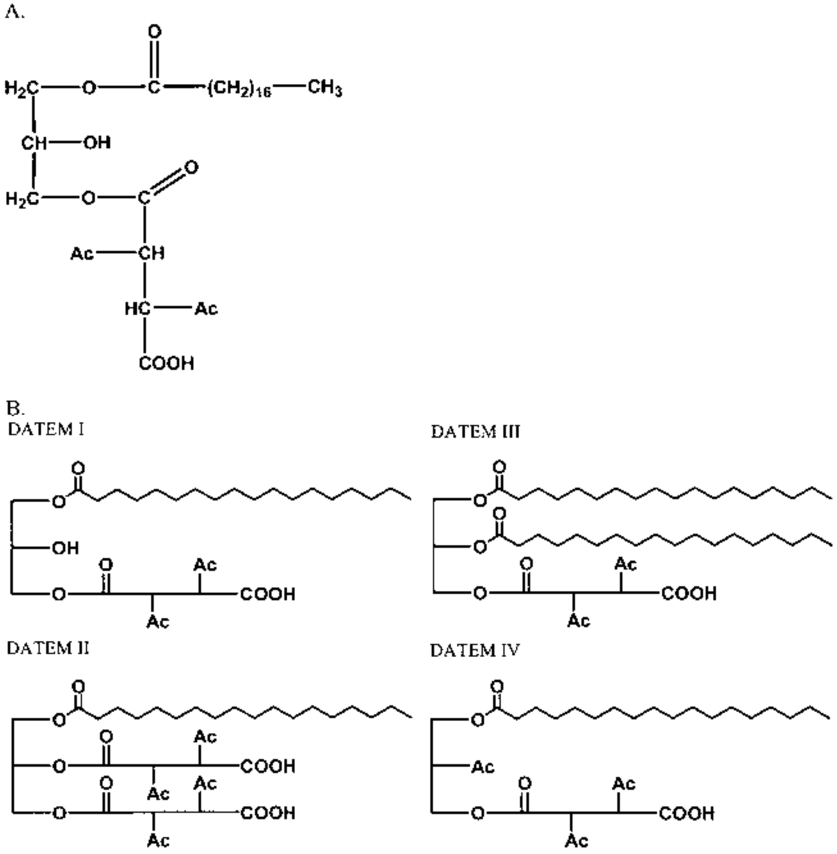

Figure 7 Chemical formulas of (A) diacetyl tartaric acid ester of 1-glycrol monostearate (DATEM) and (B) positional isomers referred to as DATEM I, II, III, and IV.

Adams (8). The main components of DATEMs are referred to as DATEM I, II, III, and IV, and their schematic molecular formula is shown in Fig. 7. Depending on the type of monoglycerides used as raw material, a DATEM can be crystallized in block, flake, or powder form or it can be semiliquid.

A DATEM of saturated, C_{16}/C_{18} monoglycerides is stable in an α crystal form with a melting point usually about 45°C. X-ray-diffraction long spacings are in agreement with a SCL packing of the hydrocarbon chains. It forms dispersions in water with low pH (2–3) due to its free-carboxyl group, and the solubility is increased if the pH value is adjusted to above 4–5 (see Section III). A DATEM is only partially soluble in oils and fats. Compared to monoglycerides, a DATEM is very surface active and has a number of applications in food emulsions. However, its main application is as a dough conditioner in yeast-raised bakery products.

According to the Food Chemical Codex in the United States, a DATEM may contain 17–20% by weight of esterified tartaric acid and 14–17% esterified acetic acid. In Europe, the EU regulation prescribes a wider variation in composition, allowing 10–40% esterified tartaric acid and 8–32% acetic acid.

F. Citric Acid Esters (CITREM)

A CITREM is manufactured by esterification of monoglycerides with citric acid in an amount 12–20% by weight of the finished product, which is often neutralized partially, forming sodium salts of CITREM. CITREM manufactured on the basis of saturated monoglycerides crystallize from melt in an α-like crystal form, and the melting point is between 55°C and 60°C.

All esters of dicarboxylic or tricarboxylic acids and monoglycerides show a high degree of long-range order in the melted state, a phenomenon well known from soaps, called thermotropic mesomorphism. Low-angle x-ray diffraction of such materials shows one or several sharp lines in the long spacing region at temperatures above the melting point. Citric acid esters exhibit this behavior, especially due to strong molecular interactions between the polar groups in the melt.

A CITREM is an extremely hydrophilic, anionic emulsifier. It forms a milky dispersion in water and is only partially soluble in oils and fats. Its main application in foods is as antispattering agent in margarine or as emulsifier in meat or beverage emulsions. CITREM based on unsaturated monoglycerides is used to reduce the yield value and plastic viscosity of a chocolate mix.

G. Succinic Acid Esters (SMG)

Succinic acid esters are produced by a reaction of succinic anhydride with monoglycerides. A SMG is an anionic emulsifier, due to its free-carboxyl group, as it appears from its chemical formula shown in Fig. 8.

A SMG based on saturated monoglycerides has a melting point of 55–60°C. When cooled from melt, it goes through a thermotropic liquid-crystalline state before crystallizing in an α-form with SCL chain packing (x-ray long spacing 38 Å). The α-form transforms to a stable β-form on storage at room temperature. The β-form has a DCL chain packing as found with monoglycerides.

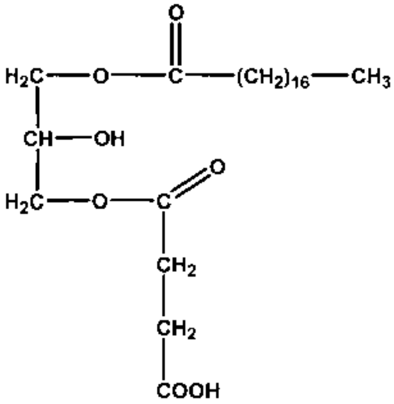

Figure 8 Chemical formula of succinic acid ester of glycerol monostearate.

Like a DATEM, a SMG is used mainly as a dough strengthener for yeast-raised baking products. However, its use in foods is limited to the United States, as EU regulations do not permit it.

H. Polyglycerol Esters of Fatty Acids (PGE)

Glycerol may be polymerised by dehydration and, by this reaction, a series of polyglycerol compounds is obtained. They can be esterified with edible fatty acids, usually palmitic stearic acid blends, forming polyglycerol esters. A structure formula of triglycerol monostearate is shown in Fig. 9. Commercial PGE products may vary considerably in composition, depending on the degree of polymerization and degree of esterification. According to EU regulations, the polyglycerol moiety should mainly be diglycerol, triglycerol, and tetraglycerol with a maximum of 10% of polyglycerols equal to or higher than heptaglycerol. In the United States, however, the U.S. FDA (Food and Drug Administration) regulation permits a polymerization degree up to decaglycerol. The composition of PGE products is very complex, with a high number of positional isomers.

A PGE with a low degree of polymerization (e.g., mainly triglycerol and tetraglycerol esters of C_{16}/C_{18} fatty acids) melts at approximately 55°C and crystallizes in a stable α-form. PGE is generally more hydrophilic than monoglycerides, but its dispersibility in water depends on polyol condensation composition and degree of esterification. PGEs are used in a number of food emulsions, ranging from margarine and dessert products to cakes and other bakery products.

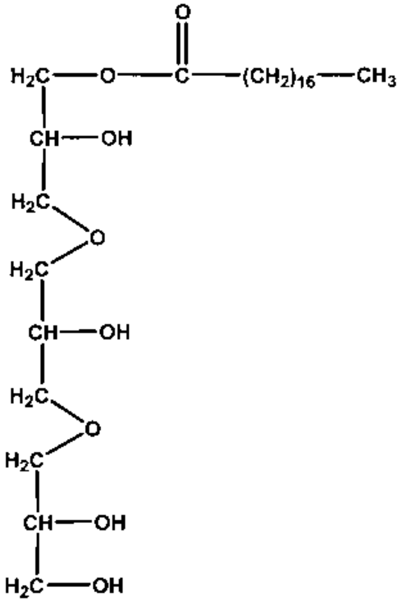

Figure 9 Chemical formula of a polyglycerol fatty acid ester [triglycerol monostearate (PGE)].

Table 6 Melting Points and X-Ray Diffraction Data of Fatty Acid Esters of Polyols and Lactic Acid (C_{16}/C_{18} ratio, 50:50)

Product	Melting point (°C)	Long spacings (Å)	Chain packing mode	Short spacings (Å)	Crystal form
Polyglycerol monostearate	56	64.2	DCL	4.13	α
Propylene glycol monostearate	39	50.7	DCL	4.15–(3.99)	α
Sorbitan monodistearate	54	54.5	DCL	4.11	α
Sorbitan monostearate	—	33.8	SCL	4.11	α
Sorbitan tristearate	56	49.8	DCL	4.13	α
Sodium stearoyl lactylate	38	37.6 (49.7)	SCL (DCL)	4.10	α

Table 6 presents the crystallographic data and melting point of polyol fatty acid esters.

Purified diglycerol fatty acid esters can be manufactured by esterification of diglycerol with edible fatty acids. The monoacyl fatty acid esters are concentrated by a molecular distillation process. The diglycerol mono fatty acid esters are more hydrophilic than corresponding monoglycerides (9). On the contrary, polyglycerol polyricinoleate (PGPR) is primarily used to stabilize low-fat water-in-oil (w/o) emulsions (spreads) or to reduce yield value in chocolate mix.

I. Stearoyl-lactylates (SSL, CSL)

Esterification of stearic acid with lactic acid in the presence of sodium or calcium hydroxides yields a mixture of stearoyl-lactylates (sodium or calcium salts), fatty acid salts, and free fatty acids. The main component of stearoyl-lactylates is shown in Fig. 10. Esters of trilactic and polylactic acids are also present in commercial products, making the composition quite complex.

The Na stearoyl-lactylates (SSL) are normally present in an α-form with a melting point of about 45°C. This form is obtained by spray-cooling the melt into a powdered or beaded product. The α-form has a single short spacing at 4.1 Å and long spacings at about 38 Å, showing the SCL packing mode with penetrating hydrocarbon chains.

The SSL is water dispersible at neutral pH. At a pH value below 4–5, solubility is limited due to the content of 15–20% free fatty acids in SSL. The CSL is less water dispersible, but more oil soluble than SSL. Both SSL and CSL are used mainly in the baking industry as dough strengtheners. SSL is also used in many emulsions such as imitation creams, coffee whiteners, filling creams, and icings.

J. Propylene Glycol Esters of Fatty Acids (PGMS)

Propylene glycol esters can be manufactured by esterifying propylene glycol with edible fatty acids under alkaline catalysis at about 200°C under

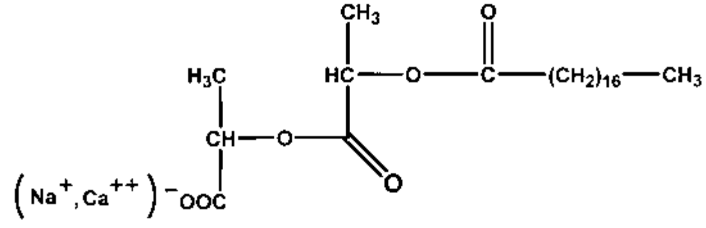

Figure 10 Chemical formula for stearoyl-lactoyl lactic acid sodium or calcium salt (SSL, CSL).

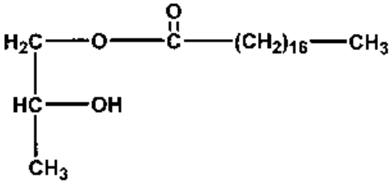

Figure 11 Chemical formula of propylene glycol monostearate (PGMS).

vacuum. After removal of excess propylene glycol, the reaction blend contains approximately 55% propylene glycol monoester and 45% diester. Structural formula is shown in Fig. 11. An alternative method is interesterification of triglycerides and propylene glycol, yielding a reaction mixture containing the propylene glycol monoesters and diesters, together with 10–15% monoglycerides and a minor amount of diglycerides as well as triglycerides. The propylene glycol monoester can be concentrated by a molecular distillation process as described for monoglycerides. Distilled PGMS contains a minimum of 90% monoesters and is normally based on saturated C_{16}/C_{18} chain length fatty acids.

Commercial propylene glycol monostearate is stable in an α-like form, as shown in Table 6. However, pure 1-propylene glycol monostearate exists in four different crystal forms (10).

The PGMS are only slightly water dispersible, but completely soluble in oils and fats. Therefore, it is used only in combinations with fats of as an α-tending emulsifier in combination with monoglycerides or other emulsifiers. PGMS is mainly used in cake shortenings and fats for whippable emulsions, toppings, and so forth.

K. Sorbitan Esters of Fatty Acids

1. Sorbitan Esters of Fatty Acids (SMS, STS)

Sorbitan is derived from sorbitol by dehydration and then esterified with fatty acids and described for PGMS, and depending on the amount of fatty acids used for the esterification, sorbitan monoesters (SMS) or triesters (STS) are produced. The chemical formulas of SMS and STS are shown in Fig. 12.

All sorbitan esters are stable in the α crystal form, but their x-ray long spacings indicate a different molecular packing depending on the degree of esterification, as shown in Table 6. Commercial sorbitan monodistearate or sorbitan tristearate crystallize with a DCL chain packing mode, whereas a concentrated sorbitan monostearate with a mono-acyl content of 80% has a long spacing of about 34 Å, corresponding to SCL chain packing.

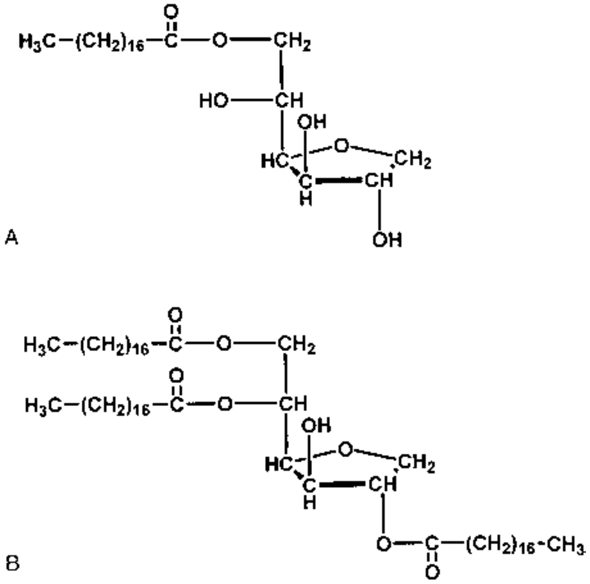

Figure 12 Chemical formula of sorbitan fatty acid esters: (A) sorbitan monostearate [6-stearoyl-1,4-anhydro-D-glucitol (SMS)] and (B) sorbitan tristearate (STS).

Sorbitan tristearate (STS) is very lipophilic and its main application is as a crystal modifier in fat-based foods (margarine, spreads, chocolate products). STSs are used to control crystallization of fats, where they stabilize the β′ crystal form, preventing formation of the higher melting β crystal form. The β crystals tends to grow very large and cause a grainy texture in margarine or spreads. In chocolate products, similar fat crystal transitions are the reason for the development of a fault referred to as "bloom," which appears as grayish spots on the surface.

Sorbitan monostearate (SMS) is dispersible in warm water and soluble in oils and fats, whereas STS is soluble in oils and fats only.

Sorbitan monostearate is used in many food products, primarily emulsions, and often in combination with the ethoxylated sorbitan esters (polysorbates).

2. Polyoxyethylene Sorbitan Esters

The hydrophilic properties of sorbitan esters can be strongly increased by ethoxylating the free-hydroxyl groups, yielding an ethoxylated sorbitan ester. Such products are referred to as polysorbates and are plastic or liquid products, completely soluble in water, where they form micelles. Their production and properties are described in detail by Benson (11).

Polysorbates are highly surface active and are used in many technical emulsions, but their application in foods is somewhat limited due to their low acceptable daily intake (ADI) value.

L. Sucrose Esters of Fatty Acids

Sucrose esters have been known for more than 30 years as esterification products of fatty acids and sucrose and other sugars, or as mixtures of partial glycerides and sucrose esters made by trans-esterification of sugars and glycerides. A great number of components from monoesters to octa-esters can exist in sucrose esters, depending on the degree of esterification.

There are several ways of producing sucrose esters (11,12) using different solvents or without solvent systems. The production may include solvent extraction for separation of esters with different hydrophilic–lipophilic characteristics. Sucrose monostearate is highly water soluble and can be used as an o/w emulsifier. Sucrose esters are generally accepted in Japan, but in other countries, the use of sucrose esters is limited in food systems.

M. Lecithin

Plant-seed lecithins are used in many foods, and lecithins from egg yolk have been used in margarine for many decades. The most common commercial lecithins today stem from soybean oil. The trade name lecithin is used commonly, although the product consists of a blend of different phospholipids.

Soybean lecithin is normally marketed as a solution of phosphatides in soybean oil containing between 60% and 70% phosphatides. Soybean lecithin can be fractionated in different ways (e.g., with acetone to remove most of the triglycerides present.

The composition of acetone-precipitated soybean phospholipids is approximately 41% phosphatidyl choline, 34% phosphatidyl ethanolamine, 19% phosphatidyl inositol, and 6% other phospholipids.

The isolated phosphatides may be further fractionated by ethyl alcohol or other short-chain alcohols, giving an alcohol-insoluble part consisting mainly of phosphatidyl choline. Lecithin may be hydrolyzed by enzyme treatment or reacted with hydrogen peroxide to make it more hydrophilic. A synthetic phosphatide for use in the chocolate industry, ‘‘Emulsifier YN,’’ is manufactured by the reaction of a diglyceride with phosphorus pentaoxide and neutralizing the reaction product partly with ammonia.

A comprehensive review of industrially produced lecithins and their applications are given by Szuhaj and List (13).

N. Structural Parameters of Emulsifiers

Long spacings obtained by x-ray diffraction analysis of homolog series of emulsifiers based on single fatty acids with varying chain lengths can give information about the molecular packing conditions in the crystalline state (14). Such data have been reported for monoglycerides, DATEMs and sorbitan esters (15). The size of the polar group in the crystalline lattice is of special interest, and for distilled monoglycerides, a value of 5.3 Å was found. This is quite similar to the polar group size of pure 1-monopalmitin (5.5 Å). The polar head group of DATEMs was found to be 9.3 Å, which is in the same range as pure 1,2-dimyristyl phosphatidyl choline (10.4 Å), as reported by Small (16). Sorbitan esters were found to have a polar head group size of 5.4 Å, quite similar to the dimension of glycerol in monoglycerides. Furthermore, the x-ray data indicate that in sorbitan tristerate crystals, the sorbitan group is oriented in the middle of the lipid bilayer, with one acyl group extended to one side and the two other acyl groups to the other. This indicates a similar structure to triacylglycerides and may explain why sorbitan tristearate is an effective crystal modifier in fat-based foods (17).

III. LYOTROPIC MESOMORPHISM

Humans have used aqueous liquid-crystalline phases in soap preparations for more than 2000 years. However, liquid crystals were first mentioned in 1904 by Lehman (18), and the structure of such polar lipid–water systems has been known only for about 50 years. Until about 1960, it was believed that both the so-called "neat" and "middle" soap phases had a lamellar-type structure. One of the first important attempts to clarify liquid crystalline structures was done by Luzzati and his co-workers in 1960 (19) when they demonstrated how to analyze lipid–water structures by low-angle x-ray diffraction. After that, numerous articles on mesomorphic lipid–water phases, their structure, phase behavior, and occurrence in biological systems have been published. Especially, soap systems and phospholipid–water systems have been studied extensively. A comprehensive review of surfactant–water liquid crystals has been given by Tiddy (20), and the phase behavior of phospholipids has been reviewed by Hauser (21); finally, the contribution by Small (16) gives the most detailed review on lipid–water interactions. Based on this background, only a brief description of lyotropic mesophases formed by polar lipids will be given here, together with a survey of the mesomorphic properties of food emulsifiers.

The molecular orientations of polar lipids in their crystalline state and a lamellar liquid-crystalline phase are shown in Fig. 13a. In their crystalline state, the lipids are orientated in bilayers with the polar groups "head to head," separated by layers of solid hydrocarbon chains usually packed in a DCL mode. Lipids with large polar groups may form crystals with penetration of hydrocarbon chains in a SCL mode as described earlier. When water is present and the temperature is above the Krafft point, T_c, water will penetrate through the polar region of the crystals. At the same time, transition from solid state to liquid state takes place in the hydrocarbon chain region, resulting in the formation of a liquid-crystalline phase. Such behavior is called lyotropic mesomorphism.

When a polar lipid in a stable crystalline form (e.g., β crystals) is mixed with water and heated to form a liquid-crystalline phase, less energy is required per mole of lipid than heating it in the absence of water to form a melt. This is demonstrated in Table 7, showing the transition enthalpy (ΔH) for β crystal transition to melt and β crystal + water transition to a liquid crystal of pure 1-monopalmitin (1-GMP) and of distilled, saturated monoglycerides ($C_{16}:C_{18}$ ratio = 35 : 65). The experimental value of ΔH are measured by differential scanning calorimetry (DSC).

It appears from Table 7 that the enthalpy values for the 1-monopalmitin transitions are higher than the corresponding values for distilled

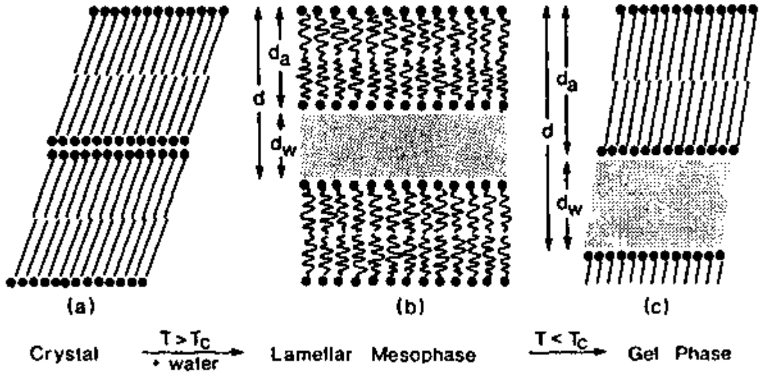

Figure 13 Structure models showing (a) the orientation of emulsifier molecules in the DCL structure in the crystalline state, (b) the formation of a lamellar, liquid-crystalline phase above the Krafft point (T_c) in water, and (c) the formation of an α-gel phase at a temperature (T) below T_c. The structure parameters d, d_a, and d_w can be measured by x-ray diffraction analysis.

Table 7 Transition Energies (ΔH) of Monoglycerides Compared to Monoglyceride–Water Systems

	Pure 1-monopalmitin		Distilled monoglycerides	
Transition scheme	Temp. (°C)	ΔH (J/g)	Temp. (°C)	ΔH (J/g)
Bulk lipid	75.9	210	70.0	172
β Crystals → melt				
Melt → α crystal	65.2	−113[a]	65.0	−105
α → Sub-α	37.7	−43	19.0	−17
Sub-α → β crystal[b]	—	−54	—	−50
Monoglycerides + water systems	60.3	203	55.0	133
β Crystals + water → lamellar lipid crystal				
Lamellar liquid crystal → α-gel phase	47.7	−84	55.0	−63
α-Gel → β crystals + water[b]	—	−119	—	−70

[a] Negative ΔH values = exothermic transition.

[b] Calculated values.

monoglycerides with a mixed fatty acid composition. This is probably due to a higher entropy in the distilled monoglycerides than in the pure 1-monopalmitin.

The latent heat of crystallization dissipated when the α-gel phase transforms to β crystals + water is a measure of the instability of the α-gel phase.

A. Lamellar Phase

The structure of the lamellar phase is shown in Fig. 13b and consists of bimolecular lipid layers separated by layers of water between the polar groups. The hydrocarbon chains are in a liquidlike state with a higher degree of motional freedom than in the corresponding anhydrous melt. The molecules in the lipid bilayer of the liquid-crystalline phases undergo several kinds of motion such as lateral diffusion, rotation, and the so-called flip-flop, which is a change in position from one side of the bilayer to another.

Figure 13b shows the structure parameters d, d_a, and d_w of the lamellar phase, which can be measured by low-angle x-ray diffraction methods.

The swelling of the lamellar phase can vary from 10 to 20 Å for the water layer thickness in pure 1-monoglyceride–water systems (22) to water layers of several hundred angstroms in commercial monoglyceride–water systems containing small amounts of ionised free fatty acids (23).

B. Phase Behavior of Monoglyceride–Water Systems

The mesomorphic behavior of emulsifiers in water depends on a number of factors:

1. *Wedge shape of the surfactant molecule* (i.e., the relative size of the polar head group to the length and degree of unsaturation of the hydrocarbon chain)
2. *Temperature* and ratio of surfactant to water
3. Degree of *ionisation* of ionic surfactants (pH). *Ion concentration* in the aqueous phase

In general, a blend of surface-active lipids (polar and nonpolar) may behave like one component, with the average polar characteristics like that of the blend. The phase behavior of surfactants in water can, therefore, be controlled by adjusting the average polarity by the addition of polar surfactants to less polar ones and vise versa.

Distilled monoglycerides, with approximately 95% 1-monoglyceride content, form similar mesomorphic phases in water as do pure 1-monoglycerides, but show different swelling properties. When saturated, distilled monoglycerides in their β-crystalline form are mixed with water and the suspension is heated to a certain temperature (Krafft point); when the melting point of the hydrocarbon chain bilayer is reached, then water will penetrate through the planes of the polar groups and a lamellar mesophase is formed with water layers alternating with lipid bilayers (see Fig. 13b).

The degree of swelling (i.e., the thickness of the water layer) may vary considerably, depending on a number of factors. The hydration force or osmotic repulsion will induce swelling of monoglycerides to a water layer thickness of about 16 Å. At this interplanar distance of bilayers, there is a balance of long-range van der Waals forces that keep the bilayers together and the hydration force. With pure monoglycerides, swelling is therefore limited to a level corresponding to a water layer thickness of 16–20 Å (22).

Electrostatic repulsions may further increase the swelling process, so the water layer thickness may increase to several hundred angstroms. This can be obtained by the incorporation of ionic polar lipids in the lipid bilayers. Swelling may then increase continuously in proportion to the water content of the system (23).

Binary phase diagrams of distilled, saturated, and unsaturated monoglycerides, pure glycerol monoelaidate, and pure glycerol mono-oleate are shown in Fig. 14. The distilled, saturated monoglycerides are based on fully

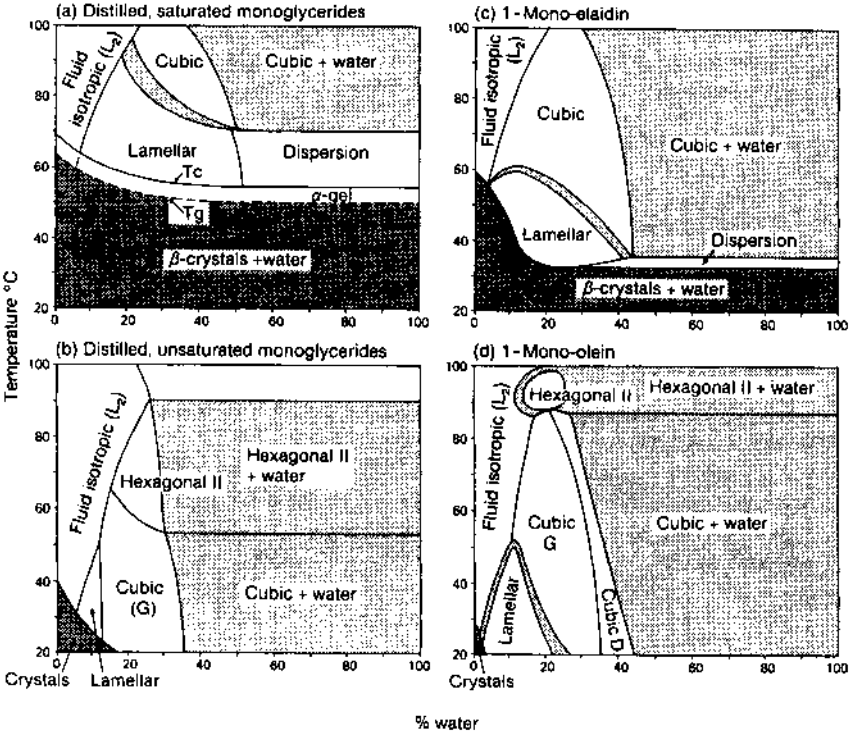

Figure 14 Binary phase diagrams of (a) distilled, saturated monoglycerides with fatty acid chain length C_{16}/C_{18} (35 : 65, DIMODAN HA, Danisco, Denmark), (b) distilled, unsaturated monoglycerides based on sunflower oil (DIMODAN U, Danisco, Demark), (c) pure 1-monoelaidin, and (d) pure 1-mono-olein. Abbreviations: $T_c =$ Krafft temperature; $T_g =$ transaction temperature for β crystal + water to α-gel; L = lamellar; G = gyroidal structure; D = diamond structure. (Modified from Refs. 24 and 25.)

hydrogenated animal fat (lard or tallow), a commercial product (Dimodan PM, from Danisco, Denmark). This product contains mainly C_{16}/C_{18} fatty acids and will be referred to as DGMS.

Studies of DGMS–water systems by means of a temperature-programmed x-ray diffraction method have shown that the phase transition from crystal + water to the lamellar phase takes place via formation of an α-gel phase. The α-gel phase exists in a temperature region of about 5°C below the region of the lamellar phase or dispersion state at high water contents. Such behavior is not found with pure monoglycerides. The phase diagram of pure 1-monopalmitin–water (22) shows a direct transition from the β-crystalline state to a lamellar phase. The formation of the α-gel phase in DGMS–water systems may be due to the mixture of different fatty acid chain lengths and the presence of a minor content of free fatty acids and free glycerol (usually below 0.5%). Apart from the formation of an α-gel phase, the DGMS–water phase diagram is quite similar to that of pure 1-monopalmitin.

The distilled, unsaturated monoglycerides referred to in Fig. 14b are made from sunflower oil. The fatty acid composition is 22% oleic acid, 64% linoleic acid, and 13% saturated C_{16} and C_{18} fatty acids. The pure 1-monoelaidate and 1-mono-oleate were made synthetically from 99% pure elaidic and oleic acid.

The phase behavior of distilled unsaturated monoglycerides is dominated by the viscous, isotropic cubic phase, which is formed at room temperature at water contents above 20%. The cubic phase is of the gyroidal type and can accommodate up to approximately 35% water (26). At higher water contents, a two-phase system of the cubic phase + water exists. At higher temperatures, from 55°C to 65°C, the cubic phase transforms to a hexagonal II phase; above 90°C, a fluid isotropic L2 phase exists with excess free water at water contents above 30%.

Monoglycerides of elaidic and oleic acids are commonly present in commercial monoglycerides based on partially hydrogenated vegetable oils. Therefore, their phase diagrams in water are shown in Figs. 14c and 14d. It can be seen from Fig. 14c that 1-monoelaidin forms a lamellar phase at 33°C and has a very narrow temperature range for the dispersion state at high water contents. The dominating mesophase in the 1-mono-olein–water system is the cubic gyroidal phase, which exists at a temperature range from below 20°C to 90°C at water contents above 20%. Two types of cubic phase are shown: the gyroidal (G) phase, which exists at water contents from 10% to about 35%, and the diamond (D) phase, which exists at higher water contents than 35% (24).

The phase behavior in water of industrial distilled monoglycerides from different manufacturers may vary slightly due to small changes in composition. It is important that the product be completely free of triglycerides, because minor quantities thereof will change the phase behavior markedly. A minor content of diglycerides (3–5%) is normally always present in distilled products and does not affect the formation of mesophases.

Saturated, distilled monoglycerides are often used in food processing as an aqueous mixture to obtain good distribution of the monoglycerides in the product. This happens particularly in cases where monoglycerides cannot be added to the product via a suitable carrier, such as fats or oils.

When DGMS–water systems were first studied (25), it was discovered that a neutral pH and a low electrolyte concentration in the water was of great importance for the formation and stability of diluted dispersions of DGMS in water. When very dilute dispersions containing 5–10% DGMS were buffered to pH 7, a clear homogeneous dispersion was obtained, and when cooled down, a stable gel could be formed. If the pH value was as low as 5–6, the dispersion was not clear, but milky, and the gel transformed quickly into a coagel (β crystals + water). In this connection, the presence of small quantities of free fatty acids plays an important role. It was later demonstrated (23) that the neutralization of the free fatty acids in DGMS increases in the swelling capacity of the lamellar phase to an optimum level.

Figure 15 shows x-ray spacings of lamellar phase of distilled monoglycerides made from fully hydrogenated fat (C_{16}/C_{18}: 30/65) in water at 60°C (23). Curve a represents system with neutralized free fatty acids (pH 7.0), and curve b represents systems with distilled water (pH 4.0), where the amount of free fatty acids (0.5%) in monoglycerides is not neutralized. There is a great difference in the swelling properties of the two system.

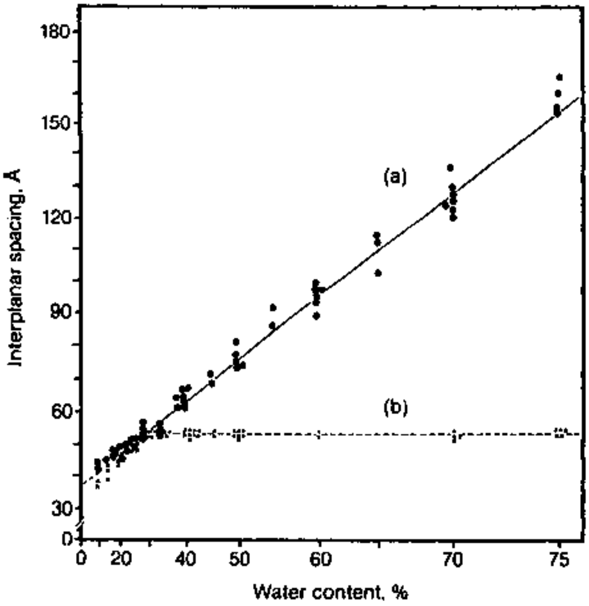

Figure 15 Swelling behavior of distilled, saturated monoglycerides (DIMODAN HA) in water at 60°C (a) with neutralization of 0.2% free fatty acids and (b) without neutralization. The interplanar spacing corresponds to the structure parameter *d* in Fig. 13b.

In the neutralized system (a), and d spacings increase in a linear relationship to the water content, showing continuous swelling behavior. Because $d_w = d - d_a$ and $d_a = 38\,\text{Å}$, it means that at a water content of 75%, the water layer thickness (d_w) is about 120 Å. The swelling of such neutralized monoglyceride–water systems continues with higher water contents, but no x-ray data are available for such diluted systems.

Contrary to the swelling behavior in neutralized water systems (pH 7.0), monoglycerides show a limited degree of swelling in distilled water with a pH below 4.0. Curve b in Fig. 15 shows a maximum d value of 54 Å, at a water content of 30%, corresponding to a water layer thickness of 16 Å. At higher water contents, no further increase in the d value is found, showing the same limited swelling behavior as found in pure 1-monoglycerides. The effect of introducing ionised amphiphilic molecules in the lipid bilayer is an increased swelling due to electric repulsion between charged groups in opposite bilayers. This repulsion effect will be reduced if the ion concentration of the water phase (e.g., $Na^+ \, Cl^-$) is increased. At concentrations above 0.3% sodium chloride in water, the effect of adding ionic active emulsifiers to the lamellar phase is inhibited (23).

C. Dispersion State and Crystalline Hydrates

All saturated monoglycerides form a dispersion as defined by Larsson (22) within the temperature region of the lamellar phase, when the water content of the system is higher than that corresponding to the lamellar phase. It is assumed that the dispersion consists of lamellar aggregates of monoglycerides in equilibrium with water.

The thickness of the water layer in the dispersion aggregates may vary considerably depending on the conditions with regard to pH, ion concentration, and purity of the monoglycerides. The dispersion state does not exist at temperatures above the transition point of lamellar phase to cubic phase. When the temperature of the dispersion is increased above that point, a two-phase mixture consisting of cubic phase + water is formed. Therefore, in diluted aqueous dispersions of monoglycerides, the temperature should always be carefully controlled in order to avoid formation of the cubic phase. Crystallization from a dispersion of monocaprin can be seen in Fig. 16, where a fragment of a β crystal is visible in the lower left corner. It can also be seen that a number of dispersion aggregates are in contact with the crystal surface. On the basis of similar observations, a specific mode of crystallization has been suggested which will lead to the formation of β crystals with unusual properties (27). It is proposed that the bimolecular lipid leaflets unfold from the dispersion aggregate into the surface of the crystal, which will then grow with discrete layers in a direction perpendicular

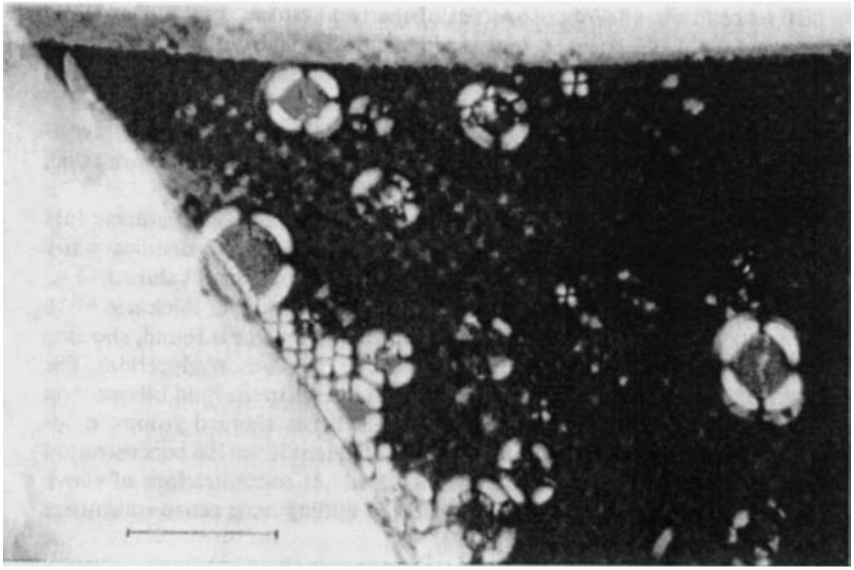

Figure 16 Photomicrograph of a dispersion of monocaprin in water, showing sperical dispersion aggregates with internal lamellar structure. A fraction of a β crystal of monocaprin is seen in the lower left corner. Bar: 30 μm, polarized light.

to the surface plane. This direction of growth can, in fact, be seen directly under the microscope in a dispersion, as shown in Fig. 16. The result of such a crystallization process will be surface consisting of the polar groups of the monoglycerides. Normally, the crystal surface consists of the lipophilic methyl end groups when crystallization takes place from the melt or from solvents. The polar surface formed when crystallized from an aqueous phase is responsible for a great water-binding capability. For example, 10 parts of monoglycerides by weight can absorb 90 parts of water; such a mixture has an ointment like consistency. Industrial products of 20–25% distilled, saturated monoglycerides in the form of β crystals suspended in water (so-called hydrates) are commercially available and are used to a great extent in the baking industry as crumb-softening or antistaling agents in bread.

The rate of crystallization initiated by cooling of the dispersion to a temperature below T_c depends on various factors such as the chain length of the monoglycerides and pH. Monoglycerides with short chain length, like monocaprin or monolaurin, recrystallize relatively quickly, compared to palmitic and stearic fatty acid monoglycerides. Pure 1-monoglycerides with chain lengths shorter than monomyristin transform directly from the lamellar phase to a β crystal + water mixture (22). At a low pH, the addition of salts and mechanical agitation will promote the formation of β crystals, and this is used in the production of monoglyceride hydrates on a commercial scale.

D. Mesomorphic Phases of Other Food Emulsifiers

In general, the phase diagrams of the commercial food emulsifiers described in this sub-section will show the typical mesomorphic phase behavior of these products without going into detail about multiphase regions that may exist.

1. Polyglycerol Esters

The composition of commercial polyglycerol esters is very complex due to variation in both the degree of polymerization and degree of esterification. This results in products containing many different components. Therefore, when polyglycerol esters of C_{16}/C_{18} fatty acids are mixed with water above their melting point, they form reversed hexagonal phases. The hexagonal phase swells up to a content of 40% water, and at higher water concentrations a two-phase mix of emulsifier and water is obtained. The reversed hexagonal phase is common, with polar lipids containing a mix of polar and nonpolar components. Monodiglycerides with a mono ester content below approximately 60% form hexagonal phases in water (22).

The dispersibility in water of such lipophilic emulsifiers can be improved by adding high-polar coemulsifiers (e.g., sodium stearate). Commercial polyglycerol esters may contain up to 6% sodium stearate; this solubilizes the hexagonal phase, making it possible to produce aqueous dispersions or gels to be used as aerating agents in food products. The emulsifier is mixed with water at a temperature above its melting point (Krafft point) until total swelling is obtained; then, the mix is cooled to ambient temperature, forming a plastic gel. Such gels are used in the baking industry to facilitate aeration of cakes of various types. The phase behavior of triglycerol and octaglycerol esters have been described elsewhere (28).

Distilled diglycerol monoacyl fatty acid esters have a unique phase behavior in water. All diglycerol esters with chain lengths from C_{12} to C_{18} form lamellar phases above their Krafft point, and in contrast to the phase behavior of monoglyceride–water systems, no other liquid-crystalline phases have been observed. Even the unsaturated diglycerol mono-olein forms a lamellar phase only in the temperature region examined. The Krafft point of distilled diglycerol esters with fatty acid chain lengths from C_{12} and C_{18} is shown in Fig. 17.

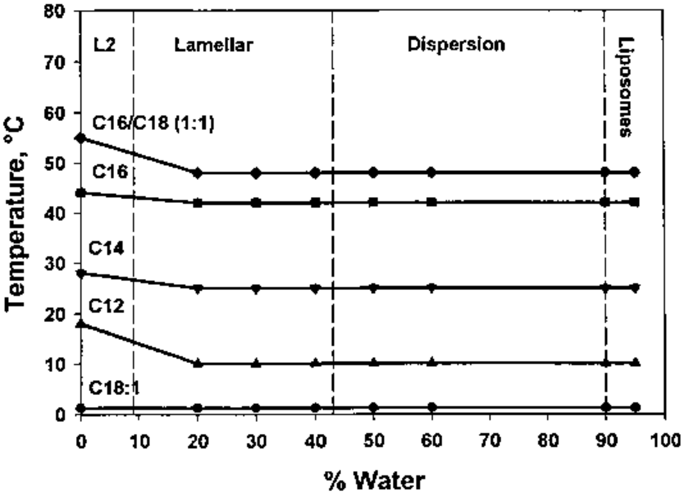

Figure 17 Krafft point lines of distilled, diglycerol fatty acid esters with fatty acid chain lengths from C_{12} to C_{18}. The formation of lamellar liquid-crystalline phases and dispersion of vesicles above the Krafft point of the emulsifiers as a function of the water content are indicated.

The swelling capacity of diglycerol esters in water is limited, and above a lipid : water ratio of 60 : 40, a stable dispersion of multilamellar vesicles is formed. The water layer thickness in the vesicles is 22–30 Å (15), corresponding to the swelling behavior of diacyl phosphatidyl choline (16). The addition of anionic coemulsifiers (e.g., sodium stearate) increases the swelling properties of diglycerol esters in a fashion similar to that of monoglycerides containing fatty acid sodium salts.

Distilled diglycerol esters of stearic or oleic acid are capable of forming liquid-crystalline films around oil droplets in o/w emulsions and can be used to stabilize protein-free emulsions (9).

2. Organic Acid Esters

The esters of dicarboxylic acids such as diacetyl tartaric acid or succinic acid and saturated monoglycerides (DATEM, SMG) contain a free-carboxyl group. Neutralization of the free-carboxyl group, by forming a sodium salt of DATEM or SMG, increases its swelling ability in water. X-ray data of the lamellar phase formed by DATEMs at 60°C show a similar swelling behavior to that of the neutralized DGMS–water systems. A schematic phase diagram of neutralized DATEMs in water is shown in Fig. 18.

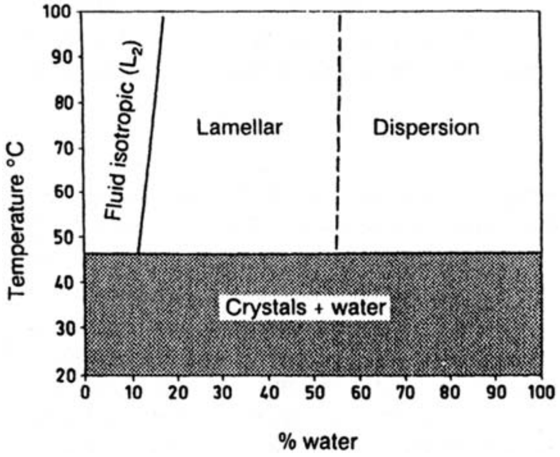

Figure 18 Schematic phase diagram of diacetyl tartaric acid ester of saturated monoglycerides (DATEMs) in water, pH 5.

A dispersion of 5% DATEMs in water has a pH value of 1–2, and at this low pH, very little, if any, swelling of DATEMs in water takes place.

An increase in pH, by adding sodium hydroxide to the water until a pH of 4.6 is reached, will give total swelling in water. The DATEMs based on saturated monoglyceride form lamellar phases above a temperature of 45°C. The DATEMs based on an unsaturated monoglyceride, such as mono-olein, form a lamellar phase at 20°C, which is stable up to above 80°C. Once the DATEM has swelled in water, it remains in its liquid, crystalline state, even when cooled below the temperature where the lamellar phase was formed. The hydrocarbon chains have little tendency to crystallize and form a gel. The DATEM esters are used mainly in the bakery industry in yeast-raised doughs, where their interactions with flour components improve the volume and texture of the finished product. The anionic emulsifiers (e.g., DATEM, SSL) are used in various o/w-type emulsions in order to increase stability towards coalescence, due to their interaction with interfacial bound proteins.

3. Stearoyl Lactylates

Sodium stearoyl lactylates (SSLs) are not neutralized completely. They have an acid value from 60 to 80, and the pH of an aqueous dispersion of SSL is therefore about 4–5. The phase behavior of SSL in water is strongly dependent on its degree of neutralization. At low pH conditions, a hexagonal II mesophase is formed at temperatures above 45°C, and this phase may

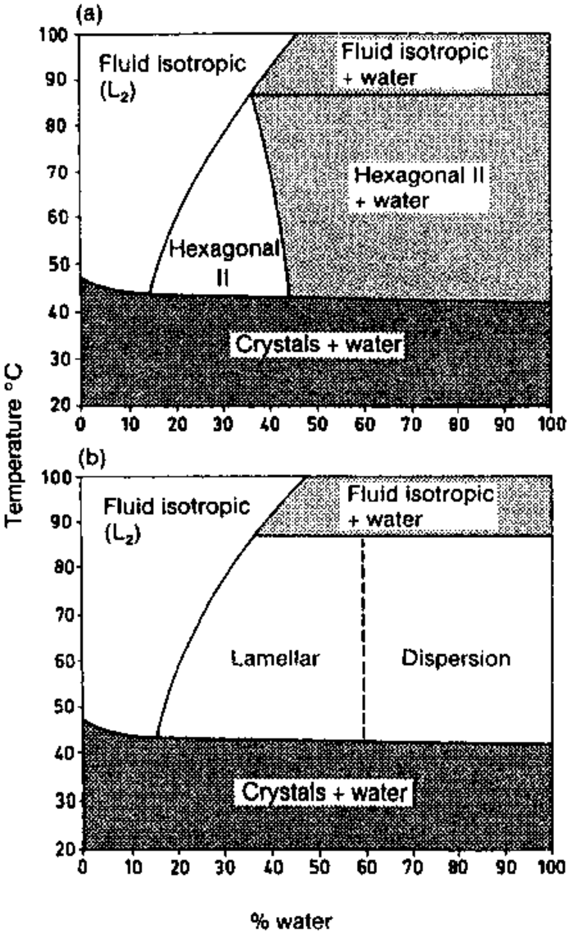

Figure 19 Schematic phase diagram of sodium stearoyl lactylate (SSL) in water (a) with partial neutralization to pH 5.0 and (b) after neutralization to pH 7.0. The figure shows an increased swelling into a lamellar phase or a dispersion of vesicles at pH 7.0.

contain 20–40% water as shown in Fig. 19a. If more water is present, the excess water will separate from the mesophase. X-ray data concerning such a hexagonal II mesophase of SSL–water systems at 60°C and pH 4.5 have shown that the diameter d_w of the water cylinders increases from 24 Å at 20% water to 40 Å at 42% water and that the specific surface in contact with water (S) increases from 25 Å^2 to 43 Å^3 with increasing water content from 20% to 42%. The structural parameters S, d_a, and d_w are very similar to data reported by Reiss Husson (29) for egg phosphatidyl ethanolamine, which also forms a hexagonal II mesophase in water. When SSL is neutralized, its phase behavior is changed, and a lamellar phase is formed, instead of the hexagonal II phase, as shown in the phase diagram in Fig. 19b. The lamellar phase of the neutralized SSL can be diluted with water to dispersion. The gel formed from the lamellar phase on cooling is very stable, and SSL may be used together with other emulsifiers (i.e., monoglycerides in order to stabilize gel phase, which are used in food processing. Due to its hydrophilic nature, SSL is used in many o/w emulsions. Both SSL and the corresponding calcium salt (CSL) are effective starch-complexing agents and are used mainly in the bakery and starch industries.

4. Lecithin

Lecithin is a natural emulsifier that has been used in foods for centuries. The phase behavior of lecithins in water was been reviewed in detail (16,21), so only a brief description of their phase behavior will be given here. Pure phosphatidyl choline forms a lamellar mesophase in water at temperatures from ambient to 100°C. The swelling of the lamellar phase is limited to a 40% water content, corresponding to a water layer thickness of about 30 Å. At higher concentrations of water, a dispersion of spherical aggregates with internal lamellar structure in the excess water (liposomes) is formed. Phosphatidyl ethanolamine (cephalin) is reported to form both lamellar and hexagonal II phases in water (29), whereas egg yolk lysolecithin exhibits a different lyotropic behavior than that of the other egg yolk phosphatides. Due to its more hydrophilic character, it forms hexagonal I phases in water in concentrations of up to about 55% water at temperature above 37°C. Commercial lecithins from soybean or rapeseed are mixtures of phospholipids with different phase behaviors in water. Mixtures of phosphatidylcholin and phosphatidylinositol form only lamellar phases, whereas the more lipophilic phosphatidylethanolamine forms reversed hexagonal phases in water. Consequently, the phase behavior of oil seed lecithins may vary with their composition.

5. Polysorbates

When fat derivatives such as monoglycerides or sorbitan esters are reacted with ethylene oxide, the resulting products become more hydrophilic in character, and their ability to form micelles in water is greatly increased. Polyoxyethylene (20) sorbitan monoleate (POESMO) forms a mesomorphic phase in water of the hexagonal I type with lipid cylinders surrounded by water, at temperatures up to 30°C, and with water contents from 30% up to 60%. POESM-stearate also produces this phase with the same amount of water, but at temperatures about 20°C higher (i.e., from 38°C to 50°C). At higher temperatures, an isotropic solution is formed. X-ray data of aqueous systems of these products (23) have shown that the specific surface *S* per molecule in contact with water is 145 Å^2, which is four times higher than the specific surface of monoglycerides in the lamellar phase, as shown in Table 8. The hexagonal I mesophase (middle) can solubilize triglycerides in small quantities. On further addition of triglycerides, a lamellar phase is formed.

Sorbitan monostearate has, in general, a similar phase behavior in water to that of glycerol monostearate, but it has not been studied in detail. It forms a lamellar phase, and when excess water is added, a liquid-crystalline dispersion is made. Sorbitan tristearate, however, does not form any mesomorphic phases in water. The use of polysorbates and sorbitan esters in emulsions of various types is reviewed by Benson (11).

E. The α-Crystalline Gel State

The term "gel" used in this context originates from the soap industry many decades ago. It was used then to describe certain soap–water systems with a clear gellike appearance. The term should not be confused with gels formed by other substances, such as starch, or hydrocolloids such as gelatin or pectin.

The gel is a crystalline state of the emulsifier with layers of water between the polar groups, as shown in Fig. 13c. The structure of the gel is similar to the lamellar phase. The difference is that the hydrocarbon chains are no longer in a liquidlike state, but are solid and orientated parallel to each other in an α-crystalline mode of packing. Consequently, the gel is characterized by a single strong x-ray diffraction line at 4.15 Å in the short spacing region, and several long spacings with an interrelation of 1 : 1/2 : 1/3 : 1/4, indicating a lamellar system. The angle of tilt of the hydrocarbon chains toward, the water layer in a gel is 54°, and the lateral packing of the chains can be described by a hexagonal subcell, where the chains have rotational freedom (22). The gel is a metastable state, and the water layer between the polar groups will be reduced in time. When all the water is expelled, a suspension of crystals + water (coagel) is formed. The so-called hydrate form of monoglycerides is a coagel. Polymorphic emulsifiers such as monoglycerides will transform into the most stable crystal form, the β-form, because an anhydrous α-form does not exist in the presence of water. Emulsifiers that are nonpolymorphic and stable in the α-crystalline form may form gels with water that are very stable. This is the case with gels of sodium stearoyl lactylates, tetraglycerol monostearates, SMG, DATEMs, and polysorbates. The stability of monoglyceride gels depends on their composition, because monoglycerides with fatty acid chain lengths of from C_{16} to C_{20} are more stable in the gel form than monoglycerides with

Table 8 X-ray Data of Lamellar Mesophases and Corresponding Gel Phases of Monoglyceride-in-Water Systems Compared to Other Emulsifier-in-Water Mesophases

Emulsifier-in-water system	X-ray spacings d (Å)	Lipid bilayer thickness d_a (Å)	Water layer thickness d_w (Å)	Specific surface in contact with water S (Å^2)
Monoglycerides				
Lamellar phase, 40% water, 60°C	63.8	38.1	25.7	32.0
Gel phase, 40% water, 25°C	93.9	54.9	39.0	22.0
Lamellar phase, 75% water, 60°C	154	38.0	116	32.0
Gel phase, 75% water, 25°C	230	55.0	175	22.0
Polysorbate-60				
Hexagonal I phase, 60% water, 45°C	90.0	59.8	30.2	145
Na-stearoyl lactylate				
Hexagonal II phase, 41% water, 60°C	59.5	19.2	40.3	42.6

shorter chain lengths. The swelling capacity and stability of industrial distilled monoglyceride gels are strongly influenced by the presence of ionic active emulsifiers and salt concentration in water (23,30).

When cooled the neutralized DGMS–water mixtures shown in Fig. 15 form gels with water contents up to about 75%, and the x-ray spacings increase in direct proportion to the water content up to about 230 Å at 75% water (30). No spacing were ever found in the region between 64 Å and 90 Å, corresponding to water contents between 20% and 40% in the neutralized system. A similar phenomenon has been described for soap–water systems by Skoulios (31), who suggested that the reason for this behavior was that certain water layer thickness cannot exist in a gel phase. When the *d* spacings of the DGMS–distilled water gels are increased up to 64 Å, corresponding to a water concentration of 20%, the *d* values remain constant at 64 Å, independent of the water concentration. The thickness of the bimolecular lipid layer d_a was calculated by analysis of the neutralized DGMS–water systems to be 55 Å (22). The value of d_a of the DGMS–distilled water systems was found to be only approximately 50 Å. The differences in thickness of the lipid bilayers may be due to a different angle of tilt of the hydrocarbon chains toward the water layer in the two systems. The d_a value of 55 Å in the neutralized systems is identical to the long spacing of the anhydrous α-form of DGMS. The water layer thickness, d_w, is 175 Å in mixtures containing 75% water. Undoubtedly, the swelling continues with a higher water content. The optical texture of neutralized DGMS gels containing 95% water indicates a lamellar structure, and such gels may have water layers of several hundred angstroms.

The microstructure of an α-gel phase and the corresponding β-crystalline coagel (hydrate) is demonstrated in Fig. 20. The α-gel has a typical lamellar structure with lipid bilayers alternating with water layers having a thickness of about 200 Å. The coagel is a tridimensional network of β-crystalline platelets suspended in water.

When a lamellar phase-of monoglyceridests cooled and a gel phase is formed, the x-ray spacings (*d*) increase, although the proportion between the water content and the lipid phase is kept constant. This phenomenon is due to the crystallization of the hydrocarbon chains in the lipid bilayer, which results in a decrease in the specific surface area (*S*) of the monoglyceride molecules in contact with the water, as shown in Table 5. The thickness of the lipid layer d_a increases from 38 Å in the lamellar phases to 55 Å in the gel phases, due to the crystallization process, whereby the hydrocarbon chains are stretched out and aligned parallel to each other. At the same time, the specific surface area *S* decreases from 32 Å^2 in the lamellar phase to 22 Å^2 in the gel phases. The crystallization of the hydrocarbon chains cannot alone account for the increase in interplanar spacings that occur on transition

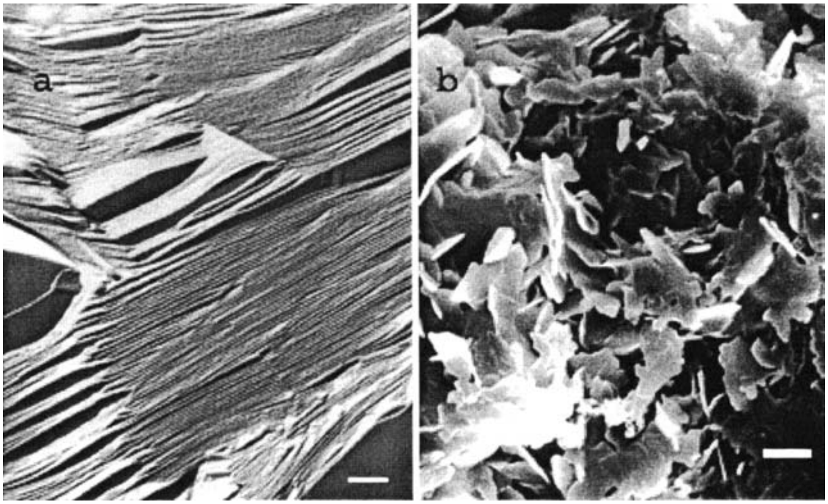

Figure 20 Microstructure of (a) an α-gel phase of distilled, saturated monoglycerides in water (25 : 75) by freeze-fracture transmission electron microscopy (bar = 0.2 μm) and (b) the corresponding coagel phases (hydrate) by scanning electron microscopy (bar = 2 μm). The water layer thickness of the gel phase was measured to approximately 200 Å by x-ray diffraction analysis. The phase (b) is a network of β-crystalline platelets of monoglycerides in water. (Courtesy of Dr. W. Buchheim, Kiel, and Danisco, Denmark.)

from the lamellar phase to the gel state. It can be seen from Table 5 that the water layer thickness increases during the formation of a gel, although the total water content is kept constant. The main reason for this extension of the water layer is the decrease in specific surface, S, of the monoglycerides in contact with the water, which is, in turn, caused by a lateral contraction of the lipid molecules. The rearrangement of the molecules during the transition from the lamellar phase to the gel phase is illustrated schematically in Fig. 13, where the relative distances for d, d_a, and d_w are shown for a lamellar phase and a gel phase containing 40% water.

Sodium salts of stearic acid added directly to DGMS increase the swelling capacity of the gel phase to the same extent found when neutralizing the free fatty acids with sodium hydroxide. The minimum concentration of soaps needed to obtain the maximum degree of swelling is about 0.5% of the DGMS. The effect of sodium and calcium soaps on the gel phase is quite different. Sodium stearate gives a high degree of swelling, whereas calcium stearate inhibits the swelling of a gel (23). The ionic active emulsifiers shown in Table 9 also increase the swelling and stability of monoglyceride gels, whereas the nonionic emulsifiers do not have this effect. Finally, it should be

Table 9 Influence of Various Additives on Swelling Capacity of DGMS and Distilled Water Systems Containing 70% Distilled Water

			Lamellar phase (60°C)		Gel phase (25°C)	
	Percent of additives by weight of DGMS	pH of aqueous mixtures	Spacings d (Å)	Water layer thickness d_w (Å)	Spacings d (Å)	Water layer thickness[a] d_w (Å)
Nonionic additives						
Tetraglycerol monostearate	4	4.7	54.1	16.0	62.3	12.3
Ethoxylated monoglycerides	4	4.6	54.6	16.5	79.1	29.1
Polyoxyethylene-(20)-sorbitan monostearate	4	4.2	61.7	23.6	67.0	17.0
Polyoxyethylene stearate	4	4.3	54.6	16.5	67.0	17.0
Lauryl alcohol polyglycol ether	1	4.3	55.1	17.0	61.7	11.7
Anionic active additives						
Succinylated monoglycerides (sodium salt)	4	5.4	123.2	85.1	156.0	101.1
Sodium stearoyl-2-lactylate	4	4.7	128.4	90.3	163.0	128.1
Sodium lauryl sulfate	1	6.3	131.2	93.1	198.0	143.1
Sodium stearate	1	6.9	131.0	92.9	184.0	129.1
Calcium stearate	1	—	130.0	91.9	62.3	12.3
Cation active additives						
Cetyl pyridinium bromide	1	4.6	131.0	92.9	192.0	137.1
Benzotonium chloride (Hyamin 1622)	1	4.6	128.0	89.9	60.5	10.5
Control						
DGMS + distilled water	—	5.0	54.1	16.0	64.0	14.0

[a] Calculations based on $d_a = 54.9$ Å for systems with ionic additives and $d_a = 50$ Å for system with non-ionic additives.

Source: From Ref. 23.

mentioned that the stability of the gel phase is very sensitive to the ion concentration in the water. The addition of 0.04% sodium chloride to the lamellar phase of monoglycerides in water inhibits the formation of a totally swollen gel at a high water content.

The stability of the monoglyceride gel structure or other emulsifiers in aqueous systems is an important factor in preventing changes in the functional effect of emulsifiers when gels are used as aerating agents.

Lipophilic, α-tending emulsifiers, such as ACETEM, LACTEM, or PGMS, and glycerol mono-olein (GMO) can swell in their crystalline state in the presence of water and form α-crystalline gel structures (32,33). This gel formation can be shown by x-ray diffraction analysis, as shown in Table 10. The emulsifiers, PGMS or GMO, are dissolved in coconut oil (Melting point = 31°C) and poured over a water phase in a beaker and then cooled to 5°C for several hours. Samples of the interfacial layer and upper bulk phase free of water are taken for x-ray analysis.

The x-ray data on the water-free bulk phase show two sets of long spacings representing (A) the PGMS or GMO and (B) the coconut oil. This shows that the emulsifiers do not cocrystallize with the coconut oil but form crystalline aggregates separately from the coconut oil crystals.

The interfacial layer also exhibits two sets of long spacings. The values of 56.1 Å and 66.0 Å represent long spacings of PGMS water gel and GMO water gel respectively, and the values of 35.4–36.1 Å represent long spacings of the coconut oil.

An interesting feature is the increase in the long spacings of the emulsifier phase (A) from the bulk system to the interfacial layer. For PGMS, the increase is about 7 Å, and for GMO, the increase is 17 Å. The changes in long spacings induced by the contact with water can only be due to water

Table 10 X-ray Diffraction of Interfacial Layers from Coconut Oil–Emulsifier–Water System at 5°C

Sample preparation	Long spacings *d* (Å) A Emulsifier	 B Coconut oil	Short spacings *d* (Å)
Interfacial layer			
Coconut oil–PGMS–water	56.1	35.4	4.18–3.83
Coconut oil–GMO–water	66.0	36.1	
Bulk phase			
Coconut oil–emulsifier (1 : 1) (melt, cooled to 5°C)	48.9	36.3	4.29–4.16–3.97–3.82–3.65

penetration through the polar regions of the emulsifier crystals driven by a hydration force, forming an α-gel structure. The hydration of GMO at ambient temperature or even lower temperatures is in good agreement with its phase diagram.

The α-gel formation is of great importance in whippable emulsions (creams, toppings), and the hydration of unsaturated monoglycerides at low temperature can be used to make powdered monoglyceride blends that are dispersible in water and used as cake emulsifiers.

F. Liquid Crystals and Emulsion Stability

Liquid crystals in emulsions were observed in 1969 by Friberg and his co-workers (34), and in 1971 (35), they demonstrated that liquid-crystalline phases may form on the surface of oil droplets in o/w emulsions and provide stability against coalescence.

The presence of liquid-crystalline mesophases in food systems is not a common feature partly due to a low concentration of polar emulsifiers and partly due to lack of stability of emulsifier–water mesophases, which may be negatively affected by other food ingredients, such as fats, proteins, carbohydrates, salts, and so forth.

An example of o/w emulsions where liquid crystals have been found by polarized microscopy is salad dressings made with egg yolk lecithins. A micrograph of such an emulsion is shown in Fig. 21. The strong birefringent layers around the oil droplets are present due to a formation of liquid-crystalline layers. Similar observations have been made with other types of emulsions (36,39).

The existence of lamellar, interfacial multilayers has been shown to provide stability to emulsions of sunflower oil in water by Pilpel and Rabbani (37,38). The emulsifiers used were sorbitan monopalmitate (Span-40) in combination with Polysorbate 40. The optimal ratio of the two emulsifiers for emulsion stability was found to be 5 mol of Span-40 to 1 mol of Polysorbate 40. With this ratio of the lipophilic Span-40 and the hydrophilic Polysorbate 40, ideal conditions for the formation of liquid-crystalline lamellar structure at the o/w interface exist. The formation of such lamellar structures around oil droplets was shown by electron microscopy.

G. Polar Lipid–Water Phases of Natural Origin

Plants contain polar and nonpolar lipids, and the polar lipids may exist in the form of liquid-crystalline phases containing water. This is the case in cereals (e.g., wheat flour), which contains about 2.5% total lipid on dry

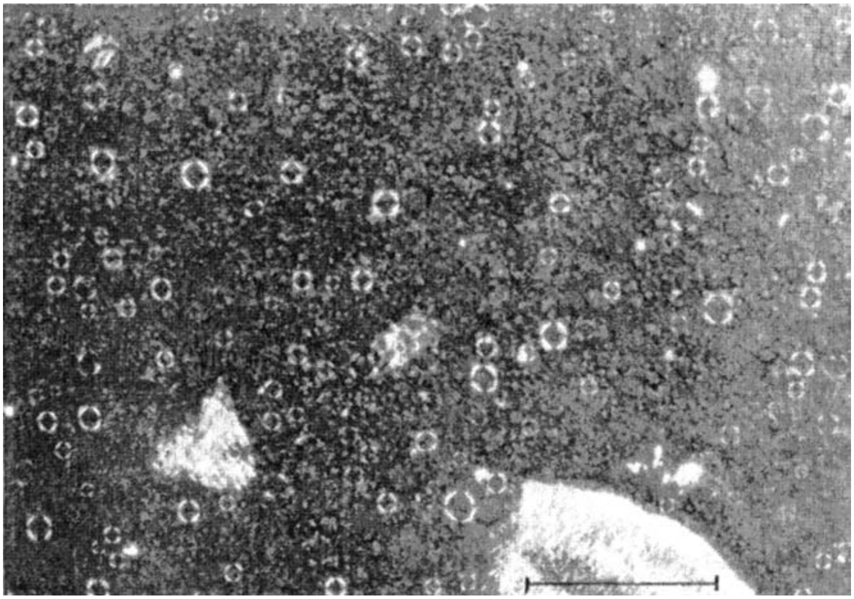

Figure 21 Commercial salad dressing made with egg yolk lecithin. The oil droplets are seen as dark spheres surrounded by liquid-crystalline layers of phospholipids, showing a strong birefringence in polarized light microscopy. Bar = 100 μm.

basis. The polar lipids in wheat flour are glycolipids, phospholipids, free fatty acids, and monoglycerides, which amount to approximately 45% of the total wheat lipids.

Carlson et al. (40) demonstrated that both lamellar and hexagonal II liquid-crystalline phases exist in ternary systems of nonpolar and polar wheat flour lipids and water. The amount of lamellar lipid water phases was found essential for the bread-baking quality of the flour. Liquid-crystalline phases of polar lipids and water have also been found in mature wheat endosperm by freeze-fracture electron microscopy (41).

IV. FUNCTIONAL PROPERTIES OF EMULSIFIERS IN FOODS

A. Emulsification and Emulsion Stability

The manufacture of o/w food emulsions often involves a homogenization process under turbulent flow conditions. The relative contribution to droplet disruption by energy input (e.g., homogenisation pressure) and the effect of emulsifiers on reduction of interfacial tension between oil and water is approximately 100 : 1. The emulsification process and final particle distribution of the emulsion are thus mainly controlled by the energy input, and the influence of emulsifiers is negligible.

In the case w/o emulsions (e.g., margarine, spreads), which is made under low-energy impeller emulsification methods, the addition of emulsifiers has a significant effect on reducing the water droplet size.

B. Interfacial Emulsifier–Protein Interactions in Emulsions

Many food emulsions contain milk proteins or proteins from plants or animal origin. The main function of emulsifiers in such emulsions is either to increase stability toward coalescence or creaming/precipitation during long-term storage (e.g., recombined milk, coffee whiteners, salad dressings, etc.) or to induce destabilization and increase whippability of emulsions to be aerated (e.g. ice cream mix, cream, toppings, etc.).

Interfacial interactions between emulsifiers and proteins in emulsions play a vital role for the physical properties of emulsions. A cooperative emulsifier–protein adsorption at the surface of fat globules may improve the surface film strength and coherence, increasing emulsion stability (17). This is found with anionic emulsifiers (DATEM, SSL) that bind proteins to the surface of fat or oil droplets via a complex formation (42). Anionic emulsifiers are therefore very effective in emulsions, where long-term stability is important.

In contrast, nonionic emulsifiers (polysorbates, monoglycerides, LACTEM, or PGMS) compete with proteins for interfacial adsorption and may displace the proteins more or less from the interface. The displacement of protein from fat globule surfaces is part of the destabilization of whippable emulsions. Other important functions of emulsifiers in the destabilization process is to enhance crystallization of the fat phase and to reduce the coherence and viscoelastic properties of the surface film, making the fat globules more sensitive to shear (43,44), increasing flocculation and partial coalescence. The formation of fat globule aggregates during whipping is enhancing the foam formation and stabilizes the foam structure of aerated emulsions (17,33,45,46).

C. Interaction with Starch Components

Food emulsifiers are used in many starch-based foods such as bakery products, processed potatoes, breakfast cereals, pasta foods, and so forth. The primary function of emulsifiers such as monoglycerides, SSLs CSLs, and others is to form a water-insoluble complex with the starch component amylose. The amylose is present in most starches in an amount of 17–25% and is the source of textural problems (stickiness, firmness) in starch-containing foods. By formation of a lipid–amylose complex, the texture of reconstituted potato products and pasta foods is improved. Monoglycerides in wheat bread are used to reduce crumb firmness and delay the staling process. Saturated monoglycerides are the most effective amylose-complexing agents and are used in bread in the form of the β-crystalline hydrates (47), or dispersible fine powders. Stearoyl lactylates (SSLs, CSLs) are also used as starch-complex agents in many products, primarily bread.

The amylose-complex formation in wheat bread may also affect the retrogradation of amylopectin, the major starch component. At low use 1evels of monoglycerides (e.g., 0.3–0.5% based on flour weight), the monoglyceride mainly interacts with the amylose fraction. At higher concentrations of monoglyceride (1–2%), they seem to interact directly with the amylopectin fraction, reducing the rate of retrogradation, which is partly responsible for the bread-firming process during storage (47).

D. Dough-Strengthening Effects of Emulsifiers

Hydrophilic emulsifiers such as DATEMs, SMGs, SSLs, CSLs, and polysorbates are used in yeast-raised doughs to increase shock-resistance fermentation stability and enhance volume of baked products such as speciality bread, fiber bread, rolls, and buns. The emulsifier function mechanism in doughs is not completely understood, although many emulsifier action models have been proposed. A relation to the physical properties of natural flour lipids may be relevant because it is known that the polar flour lipids are very important for the baking quality of flour (48). The polar flour lipids form liquid-crystalline phases in water and—especially the lamellar phase formed by polar flour lipids, such as galactolipids and phospholipids—are considered important for the baking quality of flour. Polar-lipid bilayer structures may associate with hydrated gliadin proteins at gas cell–water interfaces and improve the gas-retention capacity of the dough during fermentation.

All effective dough-strengthening emulsifiers (DATEMs SSLs, polysorbates, and lecithins) form lamellar liquid-crystalline phases in water under conditions similar to dough mixing. They may thus combine with the polar lipids in flour into biomembrane like structures and support the function of the native, polar lipids in flour. The role of lipids in bread making is extensively discussed by Eliasson and Larsson (49).

E. Legal Aspects

Before a food emulsifier is permitted for use in foods, it has to be tested in a number of toxicological studies including short- and long-term feeding trials on several animal species together with studies on metabolism.

The evaluation of emulsifiers is done by the Joint Expert Committee on Food Additives (JECFA) of the Food and Agriculture Organization World Health Organization (FAO/WHO), by the commission of the European Communities' Scientific Committee for Food (SCF), and in the United States by a department of the Food and Drug Administration (FDA).

The results of the scientific, independent toxicological evaluations are used by national health authorities for food regulations.

The acceptable daily intake (ADI) values and regulatory identification numbers for the emulsifiers dealt with here are shown in Table 1. All emulsifiers approved by local health authorities should be considered as safe food ingredients when used within their limits of the ADI values, which are given in the reports of the Joint FAO/WHO Expert Committee on Food Additives (50).

V. CONCLUDING REMARKS

The aim of this chapter is to present a general review of the most commonly used emulsifiers in the food industry. Food emulsifiers should be considered polar lipids with specific properties and functions. Their chemical composition determines their physical properties, which is of importance for their different functions in foods. Most interactions between emulsifiers and other food ingredients take place in surface monolayers or at mixed lipid–protein interfacial structures. Such interactions takes place in emulsions, resulting in increased stability of some types of emulsions and partial destabilization of others.

The capability of lipid emulsifiers to form association structures with water in form of lamellar dispersions or vesicles enhance molecular interactions of emulsifiers with water soluble food components (e.g., starch components). Furthermore, specific lipophilic emulsifiers may be incorporated in the crystal lattice of fats, thus controlling crystallization and texture of the product.

The molecular behavior of emulsifiers in all states or order, in bulk phases and at interfaces in emulsions, foams, and colloidal systems is very important to understand in order to be able to predict functional properties of emulsifiers in foods.

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