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EMULSIFIERS AS ADDITIVES IN FATS: EFFECT ON POLYMORPHIC TRANSFORMATIONS AND CRYSTAL PROPERTIES OF FATTY ACIDS AND TRIGLYCERIDES

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Abstract

The role of emulsifiers in polymorphic transformations of fats and fatty acids is treated in this paper. Their effect as crystal modifiers in solution-mediated transformations (in fatty acids) is compared to that of a dynamic controller of polymorphic transformations in triglycerides. The importance of chemical structure both in the hydrophilic and in the hydrophobic moieties of the emulsifier for an inhibitory effect on phase transitions has been emphasized. The emulsifier solubility and crystallization behavior in different solvents are probably the main factors affecting its ability to interfere with the kinetics of solution-mediated transformations. On the other hand, certain requirements for a specific chemical structure of the emulsifier which provides good structure compatibility, must be met in order to affect the kinetics and mechanism of solid-solid or melt-mediated transformations. A mechanism of emulsifier incorporation in the fat and its effect in delaying the polymorphic transformation of tristearin is proposed. It has been concluded that the presence of the emulsifier does not dictate the formation of any preferred polymorph but rather controls the mobility of the molecules and their facility to undergo polymorphic transformations.

The relationship between polymorphism in fats and presence of additives plays a major role in the food industry, because of the serious quality implications involved in phase transitions.

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Introduction

Emulsifiers, or surface-active agents, are amphiphilic molecules, usually consisting of a hydrocarbon chain and a hydrophilic moiety. Their function as stabilizers of liquid emulsions has been the main aspect which has been investigated. In spite of this, in recent years research has shown that these substances have multiple roles in food systems, not necessarily related to the decrease of interfacial tension. Commonly used emulsifiers can form a complex with starch components and improve the texture of starch-based products; they can also interact with gluten proteins and change the rheological properties of doughs (Krog, 1977). Sorbitan monostearate (SMS) is known as an antiblooming agent, since, when added to the molten chocolate mass before tempering, it delays the fat bloom during storage (DuRoss and Knightly, 1965). This specific effect has been related to its influence on the polymorphic transformations of cocoa butter, which are considered the main cause of fat bloom. The variability of the emulsifier functions enable their use in many food items like bakery products, ice cream, confectionery fats, margarine, whipped cream, etc. Proper use of an emulsifier demands a proper understanding of its action in different systems; the effect of emulsifiers on crystallization properties of fats and their polymorphic transformations needs special attention owing to the particular importance they assume for the quality of food products.

The addition of emulsifiers to aliphatic compounds can affect crystallization behavior, both in bulk and in solution. According to their effect on polymorphism, they have been designated "crystal structure modifiers", "dynamic controllers of polymorphic transformations", and "crystal modifying agents" (Perrin and Michel, 1973). The present text aims to summarize the effects of these additives on crystallization and polymorphism of fatty acids and fats, with an attempt to analyze their influence on the different systems.

Polymorphism in Organic Materials Fatty Acids and Triglycerides

Polymorphism is the ability of a compound to

crystallize in more than one crystal form. Different polymorphs of the same compound may be as different in structure and properties as two different compounds. Melting point, solubility, bulk density, X-ray diffraction pattern, crystal habit, optical and electrical properties all vary with the polymorphic form. The phenomenon of polymorphism occurs in many organic materials in which the molecules are relatively bulky and can be ordered in different arrays.

The polymorphs differ in free energy; as a consequence, spontaneous transformation occurs toward the lowest free energy state, when a metastable form is formed. Usually, in bulky molecule compounds, the difference between free energies is small and the driving force for transition is low. The formation of hydrogen bonds involves a significant drop in free energy (Kitaigorodsky, 1973). The maximal utilization of hydrogen bonding and packing density will usually lead to the metastable form.

Among pharmaceuticals, many substances have been shown to be polymorphic, like p-chlorophenol (Perrin and Michel, 1973), sulfonamides (Kuhnert-Brandstatter and Wunsch, 1969), chloramphenicol palmitate (Borka, 1970), etc. Their different internal structures can affect physical properties which determine bioavailability and solubility of the pharmaceutical.

Among the organic materials which are polymorphic, the aliphatic compounds have been extensively investigated (Small, 1986). Alkanes, alcohols, fatty acids and glycerides display different polymorphic behavior according to their chemical structures and hydrophilic moieties. In this section we will summarize the polymorphism of fatty acids and triglycerides, accentuating the mechanisms of transformation between the crystal forms and the conditions under which the different polymorphs are obtained.

Fatty Acids

The occurrence of different polymorphs in homologous long-chain fatty acids has been reported by von Sydow, 1955; Holland and Nielsen, 1962; Larsson and von Sydow, 1966; Bailey et al., 1972; Mitcham et al., 1973; Bailey et al., 1975. The effects of solvent and temperature on the crystallization of specific polymorphs have also been discussed. The different polymorphs have been characterized by means of X-ray diffraction and the unit cell dimensions computed.

Stearic acid, the most common fatty acid, has recently been investigated as a model for polymorphism (Garti and Sato, 1986; Sato et al., 1985; Beckmann et al., 1986; Garti et al., 1980; Sato and Boistelle, 1983). Three polymorphic forms are known in stearic acid. The B and C-forms are more stable thermodynamically; they have similar unit cell dimensions but differ in the geometry of the hydrogen bonding. Their stabilities interchange at 32°C. The A-form is always metastable. The nature of the solvent, together with the rate of cooling, degree of supersaturation and regime, determine the crystal form obtained (Wellner et al., 1981). Crystallization from the melt leads to the C-form only.

The main points which have been clarified led to significant progress in the understanding of polymorphism in fatty acids. The effect of solvents has been related to different solute-solvent interactions. Different solvents have different types of interactions with stearic acid: non-polar solvents interact mainly with the aliphatic part of the acid, and polar solvents form hydrogen bonds with the carboxylic acid groups. These factors affecting the occurrence of stearic acid dimers in solution determine the molecular configuration during precipitation.

The polymorphs B and C can each transform into the other via the solution phase. This transition, known as "solution-mediated transformation", occurs when the more stable polymorph (C above 32°C and B below 32°C) grows at the expense of the less stable one (Sato and Boistelle, 1984; Sato et al., 1985). The rate of transition was found to depend on the temperature and on the polarity of the solvent, since the transformation is due to dissolution of one form followed by nucleation and growth of the other form.

In aliphatic compounds, the equilibrium between hydrophilic and hydrophobic interactions determines the crystallization and polymorphic behavior. It is clear that, in fatty acids, strong hydrogen bonding between the carboxylic groups predominates during crystallization and polymorphic transformations, whereas the packing of the hydrocarbon chains has less influence.

Triglycerides

Although triglycerides are derivatives of fatty acids, their behavior is quite different. Owing to the absence of hydrogen bonds between triglyceride molecules, their crystallization pattern is dominated by the packing of the aliphatic chains; in this respect it is possible to compare crystallization of triglycerides to that of paraffins (Small, 1985). The energy barrier to transformations in triglycerides is relatively low and the phase transitions occur through the solid or melt state. This is different from fatty acids, in which the transformation has a high energy barrier and is solution-mediated. In triglycerides, the polymorphism is monotropic (Bailey, 1950), i.e., the transformation always occurs from the less stable to the more stable polymorph. Four main types of packing are recognized, in order of thermodynamical stability: orthorhombic (sub α), hexagonal (α), orthorhombic (β') and triclinic (β). The least stable hexagonal packing is usually obtained when the melt is quenched to low temperatures. In the hexagonal structure the packing between the aliphatic chains is non-specific; the chains are symmetrically arranged and have relatively high freedom of oscillation around their axes. Polymorphic transformation involves a configurational change at the glycerol moiety, which leads to denser packing. The structures of the three polymorphs have been described by Hagemann and Rothfus (1983) and characterized by several techniques: infrared (IR) (Chapman, 1956), X-ray diffraction (XRD) (Hoerr and Paulicka, 1968), scanning electron microscopy (SEM) (Okada, 1970), solid state nuclear magnetic resonance

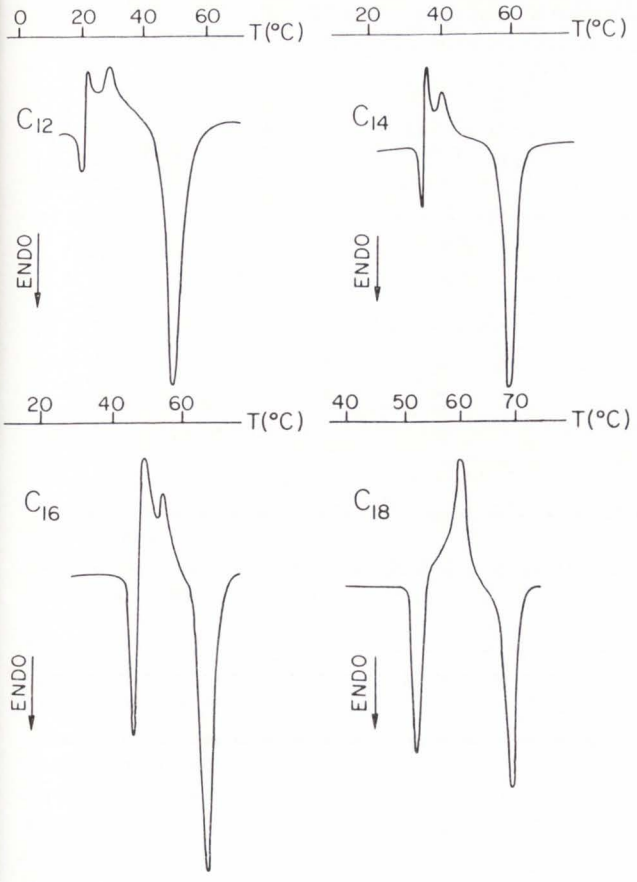

Figure 1. Thermograms of trilaurin (C_{12}), trimyristin (C_{14}), tripalmitin (C_{16}) and tristearin (C_{18}).

(NMR) (Norton et al., 1985), differential scanning calorimetry (DSC) Lutton and Fehl, 1970). By solvent crystallization only the stable β-form is obtained, and the phenomenon of polymorphism is eliminated. This is in contrast to fatty acids, in which the phenomenon of polymorphism is eliminated by melt crystallization. This difference in polymorphic behavior clearly derives from the fact that in triglycerides, van der Waals interactions predominate, while in fatty acids, mainly the interaction with the solvents determines the polymorphism.

The overall α ---> β transformation in saturated monoacid triglycerides may occur while heating at a constant heating rate or while aging at temperatures below the melting point of the α-form. During heating there are two possibilities of transformation to β. One is via the melt state, the other is through the solid state (Garti et al., 1985). In tristearin and trilaurin, two isomorphous saturated triglycerides which differ in their chain length, there are different tendencies for the α ---> β transformation (Fig. 1). In trilaurin most of the fat transforms through the solid state owing to the relatively short chain length and the low energy barrier of transformation. In tristearin the α-form melts before transforming to β, since the energy barrier for transformation is higher. This slight difference in polymorphic behavior is evident in the thermograms of the two triglycerides. Where the transformation occurs through the solid state, a low enthalpy of fusion is recorded; where the transition is liquid mediated, a high endotherm is recorded, according to the triglyceride structure and heating rate (Garti et al., 1985) (Fig. 1).

Summarizing, the polymorphic behavior derives from different possibilities of molecular packing in the crystal lattice. In fatty acids, it is mainly determined by the geometry of the hydrogen bond within the dimer. In triglycerides, the stability of the different polymorphs mainly depends on van der Waals interactions and on the packing density.

Effect of Additives on Crystallization Process

Nature offers several examples of the interference of impurities in crystallization processes. Mollusk shells, pearls, and bones demonstrate how organic molecules, at low levels, promote the formation of universal frameworks in living orqanisms. It was demonstrated that the presence of aspartic-rich protein initiated the growth of a calcite crystal that developed an unusual (001) face which was in contact with the additive (Addadi and Weiner, 1985). Polyglutamic acid promotes nucleation of calcium oxalate when the additive is present in minimal amounts (Eidelman et al., 1986); further addition of a few ppm of this oligopeptide changes its effect from crystallization initiation to inhibition. In many systems, as happens in kidney or gall stones, organic additives are known as inhibitors of crystal growth. Polyvinyl sulfonate and polyglutamic acid were found to retard the precipitation of carbonates of different metals (Sarig and Kahana, 1976a) and to interfere with the development of the crystals (Sarig and Kahana, 1976b). Also, crystal habit is modified by impurities, as shown for the crystals of strontium sulfate in the presence of polyvinyl sulfonate.

Observations in literature concerning retardation of phase transformations by organic molecules are limited. A search was made for additives that would retard crystallization of amorphous novobiocin in aqueous suspensions, protecting the pharmaceutical from losing its therapeutical effect. The best agents found were methylcellulose, polyvinylpyrrolidone and several alginic acid derivatives (Mullins and Macek, 1960). Addition of polyvinylpyrrolidone can also retard the polymorphic transformation in aqueous suspended sulfametoxydiazine (Ebian et al., 1973).

All the additives mentioned, which have an effect on crystallization of organic and inorganic compounds, do not necessarily have a molecular structure similar to the crystallizing compound, hence they adsorb onto a growing face or template for nucleation.

Commonly-used surfactants in food systems on the other hand, have a chemical structure quite similar to fatty acids and triglycerides. In the next sections we will describe in detail the effect of surfactants on the polymorphism of fatty acids and triglycerides, with an

Table 1. Qualitative nature (by X-rays diffracton) and semi-quantitative heat of phase transition (H_t by DSC) estimation of the polymorphic forms present in the crystallization mixture when pure stearic acid was crystallized from various solvents in quiescent and stirred systems at a cooling rate of 0.03°C/min.

Solvent	Condition of crystallization	Cryst. Temp. (T°C)	H_t(Cal/g) (by DSC)	Nature of Poly. (by X-rays)
Hexane	Quiescent	30.5	0	C
Hexane	Stirred	30.8	4.9	B
Benzene	Quiescent	26.7	3.2	B>>C
Benzene	Stirred	28.3	1.7	B>C
Acetone	Quiescent	26.2	0.5	C>>B
Acetone	Stirred	27.0	0	C>>>B
Ethanol	Quiescent	24.9	2.6	B>C
Ethanol	Stirred	25.7	3.6	B>>C

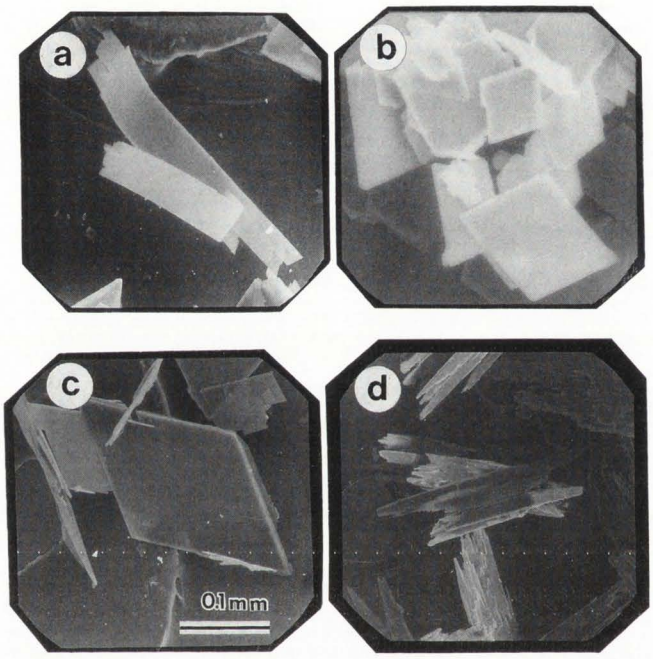

Figure 2. Stearic acid as grown from (**a**) pure acetone (A-form); (**b**) pure benzene at similar growth conditions (B-form); (**c**) pure n-hexane solution in a quiescent system at 0.03°C/min (C-form); and (**d**) benzene or acetone in the presence of 1% sorbitan monostearate.

attempt to clarify their action in solvent or bulk crystallization.

Effect of Surfactants on Crystallization and Polymorphism of Stearic Acid

Impurities or additives affect the polymorphism of fatty acids in two main ways: as crystal structure modifiers during crystallization and as retarders of solution-mediated polymorphic transformation. Differential thermal analysis (DTA) and XRD techniques were employed in order to recognize the polymorphs and to estimate their relative amounts by characteristic peak intensities.

As already mentioned above the polymorph obtained depends mainly on the solvent used. Table 1 summarizes the heat of transition of stearic acid crystals precipitated from four different solvents in quiescent and stirred systems cooled at the rate of 0.03°C/min. When pure B-form was present in the evaluated sample, a ΔHt of 4.9 cal/g was measured upon its transformation to C-form. All other values correspond to mixtures of B+C forms since much lower energies are required for the transition. In addition, an estimate of the relative amounts of the C and B-form as indicated by the peak intensities of their X-ray diffraction patterns is listed. The X-ray technique is not quantitative enough and only qualitative estimation of the amount of each polymorph present in the mixture can be given. Pure C-form was obtained from quiescent hexane solution, while pure B-form was obtained from the same solvent under stirring conditions. The B ---> C phase transition involved a latent heat of 4.9 cal/g as measured by DTA (Sato et al., 1985).

The addition of sorbitan monostearate, SMS, 1 - 5 percent by weight (wt%, refers to solute) drastically affects the crystallization of stearic acid, as can be seen in Table 2. The emulsifier induces the crystallization of the C-form, regardless of the solvent employed. However, the extent of the effect depends on the solvent. In hexane, which is strongly non-polar, the C-form is precipitated even in the absence of the emulsifiers, but when acetone or ethanol are used as solvents, 1 wt% of emulsifier promotes partial crystallization in the C-form. The presence of 5 wt% emulsifier forces the stearic acid to solidify completely in the C-form, and no phase transition is evident by DTA. When benzene is employed as solvent, the effect of the emulsifier is evident at 5 wt%.

As is evident in Table 2, supersaturation also is affected by added emulsifier. In each solvent, the supersaturation increases, the most pronounced effect being in ethanol and hexane. The crystal habit is affected by the presence of the additive as well. The characteristic crystal habit of the A, B, and C-forms changes to irregular shapes, as shown by SEM (Garti et al., 1982) (see Fig. 2).

Table 2. Crystal structure modification of stearic acid crystallized from organic solvents in the presence of emulsifier. (quiescent solution, 0.03°C min^{-1} cooling rate)

Solvent	Emulsifier Span 60 (wt%)	T (°C)	Supersaturation $S=C/C^*$	ΔH (Cal g^{-1})	Crystal Modification	
					By DTA	By X-rays
Hexane	0	27.8	1.431	0	C	C>>>B
	1.0	25.6	2.128	0	C	C
Ethanol	0	25.0	1.954	1.5	B>>C	B>>C
	1.0	24.1	2.164	0	C	C>>>B
Acetone	0	26.9	1.450	-	A,B<<C	A,B<<C
	0.5	26.8	1.472	-	A;C	A;C
	1.0	26.7	1.494	0	C;A	C>A
	5.0	-	-	0	C	C
Benzene	0	23.9	1.191	5.1	B	B
	0.5	23.8	1.217	3.5	B>>C	B
	1.0	23.6	1.244	2.9	B>>C	B>C
	5.0	23.3	1.317	0	C	C

Table 3. Effect of various emulsifiers on crystal structure and habit of stearic acid.

Trade Name	Composition	HLB	Ethanol		n-Hexane
			Polymorph		Polymorph
			X-rays	Habit change	X-rays habit
Span 20	Sorbitan monolaurate	8.6	B>>C	-	
Span 40	Sorbitan monopalmitate	6.7	C	+	C>B
Span 60	Sorbitan monostearate	4.7	C	+	C
Span 65	Sorbitan tristearate	2.1	Amorphic	Powder	C
Span 80	Sorbitan monooleate	4.3	B>>C	-	C
Span 85	Sorbitan trioleate	1.8	B>C	-	C>>>B
Tween 20	PEO sorbitan monolaurate	16.7	B	-	
Tween 21	PEO in sorbitan monolaurate	13.3	B	-	C>>B
Tween 40	PEO in sorbitan monopalmitate	14.4	B	-	
Tween 60	PEO sorbitan monostearate	14.9	B	-	C>>>B
Tween 61	PEO sorbitan monostearate	9.6	C	+	
Tween 65	PEO sorbitan tristearate	10.5	C	+	C>>B
Tween 80	PEO sorbitan monooleate	15.0	B>C	-	
Tween 81	PEO sorbitan monooleate	10.0	B>>C	-	
Tween 85	PEO sorbitan trioleate	11.0	B		

The emulsifier was tested under other crystallization conditions such as during stirring or increased cooling rate; even under drastic crystallization conditions sorbitan monostearate (SMS) is an efficient crystal structure modifier (Garti et al., 1981; Garti et al., 1982). The effect of SMS has been compared to other emulsifiers, in order to elucidate the possible mechanism of interactions between emulsifier and stearic acid.

Table 3 summarizes the effect of sorbitan esters and ethoxylated sorbitan esters, which differ in the structure of the aliphatic chain, on the polymorph obtained from ethanol and hexane and on the crystal habit.

These experiments were performed in a quiescent system at a cooling rate of 0.1°C/min. An attempt was made to connect the effect of the emulsifier to the HLB (Hydrophilic Lypophilic Balance). In the sorbitan series, SMS and SMP (sorbitan monopalmitate) were the most efficient in directing crystallization to the C-form. They both have a low HLB. Among the ethoxylated sorbitan esters, Tween 60 and Tween 61, which are ethoxylated sorbitan monostearates differing in polyoxyethylene chain length, are the most effective. Comparing different emulsifiers, no clear correlation exists between the HLB value and the performance as crystal structure modifier. During crystallization from hexane, the general efficiency of the emulsifier is increased. The influence on the crystal habit of stearic acid crystals is also summarized in Table 3.

The ability of the emulsifier to change the polymorphism of stearic acid was postulated to be connected with its molecular structure more than with the hydrophobic and hydrophilic balance. It is evident that emulsifiers with an unsaturated aliphatic chain, like sorbitan monooleate, do not affect the crystallization of stearic acid. In the same way, most of the Tweens, which consist of poly- oxyethylene chains in hydrophilic moieties, do not show any activity on the polymorphism. The fact that a peculiar chemical structure is required in order to act as a crystal structure modifier is demonstrated by the Brijs (ethoxylated fatty alcohols), characterized by linear structure, which are quite ineffective in inducing the B ---> C transformation. It seems, rather, that a bulky hydrophilic moiety can confer efficiency. In fact, of emulsifiers like the citric acid ester of glycerol monostearate (CGMS) or the diacetyltartaric acid ester of glycerol monostearate (DATAE), which have bulky hydrophilic moieties, the citric and tartaric moieties acid, respectively, show a good ability to induce the B ---> C transition.

Summarizing, the effect of the emulsifier on the crystallization of stearic acid seems to be related primarily to its specific molecular structure, and to the balance between an optimal size of the hydrophilic moiety and a linear structure of the aliphatic chain. Secondarily, it seems that the nature of the solvent can influence the performance of the emulsifier, probably by solute-solvent interactions, affecting its own solubility and crystallization properties. The HLB value, relevant to emulsion stability, seems to be a minor factor in the effectiveness of the emulsifier in inducing structure modification.

The effect of the emulsifier was tested on the solution-mediated polymorphic transformation between forms B and C. The transition in pure stearic acid crystallized from various solvents occurs when the more stable polymorph (C above 32°C and B below 32°C) grows at the expense of the less stable one (Sato et al., 1985). The rate of transition depends on temperature as well as on the polarity of the solvent. The emulsifier retards the transformation, its extent depending on the solvent. Fig. 3 compares the rate of the C ---> B transition at 22°C in methanol in the presence of SMS to that in a pure methanol solution. The transition was expressed by the change in the C-crystal fraction. AS little as 0.1 wt% emulsifier retards the transformation. The total conversion to B requires 20 minutes, in comparison to 10 minutes when pure methanol is used. When 0.5 wt% emulsifier is added, almost no transformation is detected after more than 60 minutes. Surfactant concentrations over 2 wt% were not tested, since their solubility in methanol is limited. Fig. 3 also shows the retardation effect of SMS on the B ---> C transformation in methanol at 35.5°C. It took over 72 minutes to obtain pure C-form in solution that had no surfactant. The addition of 0.5 wt% emulsifier caused only a moderate retardation. In this case a concentration over 1 wt% of SMS was needed to significantly influence the B ---> C transformation. In hexane, the B ---> C transformation rate was higher than in methanol but the retarding effect of SMS was stronger. In conclusion, it seems that this emulsifier is more effective in delaying the C ---> B transformation (at 22°C) than the opposite.

Other surfactants were tested in hexane and methanol at 22°C. Those which are liquid, like SMO (sorbitan monooleate), did not have any effect on the transformation, while those which are solid and contain a bulky hydrophilic moiety, like PGE (polyglycerol esters) or sucrose esters (SE), were very active retarding agents.

It is evident that the molecular structure of the emulsifier determines its performance. The fact that only the solid surfactants were effective suggests that they interfere with the crystallization of the stable crystal, besides dissolving the metastable crystal. The fact that solid surfactants containing a long saturated aliphatic chain and a bulky hydrophilic structure were particularly active suggests, furthermore, that a physical interaction occurs between emulsifier and fatty acid.

The solubility of the emulsifier seems to affect its activity. As is evident from the results, emulsifiers with lower solubility are more active than those with a higher solubility. For example, in methanol, STS (sorbitan tristearate), which has a low solubility in organic solvents (HLB=3.5), retards the C ---> B transformation better than SMS or PGE, which have a higher solubility and higher HLB value. On the contrary, PGE retards the C ---> B transformation in hexane, in which PGE is poorly soluble, more strongly than do the sorbitans.

The transformation between the polymorphs B and C is affected by the emulsifiers more in the C ---> B direction than the opposite. This may imply that the growth of B is more retarded than C by the addition of the surfactant, probably owing to the different structures of the active growing faces: the faces of the B crystal reveal a stepped structure due to the gauche conformation at the COOH group, while C has only flat interfaces (Fig. 4). The difference may be responsible for the preferable surfactant effects on the C ---> B transformation since there may be a favorable adsorption of surfactant molecules on the stepped portion of the B crystal faces. It is not excluded, yet, that the stronger effect of

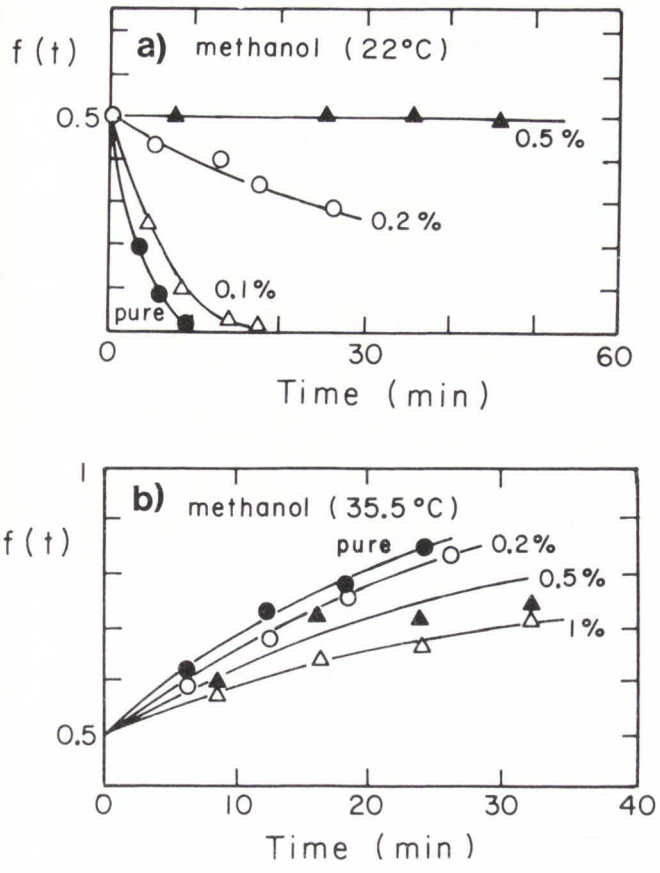

Figure 3. Transition **a**) from C- to B-form stearic acid (22°C) and **b**) from B- to C-form (35.5°C) in methanol, with and without Span 60.

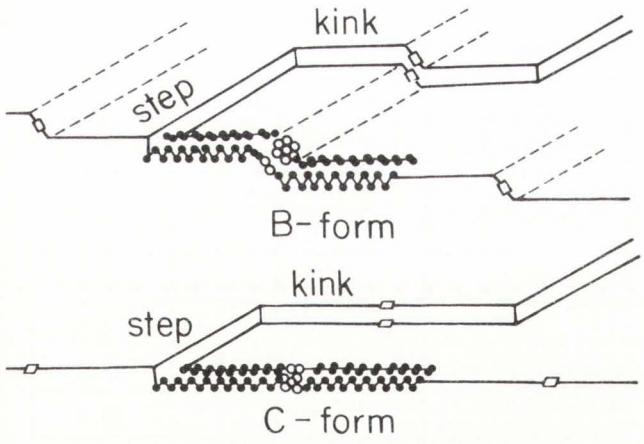

Figure 4. Molecular structures of the lateral (110) interfaces of B and C-polymorphs of stearic acid. Solid and open circles mean carbon and oxygen atoms, respectively.

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the emulsifier during the C ---> B transition is due to its lower solubility at 22°C in comparison with the B ---> C transition at 35.5°C.

Effects of Surfactants on Polymorphism of Fats

The information in the literature concerning the role of surfactants on polymorphism of saturated and mixed fats is quite limited. In an early work, Niiya et al. (1973), studied the effect of both saturated and unsaturated fatty acid monoglycerides and other emulsifiers on various hydrogenated fats. Hardened soy bean and palm kernel oils were compared to hardened beef tallow and whale oils. The saturated fatty-acid monoglycerides (monostearin, monopalmitin, monobehenin) that were incorporated into the fats increased the melting points of the vegetable fats while only slightly increasing those of animal fats. The crystal growth of the vegetable fats was slightly accelerated, but in the animal fat the crystal growth was not affected. In the presence of unsaturated monoglycerides the melting point decreased and the crystal growth was seemingly accelerated. In comparison to monoglycerides, the presence of surfactants such as propylene glycol esters retarded the crystal growth of saturated edible fats.

Some vegetable fats having a strong tendency to form β-crystals and cause sandiness in margarine were studied by Madsen and Als (1968). The addition of 0.3 wt% STS (sorbitan tristearate) was found to inhibit the β ---> β' transition.

The polymorphic behavior of low erucic rapeseed oil, composed mainly of C_{18} acids, has been found to be strongly affected by surfactants. Hernqvist and coworkers showed that the presence of diglycerides stabilize the β' form during storage (Hernqvist and Anjou (1983), Hernqvist et al. (1984)). Their conclusions were that 1 wt% diglyceride can stabilize the β' form and prolong by a factor of 2-3 the time required to reach the β-form. They also concluded that the performance of the diglyceride depends on saturation of the aliphatic chain and its length.

The use of 1,2 and 1,3-diglycerides of saturated long-chain fatty acids as crystal structure modifiers in β-tending fats has been explored and studied extensively by Krog (1977), Mostafa and deMan (1985), and Mostafa et al. (1985). It has been clearly demonstrated that addition of 1 wt% of saturated diglycerides of any kind is not sufficient to retard the β' transformation of the fat and practically no β'-form stabilization was achieved. A more realistic concentration of diglyceride is 3-5 wt%. Only the 1,2-diglycerides were found to be effective β'-stabilizers whereas 1,3-diglycerides crystallize in β-form and therefore were found to be inefficient modifiers. Commercial diglycerides, being a blend of 1,2 and 1,3-diglycerides in the ratio of 2:3, can also act as crystal structure modifiers.

Lee and deMan (1984) studied the effect of some surfactants on the polymorphic behavior of canola oil (new low erucic rapeseed oil). The surfactants tested were STS, STO (sorbitan trioleate), SMS and monoglycerides. The polymorphic transformation was measured by X-ray diffraction patterns and the crystal growth by polarized light microscopy. The most effective surfac-

tant in delaying the transition $\beta' \dashrightarrow \beta$ was STS. DSC was used to demonstrate that, during heating, the transformation to the β-form can be prevented, and it was suggested that effective surfactants co-crystallize with the fat.

It appears that STS had the best ability to delay the transformation to the β-form, but its effect is not permanent, as shown in Table 4 (Lee and deMan, 1984). Table 4 indicates that continued cycling eliminated the effect of the surfactant. The conversion to the β-form was complete after 3 cycles with the selectively hydrogenated fats; however, the same β' crystals remained in the non-selectively hydrogenated fat containing STS, SMS and STO.

The mechanism of the polymorphic transformation was suggested to involve rotation of the chains in the glyceride to a different packing. The packing of the chains in the β'-form results in two perpendicular orientations of chain planes and it was suggested that the $\beta' \dashrightarrow \beta$ transition involves a 180° rotation of chains in every second double layer (Lee and deMan, 1984). It is possible that the effective surfactants are incorporated within the fat and block this rotation.

An outstanding example of a polymorphic fat is cocoa butter. Its properties, both physical and chemical, have drawn the attention of many researchers because of the importance they assume in the confectionery industry. Some controversies in literature exist with regard to the number of polymorphs existing in cocoa butter (Wille and Lutton, 1966; Huyghebaert and Hendrick, 1971; Merken et al., 1982; Schenkel and Rufer, 1983), although generally six polymorphs are recognized. The three main sources in the literature concerning X-ray diffraction data on the different forms are Wille and Lutton (1966), Witzel and Becker (1969) and Chapman et al. (1971). The melting points of the different polymorphs range between 15°C and 36°C. It was observed (Chapman et al., 1971) that all the polymorphs can be obtained from melt crystallization except the VI form, which can be obtained only by transformation from the V form. This led to the suggestion that the transformations from polymorph I to V may be melt-mediated while the V $\dashrightarrow$ VI transformation is solid-mediated. The possibility that the VI polymorph is formed by fractionation of the V polymorph has also been suggested (Merken and Vaeck, 1980; Manning and Dimick, 1985) and is in accordance with the observation that the VI polymorph has not been crystallized from the melt.

Previous work in our laboratories showed that the addition of surfactants may affect the rate of polymorphic transformations in cocoa butter. Contrasting effects have been observed between the V $\dashrightarrow$ VI polymorphic transition and the other transitions (Garti et al., 1986). The V $\dashrightarrow$ VI transformation was retarded by solid sorbitan esters and by mixtures of sorbitan esters with ethoxylated sorbitan esters. Fig. 5 shows the heating curves of cocoa butter samples with different percentages of additive before aging (a), and after aging (b). Before aging, the thermograms clearly show that the sample is crystallized in the V form. After a period of aging, the heating curves are split, suggesting that a considerable part of the fat has transformed to the VI form. The extent of retardation is proportional to the percentage of additive. The additive also increases the liquid fraction of the V form, as evident in Table 5 (Garti et al., 1986).

Table 4. Polymorphic state of hydrogenated Canola oil as indicated by X-ray diffraction analysis.

Cycle 1 - crystallized at -15°C for 1 hour, stored at 5°C for 1 day and 20°C for 2 days

Cycle 2 - same as cycle 1 with additional 5°C for 1 day and 20°C for 3 days

Cycle 3 - same as cycle 2 with additional 5°C for 1 day and 20°C for 2 days

Sample	1	2	3
Sel-Control	$\beta' << \beta$	$\beta' << \beta$	β
STS	$\beta' = \beta$	$\beta' << \beta$	β
SMS	$\beta' << \beta$	β	β
SMP	$\beta' << \beta$	$\beta' << \beta$	β
STO	$\beta' << \beta$	$\beta' << \beta$	β
STL	$\beta' << \beta$	$\beta' << \beta$	β
AW	$\beta' << \beta$	β	β
Non-Sel-Control	$\beta' = \beta$	$\beta' < \beta$	β
STS	β	$\beta' < \beta$	$\beta' << \beta$
SMS	$\beta' > \beta$	$\beta' < \beta$	β
SMP	$\beta' = \beta$	$\beta' << \beta$	$\beta' << \beta$
STO	$\beta' = \beta$	$\beta' << \beta$	$\beta' << \beta$
STL	$\beta' = \beta$	$\beta' << \beta$	β
AW	$\beta' = \beta$	$\beta' << \beta$	β

Table 5. Melting point of form V and liquid fraction computed at 31°C, in cocoa butter with different percentages of emulsifier.

Emulsifier concentration (wt%)	Melting point temperature: top of peak (°C) before aging	Percent liquid of (31°C)
0	33.1	39.2
1.5	33.0	50.7
2	32.7	52.9
3	32.4	53.8
5	31.0	55.4
10	31.0	76.2

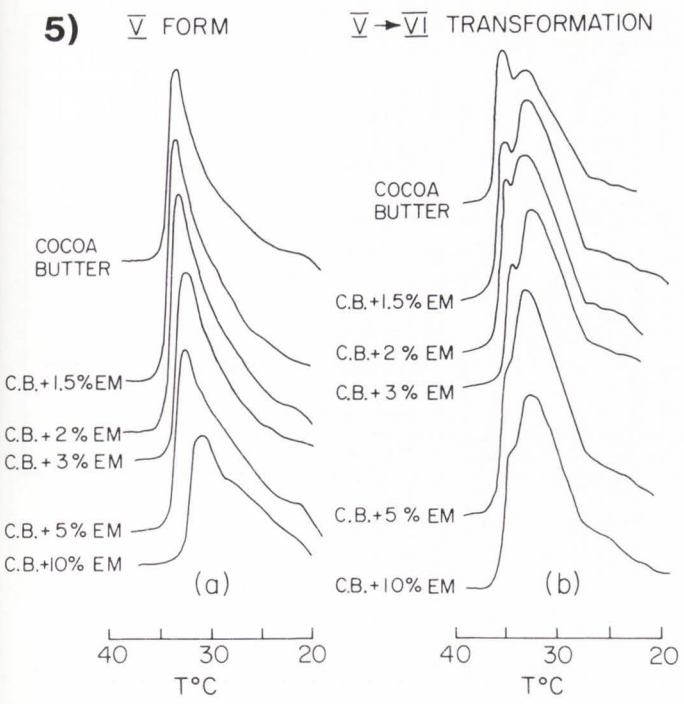

Figure 5 (above). Cocoa butter crystallized with various percentages of Span 65 (sorbitan tristearate). **(a)** DSC curves indicating presence of form V; **(b)** heating curves after temperature cycling, indicating presence of form VI.

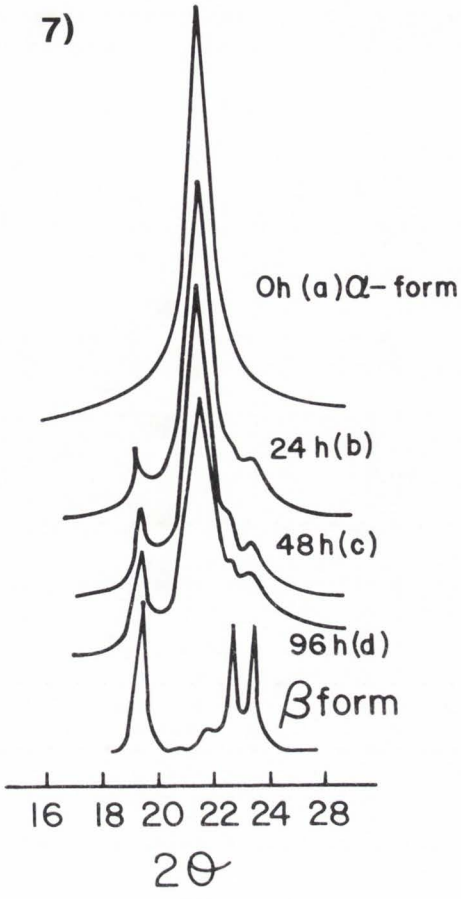

Figure 7 (at right). X-ray diffraction powder pattern of tristearin obtained by quenching melt **(a)** α-form, **(b)** pure tristearin β-form.

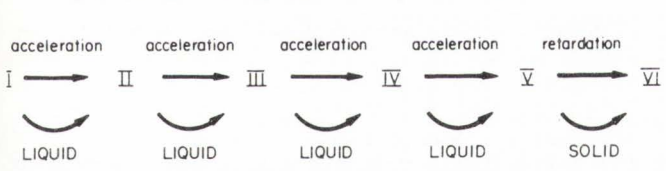

Figure 6. Effect of emulsifier on polymorphism of cocoa butter.

The III and IV forms were crystallized in the presence of the emulsifier and their heating curves, after an aging period of some hours, show an effect of promoting rather than retarding the polymorphic transformation. Also, in the case of the II form, the liquid fraction was increased.

In the same way, the lowest forms, which were crystallized in the DSC at fast cooling rates, were aged for a few minutes. Both the I ---> II and the II ---> III transitions were accelerated by the emulsifier. Fig. 6 summarizes the effect of the emulsifier on polymorphism of cocoa butter. It seems that the effect of the emulsifier is mainly to increase the liquid fraction of the fat, and in such a way as to accelerate the liquid-mediated transition and retard the solid-mediated transition. Hence, the presence of the emulsifier destabilizes the metastable forms and gives a kinetic orientation toward the stable form.

The effect of the emulsifier may be related not only to polymorphic behavior, but more generally to the possibility of affecting the segregation of high melting fractions from lower melting fractions. This can have a particular meaning in the problem of fat bloom, maybe more significant than polymorphism itself. This aspect of the emulsifier's performance has so far not been a subject for research, and therefore more attention should be directed to understanding the ability to promote crystallization of certain portions of the fat; a suggestion of this kind of influence has been presented in our recent work on crystallization of cocoa butter at very low cooling rates, in the presence of sorbitan monostearate (Aronhime et al., 1988a).

Effect of Surfactants on Polymorphism of Pure Triglycerides

Our recent work has focused mainly on the polymorphism of pure saturated triglycerides in the presence of surfactants (Schlichter et al., 1986, 1987; Aronhime et al., 1987). In pure triglycerides, generally the α ---> β transformation takes place during heating in the DSC. Under heating conditions the α-form can transform to the β-form via melting and recrystallization or directly without being melted. In short chain triglycerides (C_{12}) the direct transformation is preferred while

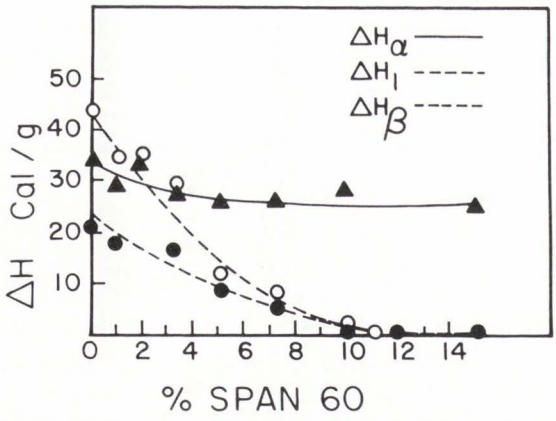

Figure 8. A plot of the ΔH_t, ΔH_α and ΔH_β values measured by the DSC for crystallized tristearin.

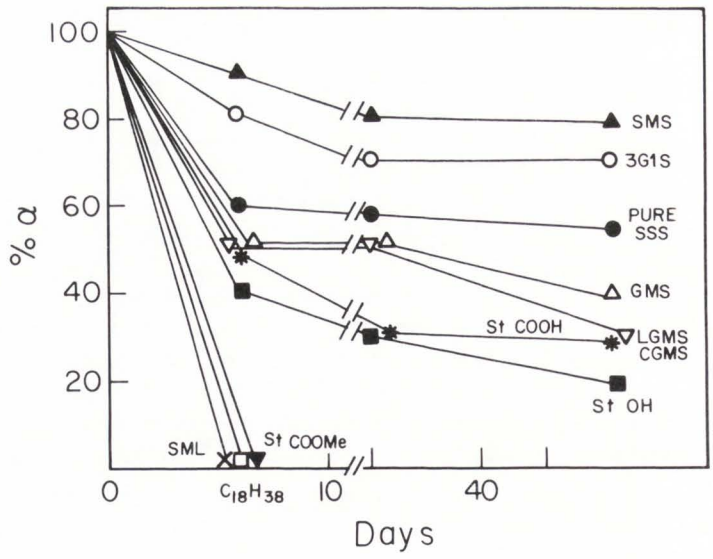

Figure 9. Aging of α-tristearin at room temperature in the presence of different additives. SMS = sorbitan monostearate; 3G1S = triglyceryl monostearate; GMS = glycerol monostearate; LGMS = lactoglycerol monostearate; CGMS = citric acid ester of monoglycerid stearate; St.OH = stearoyl alcohol; StCOOMe = methylstearate; StCOOH = stearic acid; $C_{18}H_{38}$ = octadecane; SML = sorbitan monolaurate.

for long chain triglycerides (C_{18}), due to the relatively high stability of the α-form, the transition will occur via melting.

The effect of SMS on the polymorphism of tristearin has been widely investigated. Diffractograms of tristearin obtained from rapid crystallization of the melt are presented in Fig. 7 (Garti et al., 1982). The first measurement was made immediately after crystallization. Only one reflection in the short spacings range (0.41 nm) has been obtained, indicating the α-form. The presence of 5 wt% SMS stabilizes the α-form, as can be seen in Fig. 7. After 96 hours of aging the α-form was still present (Schlichter et al., 1986). The ΔH, ΔH_α and ΔH_β values were measured from the DSC curves and plotted versus emulsifier concentration (Fig. 8). The ΔH_β (fusion enthalpy of β) and ΔH (transformation enthalpy to β) decrease with increasing percentage of additive, and the ΔH_α value (fusion enthalpy of α) does not change, indicating that the melting of the α-form occurs but the transformation to β is suppressed.

The heating rate affects the amount of β that crystallizes in tristearin and the amount of α that liquifies or transforms directly; moreover, the effect of the emulsifier also depends on the heating rate (Schlichter et al., 1987). All the solid emulsifiers prevent crystallization at high heating rates, but the inhibition of crystallization in tristearin is shown to be minimized at lower heating rates, confirming the kinetic effect of the surfactant on the α ---> β transformation (Schlichter et al., 1987). The effect of liquid surfactants differs from that of solid ones; their presence increases the ΔH_β value at higher heating rates and decreases the ΔH_α values, suggesting that they enhance rather than inhibit the transformation (Schlichter et al., 1987).

During aging at room temperature, the various emulsifiers were tested for their ability to delay the α ---> β transformation (Aronhime et al., 1988b). Fig. 9 shows that the percentage of α-form detected by X-ray diffraction decreases with time. Different additives were employed, some of them not surfactants. It can be seen that those additives which are not surfactants do not delay the transformation, but rather accelerate it. Even among the solid surfactants tested, not all of them retard the transformation. Only SMS and 3G1S (triglycerol monostearate) are effective. Unlike the liquid-mediated transformation during heating, in which all the solid surfactants inhibit crystallization, the solid-mediated transformation is affected by certain emulsifiers with a specific hydrophilic structure.

The polymorphism of tristearin was compared to that of short-chain triglycerides, like tripalmitin (C_{16}), trimyristin (C_{14}) and trilaurin (C_{12}). The effect of emulsifiers on the polymorphic transformation of these saturated isomorphous triglycerides was investigated using the DSC (Aronhime et al., 1988b). The fusion enthalpies of the α and β-forms (ΔH_α and ΔH_β, respectively) in the presence and in the absence of emulsifier were compared. The change caused in the fusion enthalpy was correlated with the change in the portion of the same polymorph which underwent melting. The values of ΔH_α^* (ratio between ΔH_α of the sample and ΔH_α of the pure triglyceride) were measured in the DSC at standard heating rates.

The effect of some solid emulsifiers on ΔH_α^* is shown in Fig. 10. The ΔH_α of tristearin is little affected by the presence of the emulsifier. The ΔH_α of trilaurin, contrarily, is affected by the solid sorbitan esters in one manner, and by other solid emulsifiers in another manner. The great enhancement of ΔH_α in trilaurin indicates that the emulsifier hinders the solid-solid

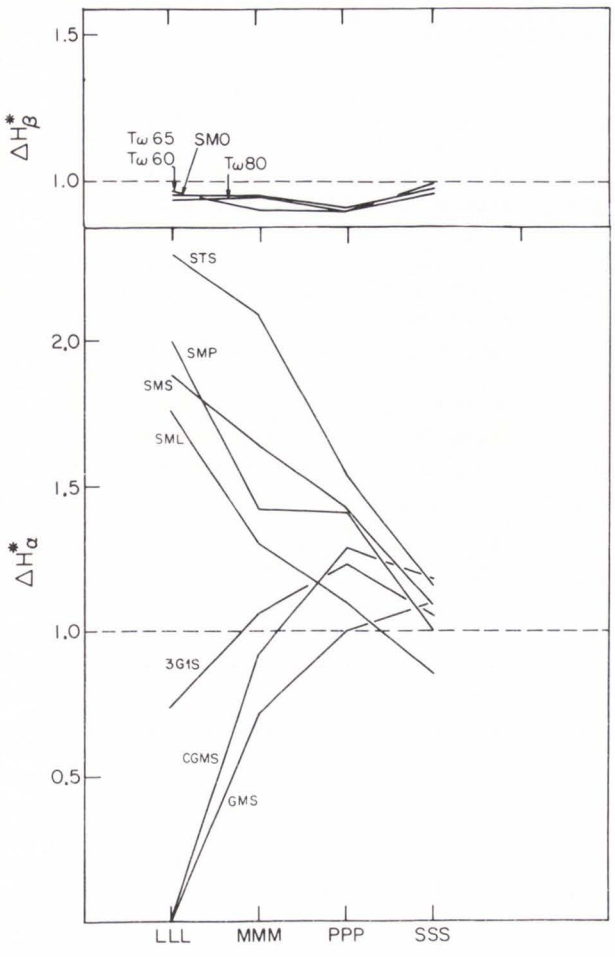

Figure 10. ΔH_α^* and ΔH_β^* values of different triglycerides in the presence of different surfactants.

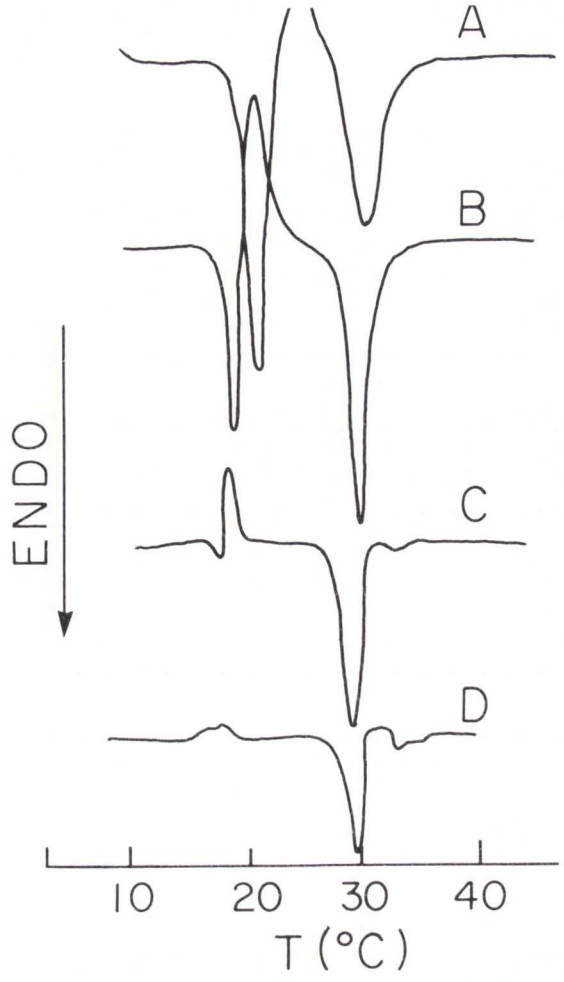

Figure 11. Heating curves of POP crystallized in the α-form. Heating rates: (**A**) 10°C/min, (**B**) 5°C/min, (**C**) 2°C/min, (**D**) 1°C/min.

transformation and allows the α-form to melt. The presence of other emulsifiers decreases the ΔH_α of trilaurin to zero, thus facilitating the solid-solid transformation. Incidentally, all those emulsifiers that increase ΔH_α are sorbitan esters. Considering that liquid surfactants decrease ΔH_α in trilaurin, the effect of SML (sorbitan monolaurate) is surprising (Aronhime et al., 1988b): in spite of being liquid at room temperature, it behaves like the solid sorbitans.

The value ΔH_α^* is an indication of the nature of transformation, but has nothing to do with the extent of β that is formed. The ΔH_β value of trilaurin was not affected by any emulsifier (Aronhime et al., 1988b). This means that their effect is specific to the step of rearrangement: sorbitan esters hinder solid-solid transformation, while CGS or GMS promote this transformation. Moreover, this confirms that the α ---> β transformation is related to the glycerol moiety since in trilaurin the effect depends more on the hydrophilic part of the emulsifier and less on the hydrophobic part. All solid emulsifiers, indiscriminately, prevent the crystallization of β in trilaurin ($\Delta H_\beta = O$), suggesting that crystallization of tristearin during heating is related mainly to the packing of the hydrocarbon chains since every solid emulsifier affects it (Aronhime et al., 1988b).

The effects of surfactants on polymorphic transformation can be summarized briefly as follows:

1. The emulsifier interferes with the kinetics of transformations without changing the crystallographic properties of the fat.
2. The effect of the emulsifier is apparently different in varying chain-length triglycerides, but is essentially based on the principle that the solid-solid transformation is delayed by the presence of a surfactant having a specific hydrophilic moiety (sorbitan esters, triglycerol-monostearate).

The effect of emulsifiers was also tested on polymorphism of dipalmitoyl-glycerol-oleate (POP), which is one of the major components of cocoa butter and displays more polymorphs than saturated triglycerides. The different polymorphs of POP, as described by Gibon and co-workers (1986), are: α_2, sub-β'_2, intermediate meso-

phase, β'_2 and β_3. Each single transformation was performed in our laboratories, in both the presence and absence of SMS. The α-form of POP obtained by chilling the melt to 0°C was heated at different heating rates in the DSC. The thermograms are shown in Fig. 11.

At the rate of 10°C/min two endotherms are seen corresponding, respectively, to α and sub-β'_2 forms, and an intermediate exotherm corresponding to the transformation. As the heating rate is lowered, the ΔH_α value approaches zero and the ΔH_F values of the sub-β' form increase. In the presence of SMS, the ΔH_α values are higher than in the pure triglyceride, and the crystallization of sub-β' is depressed (Fig. 12). The intermediate form, which appears between α and sub-β', is not reported in literature and is stabilized by the presence of SMS. The sub-β' form was aged at 26.5°C for different periods, in order to obtain the β'-form. In Fig. 13 the thermograms of pure POP show that after four hours of aging the complete transformation to β'-form occurred. With the addition of SMS, an intermediate form with melting point 31/5°C is stabilized (Jacome Guth et al., 1989). The transformation from the sub-β_2 to β_3 (at 28°C and 30°C) was also delayed by the presence of the surfactant, similar to the other transformations.

These results show that the conclusions drawn from the effect of emulsifiers on the polymorphism of saturated triglycerides, can also be applied to unsaturated triglycerides. However, more research remains to be done on different unsaturated triglycerides in order to better define the influence of surfactants on their polymorphic behavior.

Interaction Between Emulsifier and Triglyceride: Incorporation and Performance

The ability of emulsifiers to delay polymorphic transformations suggests that the additives interfere with the solidification and melting processes of the fat without detectable alterations of the crystal packing. That is, surfactants vary the kinetics of phase transformation, which are related to the mobility of the molecules, rather than changing the thermodynamics which are involved in the arrangement of the molecules.

Although solid emulsifiers do not significantly change the crystallographic features (Azoury et al., 1988, Schlichter et al., 1988), they can affect other properties, such as heat capacity (Schlichter et al., 1986). The heat capacity (Cp) of the unstable α-form of tristearin, is significantly higher than that of the stable β-form. The Cp values are affected differently by various solid surfactants. Sorbitan esters do not affect the Cp of α-tristearin at all. Heat capacities of β-tristearin are not affected below a certain temperature (Fig. 14), which is interpreted as the point of two-dimensional melting. On the other hand, other solid surfactants increase the Cp of α- and β-tristearin throughout the range of temperatures. The results suggest that the rotational freedom of the molecules in the crystal is not altered when sorbitan esters are present, probably because they fit the crystallographic dimensions of tristearin better than other surfactants.

The CGMC and GMS increase the fluctuations of the fat molecules, suggesting that some imperfections are formed in the crystal lattice. Cp measurements support the supposition of a homogeneous incorporation of the emulsifier within the fat. The modification of the heat capacity values of α- and β-tristearin by the emulsifier suggests that a new mixed crystal is formed between tristearin and surfactant, with new physical properties. The presence of the additive does not change the crystallographic dimensions of tristearin, as could be verified by X-ray powder diffraction (Schlichter et al., 1986). Moreover, no additional peaks that may belong to the emulsifier were found.

The emulsifier molecule supposedly penetrates the triglyceride hydrocarbon chains in the way described schematically in Fig. 15. According to Fig. 15, the incorporation of the emulsifier molecule creates spaces among the hydrocarbon chains, that cannot be detected by X-ray diffraction. The NMR spin-lattice relaxation time (T^1) that was measured in a previous work of ours (Azoury et al., 1988) is an indication that such holes are created. NMR T^1 relaxation time is the time required by protons aligned in a magnetic field to recover longitudinally after being subjected to a radio frequency pulse. The mobility of the molecules favors energy interchanges between protons and thus reduces the T^1 relaxation time. The addition of surfactant at different concentrations drastically decreases the T^1 value of β-form tristearin. The defect created by the introduction of the surfactant probably permits a higher mobility of the surrounding molecules at their methylenol groups in such a way that motion of the hydrocarbon chains diffuses to the neighboring molecules as a halo, thus decreasing the T^1 value even at low concentrations of additive.

The model shown in Fig. 15 is based on the assumption that the surfactant's molecule is introduced parallel to the triglyceride hydrocarbon chain in order to maximize the hydrophobic and hydrophilic interactions. The specific activity of sorbitan ester and glycerol ester in delaying polymorphic transformation is associated with the chemical structure of their hydrophilic head (Aronhime et al., 1988b).

The incorporation of SMS, which has a good structural affinity with the fat, enables formation of hydrogen bonds between the hydroxyl groups of the emulsifier and the carbonyl groups of the triglyceride; in such a way the latter molecules are temporarily held from undergoing the conformational change, and the polymorphic transformation is delayed. The presence of GMS induces the same effect, since it has two hydroxyl groups in the position mentioned above. On the other hand, molecular models of GMS and LGMS (Aronhime et al., 1988b) show that a double hydrogen bond is not feasible, owing to the chemical structure of these surfactants. This explanation is supported by the fact that in the presence of GMS and LGMS the polymorphic transformation is enhanced.

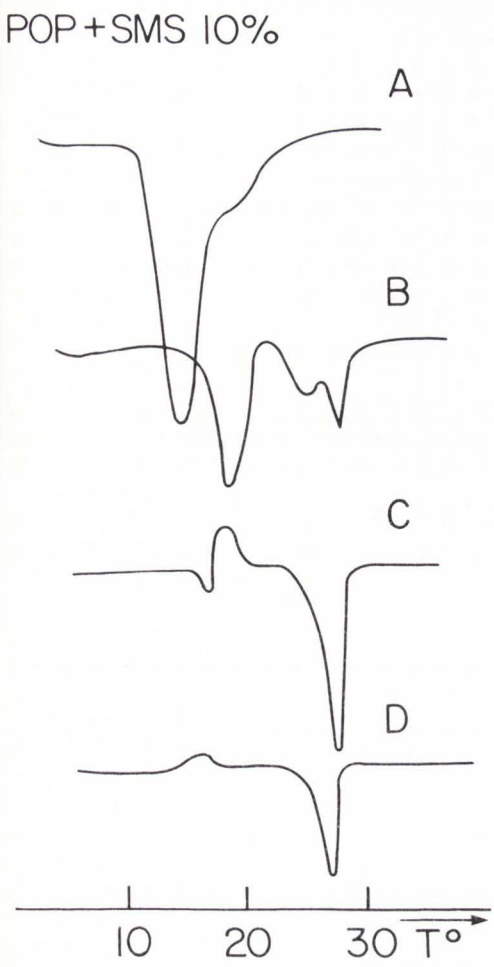

Figure 12. Endotherms of POP with SMS 10 wt% crystallized in the α-form. Heating rates: **(A)** 10°C/min, **(B)** 5°C/min, **(C)** 2°C/min, **(D)** 1°C/min.

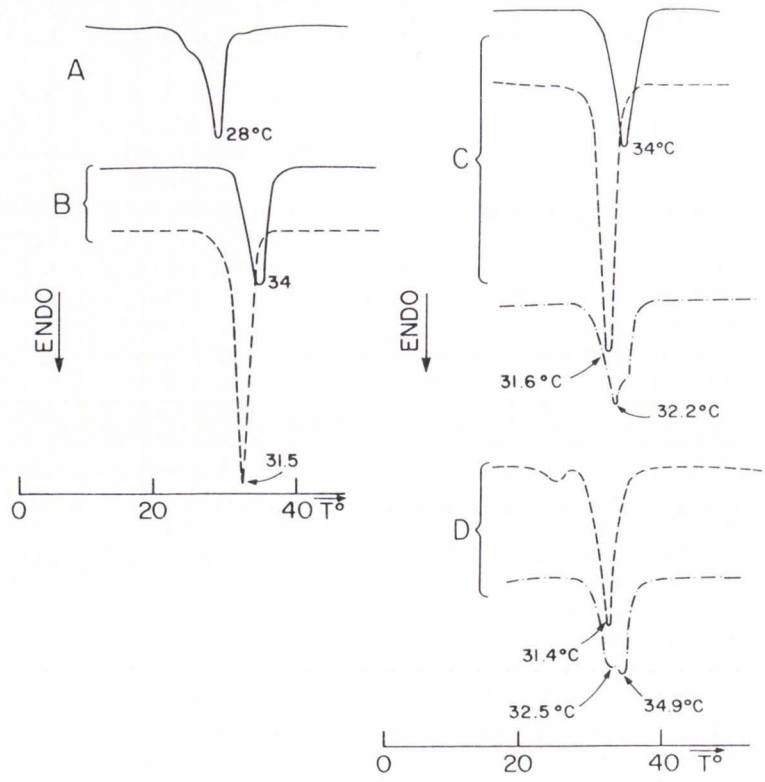

Figure 13. Thermograms of pure POP (———), POP + SMS 10% (---) and POP + GMS 10% (·---·). Heating rate = 5°C/min. **(A)** after cooling at 0.3°C/min, **(B)** after cooling at 0.3°C/min and aging for 2 hr. at 26.5°C, **(C)** after cooling and aging for 4 hr. at 26.5°C, **(D)** after cooling and aging for 18 hr. at 26.5°C.

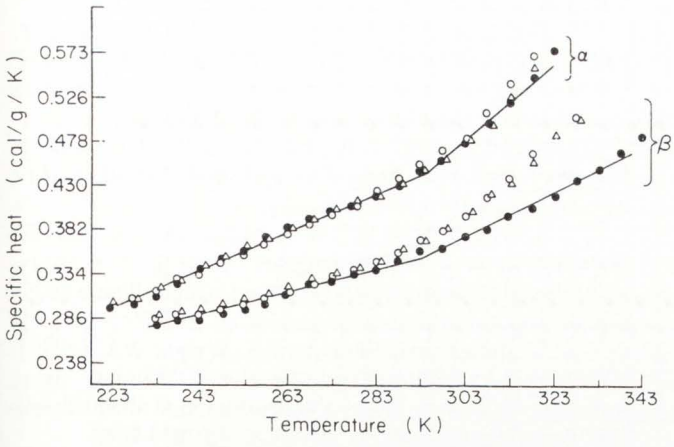

Figure 14. Specific heat of α- and β-tristearin. Neat tristearin = •, tristearin in the presence of SMS = 0, tristearin in the presence of STS = Δ.

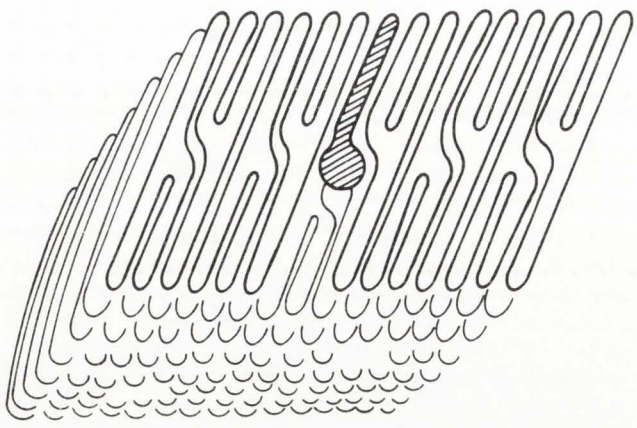

Figure 15. Schematic illustration of emulsifier incorporation in triglyceride.

Hence, the steric hindrance to the transformation suggested by Krog (Krog, 1977) does not seem to be sufficient to explain the effect. Emulsifiers which do not meet the requirements of a specific hydrophilic moiety will not delay the α-β transformation of tristearin during aging. The steric hindrance exists only on condition that hydrogen bonds between emulsifier and fat are formed in the right place. If this condition is not met the steric hindrance turns into a factor which enhances the transformation. The CGMS, GMS or LGMS, which do not have the required molecular structure, accelerate the transition.

This model clarifies why this "dynamic controller of polymorphic transformation" must be a surface-active agent. In spite of the fact that surface activity finds expression in oil/water systems, the same amphiphilic property is required for a completely different purpose.

It seems evident that differences exist between the effect of solid emulsifiers on polymorphism of fatty acids on the one hand, and of triglycerides on the other hand. As already pointed out in a previous section, polymorphic transition in stearic acid does not occur in the solid or melt phase, but rather in solvent. This means that the transition takes place through dissolution of one crystal and construction of a new one. It seems that in this case the effect of the emulsifier is connected to its solubility in different solvents, and to its efficiency of micelle formation; hence a correlation is supposed also with the HLB. The emulsifier in solution may form micellar structures and enable solubilization of stearic acid molecules. This causes a decrease in the degree of supersaturation of the acid, hence a lowering of nucleation rate. It is also possible that the emulsifier molecule may adsorb on the growing sites of the stable crystal polymorph. Both processes may occur concurrently and are independent of the direction of the transformation (if it is B to C or the opposite).

These conditions are very different from crystallization of tristearin from melt and during solid-solid transformation. In spite of this, a common denominator can be found between the effect of the emulsifier on polymorphic transformation of the two lipids. In both cases the emulsifier influences the kinetics of the transition, and the additive acts on the transition step without affecting the crystal structure. The question, whether emulsifiers can be included in the family of impurities which affect crystal growth, may be relevant, although the amount needed to delay polymorphic transformation in lipids is much higher than for impurities. In most cases, impurities are molecules which lack any structural affinity with the crystallizing substance in terms of size and shape, but their affinity is expressed in the functional groups that form bonds with growing sites of the crystal. The emulsifier, as a delayer of the polymorphic transition, also needs functional groups, but a very specific structural affinity is required to co-crystallize with the lipid molecules.

These conclusions also answer the question as to whether the amphiphilic properties of the additive are required to delay polymorphic transformations. It was found that by virtue of their molecular structures certain emulsifiers possess the chemical and structural affinity needed for this effect. This does not rule out the possibility that other kinds of molecules, not necessarily surfactants, may meet the same requirements for affecting polymorphic transformations.

Further investigation on the effect of emulsifier in different fats and solid fat emulsions will improve the understanding of this phenomenon and aid producers in controlling the physical properties of fatty products.

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Discussion with Reviewers

I. Heertje: I have considerable doubts about the interpretations of your DSC, the calculations of enthalpies and the suggested mechanism for transformation. As soon as peaks in DSC start overlapping, interpretations become very dangerous, and that is exactly what is happening in most of your work. This does not deny the important effects of emulsifiers on transformations from α to β' to β, but that should, in our opinion, be based on an another description. We think that you should not only look at what occurs at the endothermic side, but also what happens at the exothermic side. It is observed that at a high scanspeed (10; 8.5; 7°/min) the exothermic transition from liquid to β overlaps with the endothermic β melt peak. But it is questionable whether it may be concluded that this is caused by too-slow crystallization of β or by overlapping of peaks (due to the high scanspeed). Also at the low temperature side overlap of peaks can occur, in this case, of the α-melt peak and the β' crystallization peak. It is therefore unjustified to conclude that the lowering of α-melt peak is indicative for a direct solid-solid transformation from α to β, without liquefying.

Authors: We agree with you that our interpretation of the endothermic peaks is somehow misleading and simplistic since it disregards the fact that the thermogram is often a result of endotherm and exotherm overlap. However, it also seems to us that the correct interpretation of the thermogram can lead us to the same kind of conclusions. Whether the low temperature peak at scan rates 1 or O.5 °C/min refers only to the melting of the α-form or to a combination of melting and β' crystallization, it is clear that the overall endothermic reaction is small in comparison with the same reaction at high scan rates. From this we can still conclude that the overall quantity of unstable polymorph that liquifies at a certain temperature (53°C for instance) is smaller at low heating rates. Referring to Fig. 10 in our paper, the values obtained are still an indication that the solid fraction increases or decreases according to the emulsifier added. Hence, we agree with you that to state that "a larger portion of the fat transforms directly to β without liquefying" is not correct. However, it will still support the idea that the overall liquid portion of fat at a certain temperature depends on the scan rate and that this indicates a change in the transformation mechanism of the lower polymorphs.