

# Effect of Food Emulsifiers on Crystal Structure and Habit of Stearic Acid

N. GARTI, E. WELLNER and S. SARIG, Casali Institute of Applied Chemistry, School of Applied Science and Technology, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

## ABSTRACT

Several food emulsifiers have been found to serve as crystal structure modifiers for stearic acid crystallized from various organic solvents. Stearic acid that usually precipitates under appropriate crystallization conditions as the B-form is converted into the C-form when 1-5% of sorbitan esters or ethoxylated sorbitan esters of fatty acids are present in the solution. Other emulsifiers such as polyglycerol esters, substituted monoglycerides and sucrose esters of fatty acids consisting of bulky hydrophilic groups are also effective emulsifiers in preserving the C-form of the crystallized stearic acid. The active emulsifiers modify the external crystal habit of stearic acid. Mass spectrograph analysis indicates that sorbitan monostearate (Span 60) is precipitated with the stearic acid.

## INTRODUCTION

The effect of some food emulsifiers on the crystal structure of fats crystallized from melt has been known for many years (1-7). The suitable emulsifiers were found by trial and error. Only a few systematic studies have been done in order to understand the role of the emulsifiers in preventing the "blooming" phenomenon and in determining the crystal structure of the crystallized fat. It has been assumed that those emulsifiers can be accommodated by the  $\alpha$ -crystal lattice of the triglyceride and that by stearic hindrance they can prevent the formation of the more densely packed  $\beta$ -form (7).

The saturated even fatty acids constituting the hydrophobic portion of the fat can also be crystallized in several structure modifications designated A, B and C. It is believed that they can serve as a model for better understanding the ability of certain emulsifiers to cause crystal structure modifications.

In our previous studies, it was reported that crystallization conditions, as well as the nature of the solvent, can affect the crystal structure of the crystallized stearic acid (8). The effect of one selected emulsifier, sorbitan-monostearate (Span 60) was studied as a crystal structure modifier in several solvents and various crystallization conditions and it was reported that it is directing stearic acid structure toward the formation of C-form (9).

In this work, the effects of about 30 emulsifiers with different characteristics were studied and compared. Factors determining the suitability of an emulsifier to act as a modifying agent have been analyzed; predictions were tested and verified. On the basis of these data, assumptions concerning the possible mechanism of emulsifier-stearic acid interactions will be presented.

## EXPERIMENTAL

Stearic acid was purchased from BDH and was >99% pure (by gas liquid chromatographic analysis). The emulsifiers were commercially available from Atlas Europol A.p.S., Italy, and Grindsted Products of Denmark. The following types of emulsifiers were tested: Sorbitan esters of fatty acid (Spans), ethoxylated sorbitan esters of fatty acids (Tweens), ethoxylated fatty alcohols (Brijs), citric acid ester of monoglyceride (Acidan), diacetyl tartaric acid ester

of monoglycerides (DATA), sucrose monostearate (SMS) and polyglycerol esters of fatty acids (PGE).

The emulsifier concentrations were 2 wt % in ethanol and *n*-hexane solutions, and 5 wt % in benzene solutions.

The solvents for crystallization were spectroscopic grade, purchased from Malinckrodt and Baker. All experiments were done in thermostatic bath with controlled cooling profile. Crystallization temperatures were in the 20-30 C range at cooling rates of 0.03 and 0.1 C/min. Crystals obtained from *n*-hexane and ethanol solutions were filtered out 2 hr after start of precipitation. The separation of crystals from benzene solution was delayed for 24 hr after precipitation.

X-ray measurements were obtained with a Philips diffractometer using Cu radiation and Ni filter. All samples were carefully grounded and each spectrum was repeated several times.

The habit of the fatty acid crystals was inspected with a scanning electron microscope (Jeol ISM 35).

Mass spectra (MS) analysis was done on a DuPont 21-490B chemical ionization mass spectrometer.

## RESULTS AND DISCUSSION

The first step toward the elucidation of the possible mechanism of the emulsifier-stearic acid interaction was to examine the specificity of the interaction by comparing the effect of Span 60 with the effects of other emulsifiers.

Table I presents the effect of 6 Spans, 9 Tweens and 9 Brijs in a wide scope of Hydrophilic Lipophilic Balance (HLB) values, on the crystal structure and crystal habit of stearic acid crystallized from ethanol and *n*-hexane in quiescent systems, at cooling rate of 0.1 C/min, and filtered out 2 hr after precipitation.

The C-form, which is the natural stearic acid modification, crystallized in *n*-hexane at the working conditions employed is preserved in the presence of all the emulsifiers used: Spans, Tweens and Brijs.

The B-form, characteristic for ethanol solutions, undergoes transition to the C-form in varying degrees of exclusiveness in the presence of Spans and Tweens. The effect of Brijs is minor in comparison.

In the Span series, the most effective are Span 60 (sorbitan monostearate) and Span 40 (sorbitan monopalmitate). Both are similar to each other and their HLB values are close. Sorbitan monolaurate, Span 20, with shorter aliphatic chain (higher HLB value) has less effect. Emulsifiers with unsaturated carbon chains having nonlinear configurations (Span 80 and 85) also have little effect. Span 65, which consists of 3 stearic acid molecules, with very low HLB value, had a unique effect causing powder-like precipitation with very undefined X-ray patterns, suggesting an almost amorphous structure.

The Tweens have, in addition to the Span structure, polyoxyethylene chains of varying lengths. The outcome of the differences in these chain lengths is illustrated by the effects of Tweens 60 and 61 on the stearic acid structure. Tween 61 transforms the B-form into C whereas Tween 60,

TABLE I

Effect of Emulsifiers in 2% Concentration on the Crystal Structure and Habit of Stearic Acid in Ethanol and *n*-Hexane, Cooling Rate 0.1 C/min

Trade name of emulsifier	Composition <sup>a</sup>	HLB <sup>b</sup>	Ethanol		<i>n</i> -Hexane	
			X-rays	Habit change <sup>c</sup>	X-rays	Habit change
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	Amorphous	Powder	C	+
Span 80	Sorbitan monooleate	4.3	B>>C	—	C	+
Span 85	Sorbitan trioleate	1.8	B>C	—	C>>>B	—
Tween 20	POE Sorbitan monolaurate	16.7	B	—		
Tween 21	POE in Sorbitan monolaurate	13.3	B	—	C>>B	—
Tween 40	POE in Sorbitan monopalmitate	14.4	B	—		
Tween 60	POE Sorbitan monostearate	14.9	B	—	C>>>B	—
Tween 61	POE Sorbitan monostearate	9.6	C	+		
Tween 65	POE Sorbitan tristearate	10.5	C	+	C>>B	—
Tween 80	POE Sorbitan monooleate	15.0	B>C	—	C>>B	—
Tween 81	POE Sorbitan monooleate	10.0	B>>C	—		
Tween 85	POE Sorbitan trioleate	11.0	B	—		
Brij 30	POE lauryl alcohol	9.7	B>>>C	—	C>>>B	—
Brij 35	POE lauryl alcohol	16.9	B>>C	—	C>B	—
Brij 72	POE stearyl alcohol	4.4	B	—	C>>>B	—
Brij 76	POE stearyl alcohol	12.4	B	—	C>>>B	—
Brij 78	POE stearyl alcohol	15.3	B	—	C>>B	—
Brij 93	POE oleyl alcohol	4.9	B>>C	—		
Brij 97	POE oleyl alcohol	12.4	B>C	—		
Brij 98	POE oleyl alcohol	15.3	B>>>C	—		
Brij 58	POE cetyl alcohol	15.7	B>C	—		

<sup>a</sup>POE = polyoxyethylene.

<sup>b</sup>HLB = Hydrophilic Lipophylic Balance.

<sup>c</sup>+: Change in habit structure; —: no change in habit structure.

with a long hydrophilic chain as reflected by its high HLB value, has no effect. However, it is not self-evident that a long hydrophilic chain is enough to decrease effectiveness—in Tween 65, the addition of the long hydrophilic chain to sorbitan tristearate induced activity (compared to Span 65). It seems that the balance between the constituents is more important than their particular nature.

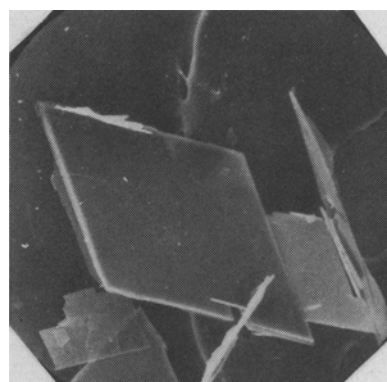
The Brij, characterized by linear structure, are quite ineffective in inducing B to C transitions.

Additional information included in Table I concerns the change in the habit of the stearic acid crystals induced by the emulsifiers. In our previous study (8), it has been shown that each crystal form of stearic acid, precipitated from a pure solution, has its own individual crystal habit and no deviation from the straightforward correlation has been found. Nevertheless, the C-form crystals obtained in the presence of the Span 60 have a completely different shape, as illustrated in Figure 1, a and b.

In this work, it was found that any emulsifier that affects the crystal structure modification caused, at the same time, similar change in the crystal habit (Fig. 1b). Moreover, when the same emulsifier is added to systems in which C modification is formed naturally, the crystal habit completely changes, though the crystal structure is unaffected.

The effects of representative emulsifier from the 3 groups were tested on crystals grown from benzene and the results are presented in Table II. In benzene, the pure B-form is obtained only after several hours of contact with the mother liquor (10). When Span 60 and Tween 61 were added, the crystals changed into the C-form, as could have been expected. When Span 65 and Brij 35 were added, no change was noticed.

At this stage, it could be summarized that effectiveness to induce the crystal structure and habit modification



A



B

FIG. 1. (a) The habit of C-form of stearic acid obtained from pure solution; (b) habit modification of stearic acid C-form obtained in the presence of Span 60.

depends on the structure of the emulsifier. It seemed that effective emulsifiers, among other characteristics, had a bulky hydrophilic group. In order to verify this assumption, several specific emulsifiers were tested and the results are given in Table III. The solvent used was ethanol, in which, as already mentioned, the natural structure is the B-form. Glycerol monostearate was ineffective, but triglycerol and decaglycerol monostearate were effective, confirming the assumption that bulkiness of the hydrophilic group is essential for the ability of the emulsifier to cause structure transition in stearic acid. The assumption is further enhanced by the fact that addition of Acidan and DATA, in which the bulkiness of the hydrophilic group is due to the structure of the citric and tartaric acids, respectively, also caused the transition to the C-form. Although it seems that the bulkiness of the hydrophilic group is an important factor, the right balance between the 2 parts of the emulsifier also has bearing on the effectiveness of the emulsifier to induce structure modification.

It may be important to note that although B and C forms of stearic acid are monoclinic with orthorhombic sub-cell packing, there is a substantial difference in the position of their carboxylic groups: in the C-form, they are aligned in the aliphatic chain plane whereas in the B-form, they are perpendicular to this plane. It may be assumed that the probable emulsifier-stearic acid interaction is through the carboxylic group of stearic acid, the emulsifier forcing the carboxylic groups and aliphatic chains into the same plane.

It seems significant that structure transitions are invariably accompanied by a particular habit transition. The normal mode of stearic acid crystal growth through regular 001 planes is interrupted and disorderly agglomerates of needle-like crystals are formed.

Crystals formed in solutions with the admixture of different emulsifiers were analyzed by MS. In crystals formed in the presence of Brij 78, which does not affect structure and habit, no fragments of molecular weight (MW) higher than the 284 (MW of stearic acid), were detected, whereas in crystals grown in the presence of Span 60, a well developed peak corresponding to the  $414 \pm 2$  MW was detected, together with a series of peaks between MW 284 and 414. The MW of 1,4-sorbitan-monostearate is 430 whereas 1,4-isosorbite-monostearate has an MW of 412. MS of the commercial emulsifier itself shows parent peaks at 430 and 412. The fact that stearic acid precipitated in the presence of Span 60 showing a series of peaks beyond the  $m/e = 284$  indicates that the emulsifier was incorporated in the fatty acid.

TABLE II

Effect of Emulsifiers in 5% Concentration on Crystal Structure and Habit of Stearic Acid in Benzene, Cooling Rate 0.1 C/min

Emulsifier	Composition	X-rays	Habit
—	Control (no emulsifier)	B	
Span 60	Sorbitan monostearate	C	+
Span 65	Sorbitan tristearate	B>>>C	—
Tween 61	POE Sorbitan monostearate	C	+
Brij 35	POE lauryl alcohol	B>>>C	—

TABLE III

Effect of Emulsifiers in 2% Concentration on Crystal Structure and Habit of Stearic Acid in Ethanol, Cooling Rate 0.1 C/min

Emulsifier	HLB	X-rays	Habit
Sucrose monostearate	—	C	+
Glycerol monostearate	—	B	—
Triglycerol monostearate	8.8	C	+
Decaglycerol monostearate	14.5	C	+
Acidan (citric acid ester or glycerol monostearate)	6	C	+
DATA (tartaric acid ester of glycerol monostearate)	—	C	+

Whether the mechanism of incorporation of the emulsifier in the fatty acid crystal is through absorption during growth or by the formation of associates composed of emulsifier and acid molecules as precursors of the precipitate in the solution is to be further studied.

## REFERENCES

1. Campbell, L.B., and P.G. Keeney, *Mfg. Confect.* 48:177 (1968).
2. Chapman, G.M., *JAOCS* 48:824 (1971).
3. Easton, N.R., D.J. Kelly and L.R. Buton, *Food Technol.* 6:21 (1952).
4. Ludwig, K.G., *Fette Seifen Anstrichm.* 71:672 (1969).
5. DuRoss, J.W., and W.H. Knightly, *Mfg. Confect.* 45:50 (1965).
6. Kleinert, J., *Rev. Int. Choc.* 16(5):201 (1961).
7. Krog, M., *JAOCS* 54:124 (1977).
8. Garti, N., E. Wellner and S. Sarig, *Cryst. Tech.* 15:1303 (1980).
9. Garti, N., E. Wellner and S. Sarig, *J. Crystal Growth* (in press).
10. Garti, N., E. Wellner and S. Sarig, *Cryst. Tech.* 16:1283 (1981).

[Received March 17, 1980]