

## EFFECT OF SURFACTANTS ON CRYSTAL STRUCTURE MODIFICATION OF STEARIC ACID

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Stearic acid can exist in three main crystal structure modifications. The crystal structure is determined by solute-solvent interactions. When changes occur in the growth conditions, for instance in flow regime or by increased cooling rate, the crystal modification is affected. Addition of small amounts of surfactants will force the stearic acid to crystallize in only one modification regardless of the crystallization conditions and the nature of the solvent.

### 1. Introduction

Normal fats and fatty acids are polymorphic and can exist in more than one crystalline form [1-3]. An industrial phenomenon known as "blooming" occurs when fat, crystallized from melt, converts to the undesirable modification which is the most thermodynamically stable form [4]. Several manufacturers noticed that suitable growth conditions or addition of small amounts of emulsifiers to the molten fat will prevent "blooming" [4].

Stearic acid, which is a saturated common fatty acid, was chosen as a model material for a study of these phenomena.

The relationship between the polymorphism and the growth conditions of stearic acid has been examined by several investigators. It has been mentioned, for example, by Piper [5] that the B-form is obtained by slow crystallization from nonpolar solvents and that rapid crystallization from polar solvents produces the C-form. Stearic acid crystallizes as C-form from melt and the A-form appears by pressing the same crystals on a glass plate [5]. Holland et al. [6] obtained pure C-form from isopropyl ether by evaporation at 27°C. Evaporation of CS<sub>2</sub> at 18°C gave B-form, while evaporation at -9°C yielded a mixture of B- and A-forms [7,8].

Bailey [9,10] recently concluded that the crystal

structure of stearic acid obtained by evaporation is governed by the temperature of crystallization in any crystallizing solvent.

Sato and Okada [11] tried to clarify the relationship between polymorphism of the fatty acid and the growth conditions in order to find the best conditions to obtain large single crystals. They concluded that polymorphic modifications are affected more strongly by the growth rate than by the solvent; whether the solvent is polar or non-polar is not the determining factor. Unfortunately, their study is incomplete and thus their conclusions are not yet comprehensive.

Our previous studies [12,13] demonstrated that in quiescent solutions the crystalline modification of the acid is determined by solvent-solute interactions. When growth conditions (e.g., cooling rate, flow regime) are changed, the fatty-acid modification is changed. Thus, it appears that one can obtain a desired form by choosing the right solvent and growth conditions. However, since the system is extremely sensitive, it may prove to be quite difficult to obtain satisfactory predictability in practice.

To the best of our knowledge, no attempts have been described in the literature to evaluate the effect of impurities, nucleating agents or other crystal modifiers on the crystal structure and habit of the fatty acid. In this study, we sought to find dependable ways for controlling the crystal struc-

ture and habit of the fatty acid. The effect of small amounts of emulsifiers (1–5%) on the crystallization of stearic acid has been examined, to find out whether predictability may be increased by the use of additives.

## 2. Experimental

### 2.1. Materials

Stearic acid from BDH Chemicals was purchased at >99.5% purity and was used without further purification. The absence of significant quantities of other impurities than palmitic acid (<1%) was established by gas chromatography. The melting point was 69.5°C. The fatty acid as received was in the C-form according to X-ray measurements.

The solvents for crystallization were spectroscopic grade purchased from Mallinckrodt and from J.T. Baker.

The emulsifier, sorbitan monostearate (Atlas Erupol, S.p.A.), was commercially available and used without any further purification.

### 2.2. Crystallization techniques and analytical methods

All the experiments were carried out in a thermostatic bath with controlled cooling profile. Crystallization temperatures were in the 20–30°C range.

Simultaneous Differential Thermal Analysis (DTA), Thermo-Gravimetric Analysis (TGA) and Differential Thermal Gravimetry (DTG) determinations were carried out on a Mettler Thermoanalyzer under controlled dry nitrogen flow of 5 l h<sup>-1</sup>. The samples were in the range of 50–70 mg and the heating was at the rate of 2°C min<sup>-1</sup>.

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

The habit of the fatty acid was carefully inspected with a Scanning Electron Microscope (SEM).

## 3. Results

The solubility curves of pure stearic acid in four organic solvents were determined prior to any addition of emulsifier (see fig. 1). It can be seen that at 30°C the solubility of stearic acid in benzene is 12.4 g/100 g solvent while in acetone, ethanol and hexane the solubilities are much smaller (4.93, 3.42 and 3.96, respectively). The solubility of stearic acid with temperature increases significantly with all the solvents. The supercooling of pure stearic acid in hexane, ethanol, acetone and benzene are given in table 1 for quiescent solutions and cooling rates of 0.03°C min<sup>-1</sup>, and the supercooling values for stirred and quiescent solutions in benzene for 3 different cooling values are given in table 2. The stearic acid recovery after each crystallization experiments was almost quantitative since the filtration process was accomplished 6 h after appearance of the first crystals in the vessel. The amounts of stearic acid precipitated in hexane, ethanol and benzene were measured and found to be 95, 90 and 80% respectively, of the initially dissolved stearic acid.

The precipitated forms of stearic acid obtained from each solvent from quiescent and stirred solutions at several cooling rates were examined care-

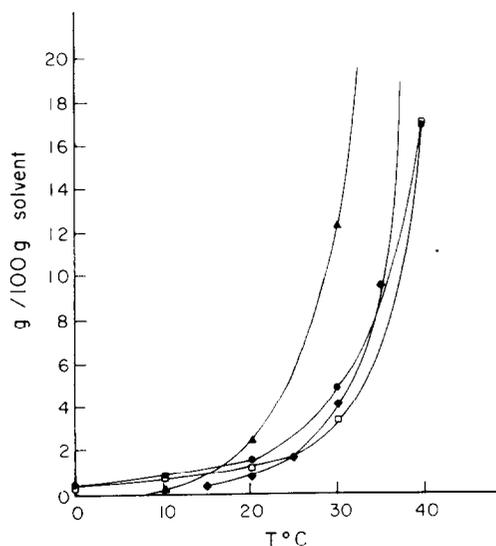


Fig. 1. Solubility curves of pure stearic acid in (◆) hexane, (□) ethanol, (●) acetone, (▲) benzene.

Table 1

Crystal structure modification of stearic acid crystallized from organic solvents in the presence of emulsifier (quiescent solution,  $0.03^{\circ}\text{C min}^{-1}$  cooling rate)

| Solvent               | Emulsifier<br>SPAN 60 | $T^*$<br>( $^{\circ}\text{C}$ ) | Supersaturation<br>$S=C/C^*$ | $\Delta H$<br>( $\text{cal g}^{-1}$ ) | Crystal modification |           |
|-----------------------|-----------------------|---------------------------------|------------------------------|---------------------------------------|----------------------|-----------|
|                       |                       |                                 |                              |                                       | By DTA               | By X-rays |
| Hexane <sup>a)</sup>  | 0                     | 27.8                            | 1.431                        | 0                                     | C                    | C>>>B     |
|                       | 1.0                   | 25.6                            | 2.128                        | 0                                     | C                    | C         |
| Ethanol <sup>b)</sup> | 0                     | 25.0                            | 1.954                        | 1.50                                  | B>>C                 | B>>C      |
|                       | 1.0                   | 24.1                            | 2.164                        | 0                                     | C                    | C>>>B     |
| Acetone <sup>b)</sup> | 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 <sup>a)</sup> | 0                     | 23.9                            | 1.191                        | 5.11                                  | B                    | B         |
|                       | 0.5                   | 23.8                            | 1.217                        | 3.51                                  | B>>C                 | B         |
|                       | 1.0                   | 23.6                            | 1.244                        | 2.89                                  | B>C                  | B>C       |
|                       | 5.0                   | 23.3                            | 1.317                        | 0                                     | C                    | C         |

<sup>a)</sup> Saturation temperature  $25^{\circ}\text{C}$ .

<sup>b)</sup> Saturation temperature  $30^{\circ}\text{C}$ .

fully by DTA, X-rays, SEM and IR techniques as described elsewhere [12].

When 1 to 5 wt% of sorbitan monostearate (SPAN 60) (referred to solute) was added to the

crystallizing solvent a dramatic change was observed: the C-form was obtained regardless of growth conditions (table 1).

The stearic acid precipitated in the presence of

Table 2

The effect of 3% SPAN 60 on the crystal structure of stearic acid grown from benzene at various cooling rates in stirred and quiescent solutions

| Flow regime | Cooling rate<br>( $^{\circ}\text{C min}^{-1}$ ) | Emulsifier<br>SPAN 60<br>(%) | $T^*$<br>( $^{\circ}\text{C}$ ) | Supersaturation<br>$S=C/C^*$ | Crystal modification<br>by X-rays |
|-------------|---|------------------------------|---------------------------------|------------------------------|-----------------------------------|
| Quiescent   | 1   | 0                            | 18.5                            | 3.027                        | B                                 |
|             | 1   | 3                            | 18.0                            | 3.294                        | B>>>C                             |
| Stirred     | 1   | 0                            | 21.3                            | 1.806                        | B                                 |
|             | 1   | 3                            | 21.9                            | 1.947                        | B=C                               |
| Quiescent   | 0.5   | 0                            | 20.2                            | 2.213                        | B                                 |
|             | 0.5   | 3                            | 20.3                            | 2.213                        | B>C                               |
| Stirred     | 0.5   | 0                            | 22.2                            | 1.577                        | B                                 |
|             | 0.5   | 3                            | 21.5                            | 1.696                        | B<C                               |
| Quiescent   | 0.1   | 0                            | 21.2                            | 1.867                        | B                                 |
|             | 0.1   | 3                            | 21.1                            | 1.898                        | B>>C                              |
| Stirred     | 0.1   | 0                            | 23.4                            | 1.302                        | B                                 |
|             | 0.1   | 3                            | 23.0                            | 1.389                        | B<<C                              |

emulsifier was collected and examined. The elemental analysis for C, H, IR, NMR and m.p. of the product did not show any significant change. The recoveries of stearic acid in each of the solvents were close to the values obtained without the emulsifiers.

When hexane, cyclohexane and other nonpolar hydrocarbon compounds were used as solvents, in quiescent solution at slow cooling rate ( $0.03^{\circ}\text{C min}^{-1}$ ), the C-form was obtained without the addition of the emulsifier. The crystal habit of the C-form can be seen in fig. 2. DTA showed only one endothermic peak at its melting point (fig. 3 (1)). The X-ray diffraction pattern was typical of the C-form (fig. 4).

Under the same growth conditions, when benzene was the crystallizing solvent the B-form was obtained (figs. 5 and 6). Addition of 0.5 and 1% emulsifier forced part of the stearic acid to crystallize in the C-form (see table 2). The microscope showed a mixture of typical B-form and C-form crystals. X-ray diffraction as used here can yield only qualitative data with regard to the composition of a solid mixture: both samples showed bands of the C-form with the main B-form (fig. 7). DTA measurements provided a clearer interpretation. The phase transition of the B-form into C-form was accompanied by an endothermic peak at  $54^{\circ}\text{C}$  with  $\Delta H$  values between  $2.8$  and  $3.5 \text{ cal g}^{-1}$  (table 1). For the pure B-form an endothermic peak was found at the same temperature with  $\Delta H$

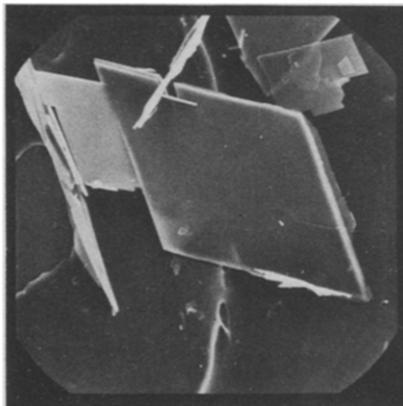


Fig. 2. C-form stearic acid grown from pure n-hexane in quiescent system at  $0.03^{\circ}\text{C min}^{-1}$  cooling rate. Magn.  $\times 160$ .

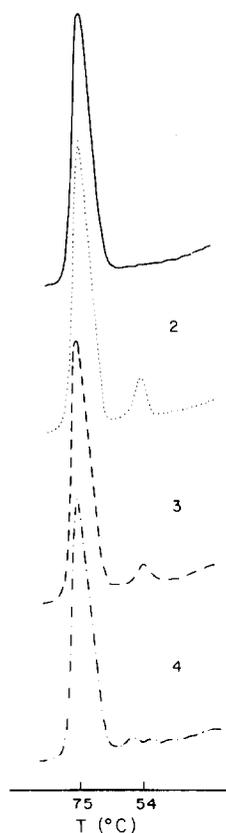


Fig. 3. DTA thermograms of pure C-form (1), pure B-form (2), mixture of B- and C-forms (3) and mixture of A-, B- and C-forms (4) of stearic acid.

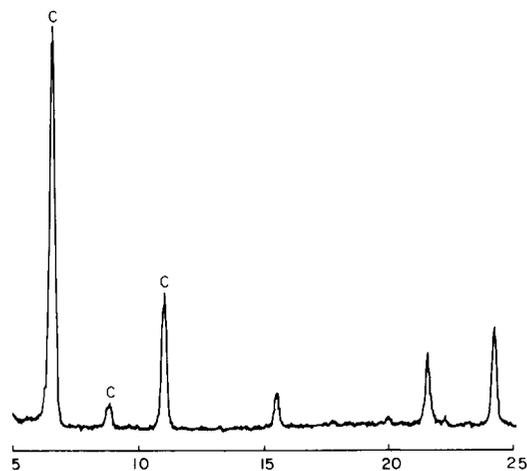


Fig. 4. X-ray diffraction pattern of stearic acid crystallized from hexane with or without emulsifier.

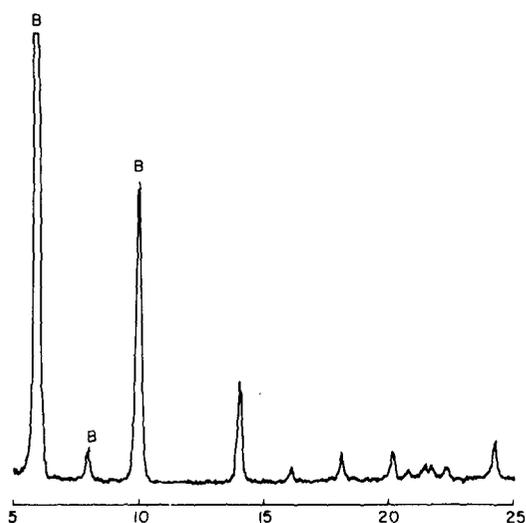


Fig. 5. X-ray diffraction pattern of stearic acid crystallized from pure benzene.

value of  $5.11 \text{ cal g}^{-1}$  (compare fig. 3 (2) and fig. 3 (3)). Thus it was possible to estimate the amount of C-form in the mixture. Addition of 5% emulsifier to the benzene resulted in stearic acid crystals which showed no indication of phase transition during heating and a typical C-form X-ray diffraction pattern.

Similar results were obtained when acetone and ethanol were used as solvents. In acetone the presence of the A-form was detected by X-ray diffrac-

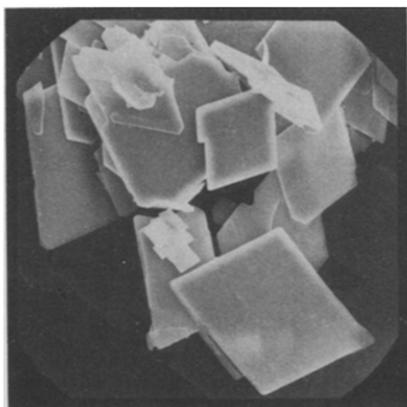


Fig. 6. B-form of stearic acid grown from pure benzene in quiescent system at  $0.03^\circ\text{C min}^{-1}$  cooling rate. Magn.  $\times 80$ .

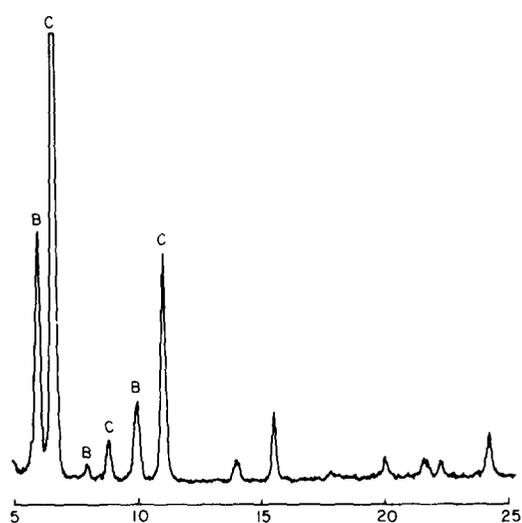


Fig. 7. X-ray diffraction pattern of stearic acid crystallized from benzene in the presence of 1% emulsifier.

tion (fig. 8) and DTA measurements (fig. 3 (4)). The presence of 5% emulsifier prevented both the B- and A-forms from precipitating and only the C-form was obtained.

The presence of the modifier in the crystallization system caused an increase in the supersaturation values for each solvent. The most pronounced effect was for ethanol and hexane and only a marginal effect was recorded for benzene and ace-

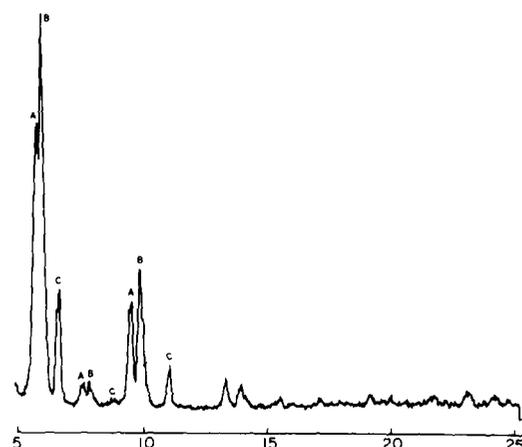


Fig. 8. X-ray diffraction pattern of stearic acid crystallized from acetone in the presence of emulsifier.

tone (table 1). Examination by SEM of the crystals obtained from the pure solvents in comparison with the crystal prepared in the contaminated systems revealed that the crystal habit of the acid changed from that in typical A-, B- or C-forms (figs. 2, 6 and 9) into an irregular shape, as illustrated in fig. 10.

The effect of the emulsifier SPAN 60 was examined also under other controlled crystallization conditions such as increased cooling rates and increase in turbulence of flow. Tables 2 and 3 summarize those results. It can be clearly seen that sorbitan monostearate is an efficient modifier for stearic acid even under drastic crystallization conditions.

Table 2 presents the results from crystallization processes carried out at various cooling rates in quiescent and stirred solutions. It can be seen that for quiescent solutions when no emulsifier was added, although the supersaturation values increased considerably with increase in the cooling rate (1.867, 2.213 and 3.027), no significant change was obtained in the crystal structure, and modification B precipitated predominantly. The addition of 3% emulsifier caused only part of the acid to crystallize as C-form ( $B > C$ ).

For stirred solutions, the effect of cooling rate was similar but more pronounced. When no emulsifier was present in the system, in spite of the increase in the supersaturation values (1.302, 1.577 and 1.806), only B-form was detected. However, significant amounts of the C-form were found when 3% emulsifier was present in the solution ( $C > B$ ).



Fig. 9. A-form of stearic acid grown from pure acetone in quiescent system at  $0.03^{\circ}\text{C min}^{-1}$  cooling rate.



Fig. 10. C-form of stearic acid grown from acetone in quiescent system at  $0.03^{\circ}\text{C min}^{-1}$  cooling rate in presence of 1% SPAN 60 emulsifier. Magn.  $\times 80$ .

Table 3

The effect of the emulsifier on the crystal structure modifications of stearic acid crystallized in stirred solutions

| Solvent | Cooling rate<br>( $^{\circ}\text{C min}^{-1}$ ) | Emulsifier SPAN 60<br>(%) | $T^*$<br>( $^{\circ}\text{C}$ ) | Crystal modification<br>by X-rays |
|---------|---|---------------------------|---------------------------------|-----------------------------------|
| Benzene | 0.5   | 0                         | 26.7                            | B                                 |
|         |   | 5                         | 26.8                            | C                                 |
| Hexane  | 0.5   | 0                         | 27.7                            | B                                 |
|         |   | 1                         | 24.5                            | $C > B$                           |
| Ethanol | 0.03  | 0                         | 25.4                            | B                                 |
|         |   | 1                         | 24.1                            | C                                 |

When hexane and ethanol were used, in which some C-form is produced even in the absence of the emulsifier, it was found, as expected, that at accelerated cooling rates the C-form was precipitated predominantly.

Table 3 clarifies the effect of the emulsifier with other solvents as well, with 5% emulsifier at a  $0.5^{\circ}\text{C min}^{-1}$  cooling rate. With benzene, only C-form was observed. When hexane and ethanol were used, 1% of emulsifier was sufficient to stabilize the formation of C in place of the B-form.

The presence of the emulsifier in the stearic acid was demonstrated by mass spectrometry since fragments of molecular weights close to the emulsifier's formula ( $mw = 414$ ) have been detected. The amount of the emulsifier present in the stearic acid is not yet known. Analysis of the product by High Performance Liquid Chromatography is in progress in order to determine the emulsifier concentration in the fatty acid.

#### 4. Discussion

Sorbitan esters of fatty acids are known as crystal structure modifiers for fats crystallized from the melt. They tend to stabilize the formation of thermodynamically unstable modifications. To the best of our knowledge this is the first study which demonstrates that emulsifiers can serve as crystal modifiers for stearic acid crystallized from various solvents and at various conditions. Whereas stearic acid crystallizes in the stable C-form from melt, all forms may crystallize from solutions. SPAN 60 will stabilize the formation of modification C in crystals formed in solution.

It has been shown that in quiescent solutions the main factors affecting the crystal structure are solvent-solute interactions, as well as the nucleation and crystal growth rates [12]. For solvents such as hexane and acetone it was demonstrated in previous work that the solvent-solute interactions had only a limited effect. In the present study it was found that the addition of emulsifier in minor concentrations caused the stabilization of the C-form. When benzene and ethanol are used, significant solvent solute interactions take place, directing

the precipitation to the B-form. It seems to signify that an increased amount of emulsifier, up to 5%, was needed to stabilize the formation of C-form in these cases. However, when drastic conditions were applied to the system the formation of the C-form was only partial. It appeared admixed with the B-form.

For solvents such as hexane and acetone, 1% of emulsifier was sufficient to produce the pure C-form in stirred solution and at increased cooling rates. For benzene, 3% of emulsifier yielded mixtures of B and C and the pure C-form was obtained only with 5% emulsifier.

At increased cooling rate, increased supersaturation is stabilized, and thus one would expect the formation of the thermodynamically unstable modification B, since in a given solvent the interplay of both nucleation rates and supersaturation values is responsible for the formation of the preferred modification. Thus it will be advisable to check both parameters before any prediction is made of the modification to be formed. In benzene, in spite of the fact that the supersaturation values increased by increasing cooling rates, modification B was formed in quiescent and stirred solutions and only 5% of emulsifier helped the formation of the C-form.

The mechanism by which the formation of the C-form is facilitated is not yet clear but the fact that a change in the habit is brought about by the emulsifier by which irregularly shaped crystals are produced, is a hint at possible absorption of the emulsifier on the precipitated stearic acid. Work on that mechanism is in progress and will be reported soon. Other emulsifiers and their effect on the crystal structure are being studied and their effect will be discussed separately.

#### List of symbols

- $C^*$  Concentration at the onset of crystallization
- $C$  Saturation concentration
- $S$  The supersaturation  $C/C^*$
- $T^*$  The observed temperature of crystallization
- $T$  Saturation temperature

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