Synergism between Span 60 and Tween 60 may suggest that the emulsifiers do not function in a complete molecular dispersion, but are solubilized one into the other.

A relation between emulsifier structure and the ability to retard V-VI transformation has been demonstrated. It may be suggested that the effect on IV-V transition is due just to the increase in liquid fraction, but the effect on V-VI transition in addition is related closely to the emulsifier physical structure. We may imagine that a high melting point emulsifier will have its carbon chains tightly packaged, producing a rigid structure. Any polymorphic transition through solid phase, associated with slight movement of fat molecules will be hindered by the rigidity of that structure. Lack of rigidity will allow eventual undulation of the carbon chains, thus permitting the slight movement of the fat molecules.

Much work still must be performed to elucidate the action of the emulsifier; further results on the subject will be published later.

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Effects of Surfactants on Transition Kinetics of Stearic Acid Polymorphs

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The effects of some nonionic surfactants on the kinetics of the solution-mediated transition of stearic acid of B and C polymorphs were studied. Some surfactants were found to retard the transition of the thermodynamically unstable stearic acid modification to the stable form in methanol, n-hexane and decane solutions. The surfactants consisting of large hydrophilic moieties revealed a significant retardation effect. The effect also depends on the solvent; the lower the solubility of the surfactant in the solvents, the more the transition rate was decreased. Finally it should be noted that the C→B transition was more affected than the B→C transition with a given surfactant.

Surfactants have been known to be useful agents for controlling the polymorphic behaviors of fats and oils (1,2). The microscopic features of the surfactants' effects, however, have never been clarified. To elucidate this effect, we tried to examine the retardation of transition kinetics of different polymorphs of stearic acid crystals. As reported very shortly (3), two typical polymorphs, B and C, of stearic acid can transform to one another in the solution phase (solution-mediated transition). This transition occurs when the more stable polymorphs (C above 32 C, and B below 32 C) grow at the expense of the less stable ones (4). The rate of transition depends on temperature as well as on the solvent. The polarity of the solvent was found to be very important. The modification transitions were used as a model system to examine the effects of various surfactants, such as sorbitan esters, monoglycerides, polyglycerol esters and sucrose esters, on the kinetics of the polymorphic transition at low and high temperatures in polar and nonpolar solvents. By doing so, the effect of surfactant as a crystal-structure modifier could be examined in detail.

MATERIALS AND METHODS

Stearic acid of more than 99% purity from Ishizu Pharmacy was employed. The following solvents were utilized: nonpolar aprotic n-hexane (Yoneyama Pharmacy, 99.6%) and nonpolar aprotic decane (Tokyo Kasei Inc., 99%), and polar protic methanol (Yoneyama Pharmacy, 99.8%).

The transition rate was defined as the rate of change in fractional concentrations of C and B powdered crystals suspended in the solution. Stearic acid was crystallized in both forms, and the crude crystals were carefully ground for several hr prior to each experiment to obtain crystals of optimal small size. The particle size distribution was determined by optical microscope in the suspended solution of n-hexane at 10 C. As the solubility of stearic acid at this temperature is very low (0.1 g/100 g solvent), no appreciable dissolution occurred during the examination of the particle sizes, which was done within about 20 min. Thus, the average particle size was found to be about 30 μm for both polymorphs. The same samples were used throughout the experiments. A mixture of B and C powders was put into the solution, which had been saturated to the more stable form at a given temperature.

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The saturated solution was prepared by stirring the solution, in which either the unstable or stable crystals were precipitated due to their high initial concentration, for one night. Since the solution-mediated transition in the pure solutions completes within that duration, the resultant solution was perfectly saturated with respect to the more stable one. Thereafter, the top solution was picked up after stirring was stopped. The amounts of solution and powder were always 15 g and 1.5 g, respectively. The suspension was stirred with a magnetic stirrer (about 300 rpm). The temperature of the suspension was kept constant within ±0.1 C via the temperature-controlled water bath surrounding the growth cell.

The 1.5 cc samples were withdrawn, filtered and dried as quickly as possible. The ratio of the B and C concentrations was measured as a function of time from X-ray spectra (Rigaku diffractometer). The (003) reflection was chosen as a reference. The concentrations were determined at intervals ranging from 3 to 10 min, depending on the temperature. When the surfactants were present, they were dissolved in the solution prior to the addition of B and C powdered mixture. Different amounts of surfactants were added to examine the effect of concentration.

RESULTS AND DISCUSSION

Figure 1 compares the rate of the C→B transition (C→B) at 22 C in methanol in the presence of 0.1-1.0 wt% sorbitan monostearate (span 60) to that in pure solution. The transition was expressed by a change in the C-crystal fraction. Even at 0.1 wt%, span 60 retards the transition. The total conversion to B required 20 min, in comparison to 10 min when pure methanol was used. When 0.5 wt% of span 60 was introduced, almost no transition was detected after more than 60 min. Yet, if the solution was stirred continuously for 10 to 12 hr, all of the C crystals transformed to B. Surfactant concentrations over 1 wt% could not be tested, because their solubility in methanol at the given temperature is restricted.

The results in n-hexane are shown in Figure 2. The nonpolar solvent n-hexane has almost no interaction with solutes, either of stearic acid or of surfactant. Therefore, dimerization of stearic acid molecules is achieved under the conditions examined (5,6). Almost 25 min are needed to obtain the full C→B transformation. Higher concentrations of surfactant showed, as expected, a more pronounced effect. Comparison of the effect at 0.5 to 1.0 wt% span 60 on C→B in methanol and in n-hexane at 22 C reveals that, in spite of the fact that in pure methanol the transition is faster, C→B was more retarded in the presence of span 60 in methanol than in n-hexane.

Figure 3 demonstrates the retardation effect of span 60 on B→C in methanol at 35.5 C. The transition took over 72 min to obtain pure C form in the pure solution. The addition of 0.5 wt% of span 60 caused only a moderate retardation. A concentration of over 1 wt% of span 60 was needed to significantly influence the B→C transition.

When n-hexane was used as the solvent, the B→C rate was higher than in methanol. However, the addition of span 60 in n-hexane caused more retardation than in methanol. As a result, the rate was significantly decreased as shown in Figure 4.

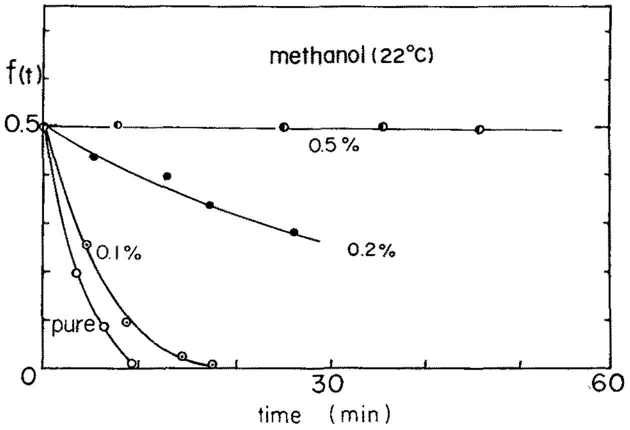

FIG. 1. Transition from C to B (C→B) polymorphs of stearic acid in methanol with and without span 60 at 22 C.

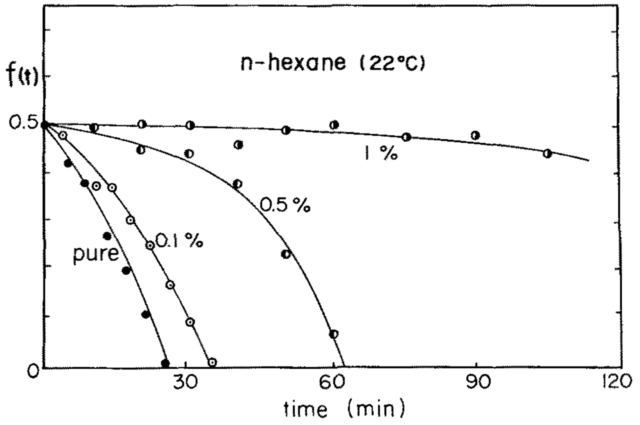

FIG. 2. C→B transition in n-hexane with and without span 60 at 22 C.

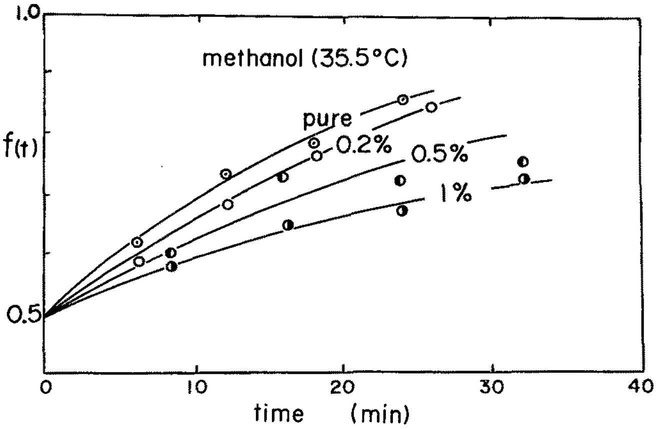

FIG. 3. B→C transition in methanol with and without span 60 at 35.5 C.

To summarize, Figure 5 shows the effect of 0.5 wt% span 60 in the two solutions and at two temperatures. It appears noticeable that span 60 was more effective at 22 C than at 35.5 C in both solvents. This means that the C→B transition was more influenced than B→C.

The effect of both span 60 and span 65 (sorbitan tristearates) on C→B was examined in decane at 22 C.

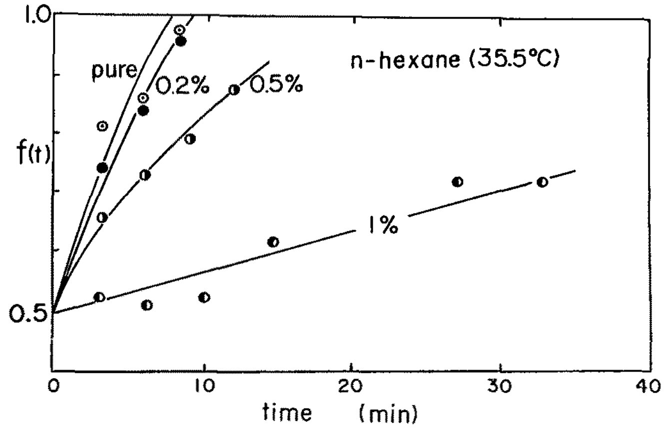

FIG. 4. B→C transition in n-hexane with and without span 60 at 35.5 C.

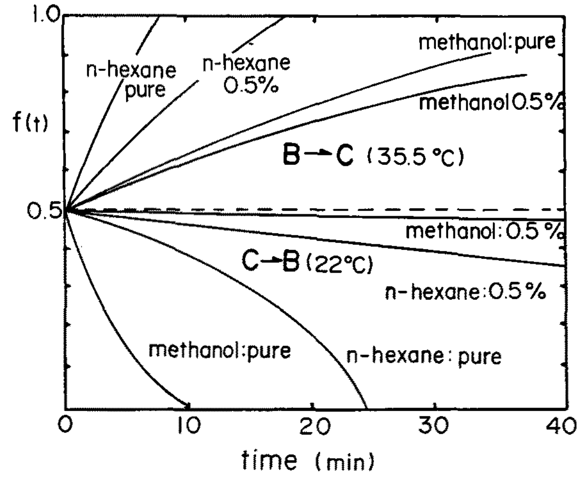

FIG. 5. Retardation by span 60 in polar (methanol) and nonpolar (n-hexane) solvents for both C→B and B→C.

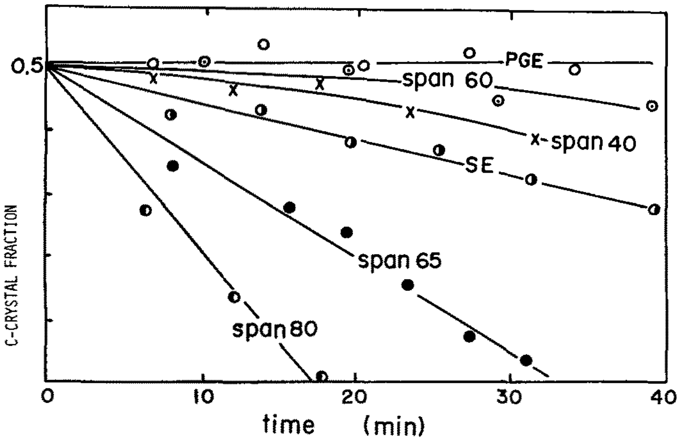

FIG. 6. Retardation effects of span 80, polyglycerol ester (PGE), sugar ester (SE), span 40, span 65 in addition to span 60 in n-hexane solution at a fixed 0.2 wt% at 22 C.

Retardation was also revealed, but it was less significant than when the other solutions were employed. This results from lower solubilities both of stearic acid and surfactants in decane solvent.

Lastly, we examined various surfactants at a fixed 0.2 wt% in n-hexane solutions at 22 C (Fig. 6). Span 80 (sorbitan monooleate), being a liquid emulsifier, did not cause any retardation. Span 20 (sorbitan monolaurate), consisting of C12 fatty acid (lauric acid) with a short hydrophobic moiety, did not retard C→B. When the surfactants consisted of a large hydrophobic portion (sorbitan monopalmitate, span 40), the rate of transition slowed significantly. Nevertheless, the retardation was smaller than with span 60. Monoglyceride of stearic acid (distilled, 90% mono) caused no retardation. This is in good agreement with our previous findings on tristearin (1) and on stearic acid (2). Sucrose esters (SE) and polyglycerol esters (PGE), consisting of bulky hydrophilic groups and long-chain fatty acid hydrophobic moieties, were very active retarding agents. To summarize, the retardation effects of these emulsifiers are compared in the following sequence:

PGE > span 60 > span 40 > SE > span 65 > span 80

Similar experiments were carried out in methanol for C→B with 0.2 and 0.5 wt% of emulsifiers at 22 C. The following sequence of the retardation effects was obtained:

span 65 > PGE > span 60 > SE > span 40 > span 20 > span 80

In spite of some overlapping, there is a distinct difference in retardation effects between n-hexane and methanol. Yet, it is clear that PGE retard the transition most efficiently in both solutions.

We have examined the effects of some well-known crystal structure modifiers (surfactants) on the kinetics of the transition of stearic acid polymorphs. Some of them had significant retardation effects both on B→C and on C→B.

The nature and structure of the surfactant is significant. Only solid surfactants were proven to have measurable effects, which suggests that the effect is not only in the dissolution stage of stearic acid but also in nucleation or crystallization. In order to obtain a transformation from B to C or vice versa, the stearic acid crystals must dissolve and regrow on the new lattice. The surfactants can interfere either in the dissolution or reorganization stage when the crystal growth occurs. The fact that only very specific surfactants were active (solid compounds, with long-chain fatty acid moieties, and with bulky hydrophilic groups) suggests that a strong surfactant-stearic acid interaction is needed.

With respect to the solvents used, emulsifiers with a lower solubility were more active compared to those with a higher solubility. For example, sorbitan tristearate, very hydrophobic with HLB = 3.5 and very low solubility in polar solvents, retarded C→B better in methanol than similar concentrations of sorbitan monostearate of PGE having a higher HLB value and higher solubility. On the contrary, PGE caused stronger retardation on C→B in comparison to span 65 and span 60 when n-hexane was used as solvent, with its solubility in the nonpolar sol-

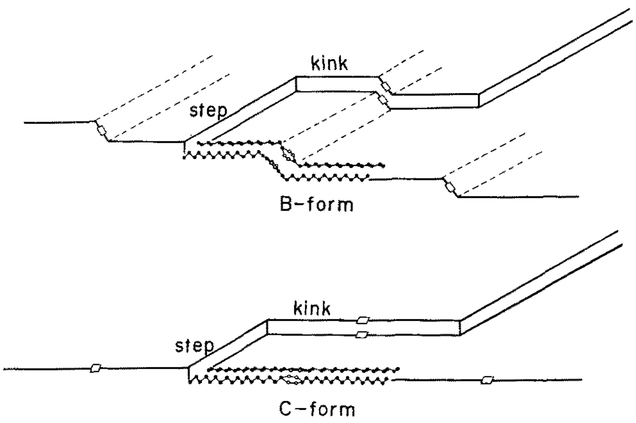

FIG. 7. Lateral surface structures of B and C crystals of stearic acid.

vent significantly lower than the latter two emulsifiers.

Finally, the comparison of C→B with B→C should be mentioned. Whatever the solvents and emulsifiers employed, C→B was always more effected than B→C at the same concentration level. This means that the growth of B was more retarded by the addition of the surfactants. The lateral faces, which are most active growth faces, of the B crystal reveal the stepped structure due to the gauche conformation at the COOH group (7). Meanwhile, C has only flat interfaces (8). Figure 7 shows the different lateral crystal surfaces. This difference may be responsible for the preferable surfactant effects on C→B more than B→C through favorable adsorption of surfactant molecules on the stepped positions on the B crystal faces.

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Laboratory and Pilot Solvent Extraction of Extruded High-Oil Corn

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Oil extraction of flakes and extrudates of high-oil (HO) corn was studied, using hexane as solvent. HO corn contained 19.5% oil, 70% of which was located in the germ. Microstructures of starchy endosperm and germ were analyzed by scanning electron and light microscopy. Conventionally extruded samples extracted faster and to a lower residual oil content than flakes and steam-injected extrudates. Ultrastructural disruption and cooking of conventionally extruded material was adequate to free the oil from the spherosomes and produce a porous pellet with a high proportion of "surface oil." Encapsulation of the oil within a gelatinized starch matrix made it partly unavailable in steam-injected extrudate samples. Data presented for laboratory and pilot plant runs demonstrate that conventional extrusion is a promising pretreatment for solvent extraction of high-oil, starchy materials.

Only about 3% of total oil produced in the U.S. is from corn. Corn oil is a by-product of wet or dry milling of corn and, presently, is recovered economically only from separated germs.

Total oil content in regular corn is about 4.5%, and that of the germ averages about 35%. Limited quantities of high-oil corn (HO corn) hybrids are available where oil content in the whole kernel is as much as 20%. About 90% of the oil is in the germ and the rest in the endosperm (1). At this oil content, it may be economically feasible to solvent-extract the oil directly from the whole kernel.

Conventional solvent extraction of low-oil containing oilseeds (e.g., soybeans) involves preparation of the seed to disrupt its internal structure and to shorten the distance that the miscella has to diffuse within a particle. This is accomplished by a sequence of conditioning, tempering and flaking. The cooking step coagulates the protein, causing coalescence of oil droplets and making the seed more permeable to diffusion extraction of oil (2).

Extruders have been introduced recently to enhance oil extraction from soybeans and cottonseed. New processes consist of conditioning, flaking, extrusion with steam injection and drying of the pellets before solvent extraction (3). Major advantages of extrusion are: (i) the density of the pellet is augmented, and extraction capacity and draining are enhanced; (ii) less solvent is used per weight of oilseed; and (iii) more complete cooking of the components is achieved (4).

The objective of the reported work was to evaluate extrusion as a pretreatment to enhance extractability of oil from high-oil corn hybrids and to precook the starch fraction in the meal. The study was divided into two parts: a set of bench-top experiments to identify important

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