Crystallization of Hydrogenated Sunflower-Cottonseed Oil

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Crystal structures formed during solidification of hydrogenated cottonseed oil, sunflowerseed oil and their blends were analyzed by using an X-ray diffraction technique, differential scanning calorimetry (DSC) and polarized light microscopy. Temperatures and times of crystallization under conditions which tend to produce β' type structures were determined in terms of refrigeration parameters. Microscopy with polarized light also helped clarify some aspects of the tridimensional network of crystals that contribute to the consistency of products made from hydrogenated oils.

The rheological characteristics (consistency, spreadability, etc.) of margarines, shortenings or spreads are related to a series of transformations which must be controlled by means of the formulation and processing of the product. Formulation allows control of the solid content which, for identical processing conditions, is directly related to the consistency (1) and type of crystalline structure formed (2,3). Conditions of processing (rate of cooling, mechanical work applied, final temperature of product, etc.) regulate both the type of crystal formed and the morphology and extent of intertwining of the solid structure which holds the liquid oil. Fats solidify in more than one crystalline type. It is generally accepted that triglycerides exhibit three main types, α, β' and β, with increasing degrees of stability and melting point. Intermediate types also have been described in cocoa butter (4). Under fast cooling conditions, such as those used in the manufacture of margarine, it is believed the α phase is the first one formed and that it is transformed rapidly into the β' type. This latter crystalline type is desirable because under certain conditions it tends to structure as a fine tridimensional network capable of immobilizing a large amount of liquid oil. Under conditions of high storage temperatures, or as a consequence of the use of inadequate formulations, quite large crystals can be formed. Such crystals do not tend to give a tridimensional structure; therefore, they introduce a coarse, sandy texture to the product. In severe cases this can lead to separation of the oil.

The formulation has a marked effect on the crystalline form attained by the margarine or shortening. Hydrogenated oils have been reported as having a β' or β tendency, according to the crystalline structure to which they lead. It is even accepted that the incorporation of a hydrogenated oil which has a β' tendency to a base with a β tendency can induce the crystallization of a blend of the β' type. Sunflowerseed, soybean, corn, olive, coconut and peanut oils show a β tendency, whereas cottonseed, palm, rapeseed, etc., have been reported to have a β' tendency (2,5). Substances such as diglycerides (3) and sorbitan tristearate (6), which contribute to the stabilization of the β' form, also have been reported.

The consistency of a margarine is determined mainly by a tridimensional structure of the fat crystals. These crystals have the shape of small needles or rods, their lengths varying from 0.1 μm to more than 20 μm. Generally, they show a great tendency toward aggregation due to mutual attractions attributed to Van der Waals-London forces (7,8). As a result of this flocculation, and depending on the resulting crystalline form obtained, highly branched and intertwining long chains are formed. These chains constitute a tridimensional network that holds the liquid. Primary and secondary bonds have been distinguished in this network (7). Secondary bonds are weak and break easily by applying mechanical work, but they are readily restored once the strain has been removed. On the other hand, primary bonds are strong and are not readily re-established once they have been broken. It is thought that they are the result of a strengthening of the tridimensional network at certain sites due to the crystallization of insoluble glycerides (8). Parallel to the tridimensional structure, loose crystalline aggregates can be located within the network together with drops of the margarine aqueous phase. It is estimated that fast cooling rates yield a product of higher stability and better spreadability.

In the present work we studied the polymorphism and crystalline habits by which hydrogenated sunflower and cottonseed oils and their blends crystallize, in order to obtain information which can contribute to the determination of the most suitable processing conditions and formulations for this type of product.

MATERIALS AND METHODS

Samples. Studies were performed on a commercial margarine containing 82% fat phase, formed from hydro-

TABLE 1

Fat Phase Formulation and Fatty Acid Composition

A. Fat Phase

Components	WMP (C)	(%)
Hydrogenated sunflowerseed oil (HSFO)	35.9	57
Hydrogenated cottonseed oil (HCSO)	44.7	23
Sunflowerseed oil (SFO)	–	20

B. Fatty acid composition

Fatty acids (%)	HSFO	HCSO	SFO	Fat Phase
14:0	0.08	0.70	0.07	0.21
16:0	6.92	23.86	6.70	10.26
18:0	11.21	16.30	3.80	10.40
18:1	71.59	58.90	30.54	60.54
18:2	9.19	–	57.80	17.93
20:0	0.34	–	–	0.11
22:0	0.58	0.19	0.79	0.51
others	0.09	0.05	0.30	0.04

WMP, Wiley melting point.

genated cottonseed and sunflowerseed oils and from liquid sunflowerseed oil. Runs were also made with the fat phase and the individual hydrogenated oils. Hydrogenated cottonseed oil [Wiley Melting Point (WMP) 44.7 C] and hydrogenated sunflowerseed oil (WMP 35.9 C) were used. Fatty acid compositions obtained by GLC (9) and other characteristic indices are shown in Table 1.

Microscopy. A Leitz microscope with a thermoregulated platform was used for the microscopic observation of crystalline morphology; determination of temperature; time of appearance of crystals, and observation of crystal growth. The temperature of the fluid used for regulation of the platform temperature (ethyleneglycol-water, 3:1) was controlled by means of a cryostat Lauda UK 30 at a constant temperature or according to a previously designed program. The sample, about 50 μm thick, was placed between two slides and its temperature determined continuously by means of a 0.05 mm i.d. copper-constantan thermocouple connected to a potentiometric recorder. When temperatures below room temperature were used, moisture condensation was avoided by means of a slight flow of dry air circulating over the slide. Observations were done under polarized light, and microphotographs of the fields were taken.

Melting point determinations. Melting points of hydrogenated cottonseed oil, hydrogenated sunflowerseed oil and their blends were determined by microscopy and the Wiley technique (10).

Differential Scanning Calorimetry (DSC). A Du Pont DSC 910 Differential Scanning Calorimeter was used. Calibration of temperature and cell constant were made using Indium as standard. Samples weighing between 12 and 20 mg were placed in hermetically sealed aluminum pans and run against air as reference. Heating rate was 10 C/min.

X-ray diffraction. X-ray diffraction spectra were obtained by means of a Phillips 1730 instrument fitted with a system for temperature control. The sample holder placed within the refraction chamber was maintained at a constant temperature with a 3:1 solution of ethyleneglycol coming from a Lauda UK 30 cryostat. Radiations K $\alpha 1$ $\alpha 2$ from copper with 40 KV, 20 mA and a scanning velocity of 1°/min were used.

Cooling conditions. Cooling conditions were carefully controlled whether the crystallizations were carried out on the microscope platform or not. In order to simulate the thermal history of a margarine in a scraped surface exchanger, where the temperature decreases in an approximately exponential way, samples were cooled according to an equation of the type:

$$T=T_f+(T_i-T_f)\,e^{-Kt} \qquad (1)$$

Where T_f is the temperature of the fluid used to refrigerate the sample, T_i the initial temperature of the sample and K a constant which represents the ease of heat transfer from the sample to the refigerating fluid. Cooling experiments were started in all cases from $T_i=54$ C, with the fat completely melted; then, according to Eqn. (1), the thermal histories of the samples were completely characterized in terms of K and T_f. Values of K were obtained from the cooling recordings by plotting 1n $(T-T_f)/(T_i-T_f)$ against t and calculating the slope of the straight line obtained.

RESULTS AND DISCUSSION

Polymorphism, hydrogenated sunflowerseed oil (HSFO). Figure 1 shows the X-ray diffraction spectra of hydrogenated sunflowerseed oil crystallized either slowly ($K=3\times10^{-4}$ sec^{-1}; $T_f=20$ C) or quickly ($K=2\times10^{-2}$ sec^{-1}; $T_f=-25$ C). In the upper spectrum (slow crystallization) peaks of d=3.66, 3.88 and 4.56, characteristic of

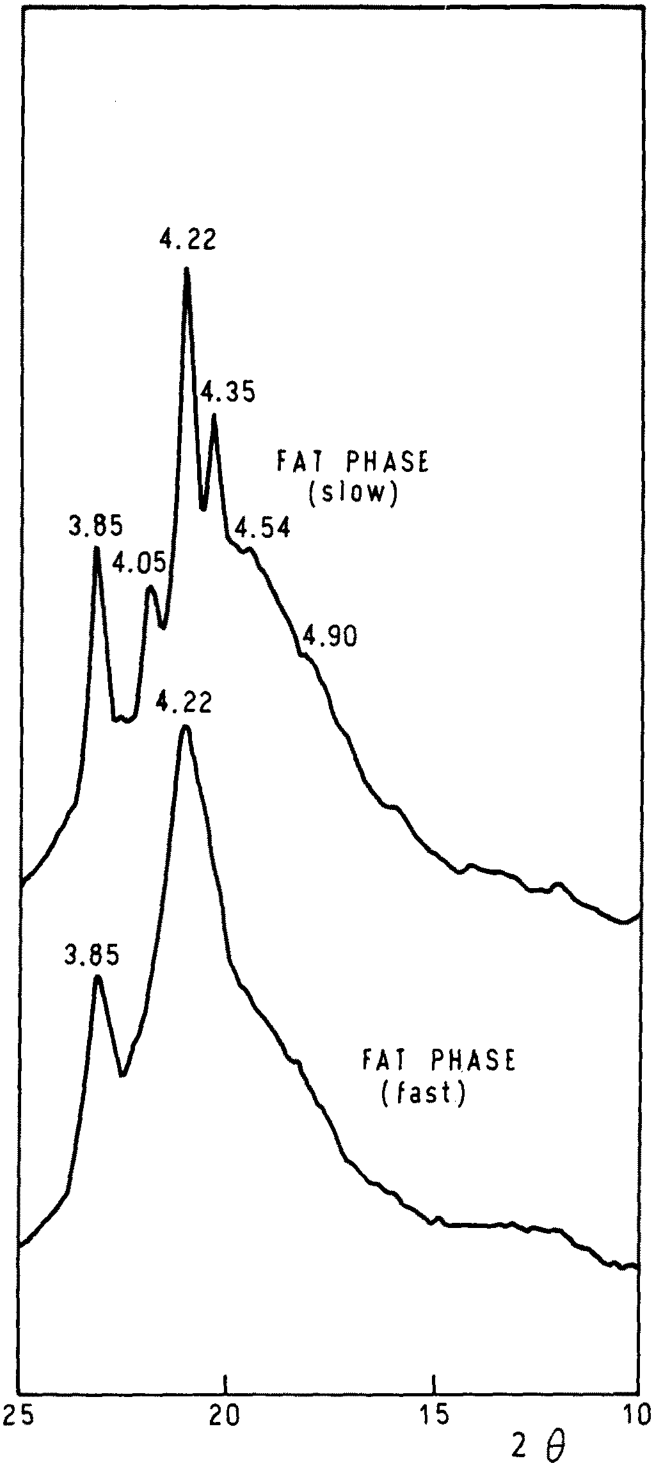

FIG. 1. X-ray diffraction spectra of hydrogenated sunflowerseed oil crystallized either slowly ($K=3\times10^{-4}$ sec^{-1}; $T_f=20$ C) or quickly ($K=2\times10^{-2}$ sec^{-1}; $T_f=-25$ C).

the β type can be seen. By contrast, the lower spectrum shows peaks of d=3.88 and 4.25, typical of the β' type (4,11). This shows that as the rate of cooling increases, the tendency to crystallize in the β' form also increases. The differential scanning calorimetry of both samples, which were started at -10 C, also detects differences between the samples (Fig. 2). Thermograms show two melting peaks, one at low temperature (with a maximum at 4-6 C) and another at 25 C for the rapidly cooled sample and at 32 C for the slowly crystallized one. This result is in agreement with the higher melting point attributed to the more stable β form.

In order to determine the cause of the peak of low temperature melt (4-6 C) which appears in the DSC thermograms, a sample of hydrogenated sunflowerseed oil that melted at 54 C was cooled to 17 C and filtered. All the solids which crystallize above that temperature were thus separated. The filtrate, which included the compounds which gave rise to the peak melting at 4-6 C, was crystallized either slowly or quickly at -25 C and 12 C, respectively. X-ray diffraction spectra were

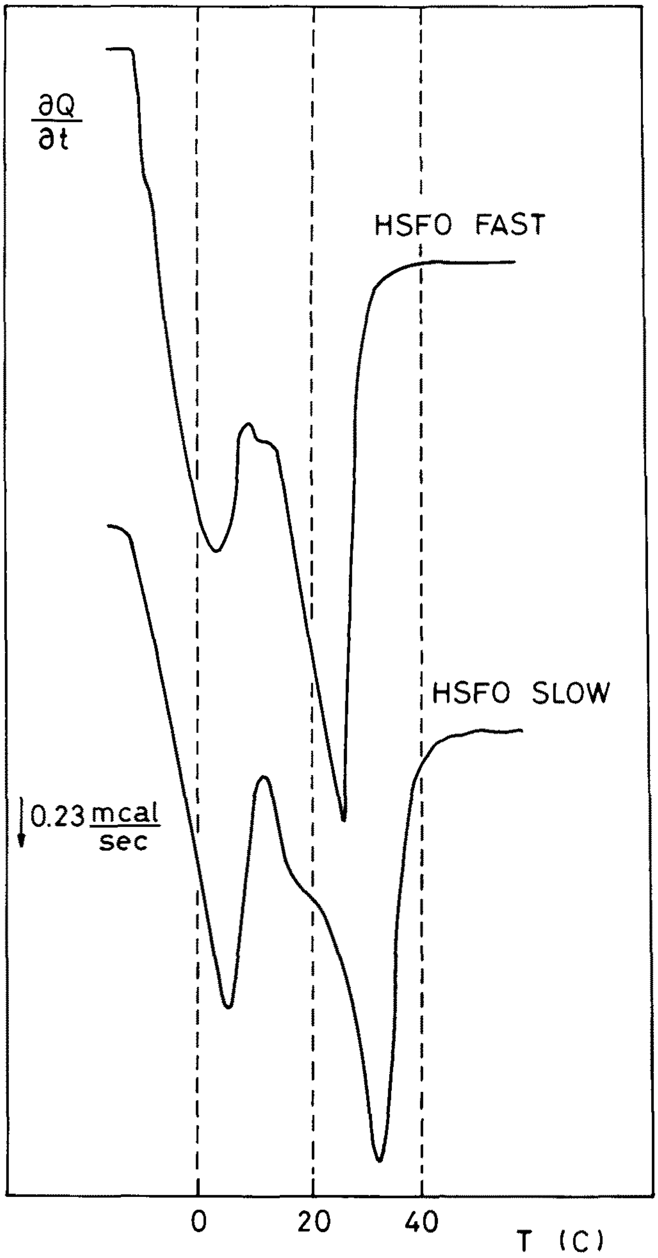

FIG. 2. DSC thermograms of hydrogenated sunflowerseed oil crystallized either slowly ($K=3\times10^{-4}$ sec^{-1}; $T_f=20$ C) or quickly ($K=2\times10^{-2}$ sec^{-1}; $T_f=25$ C).

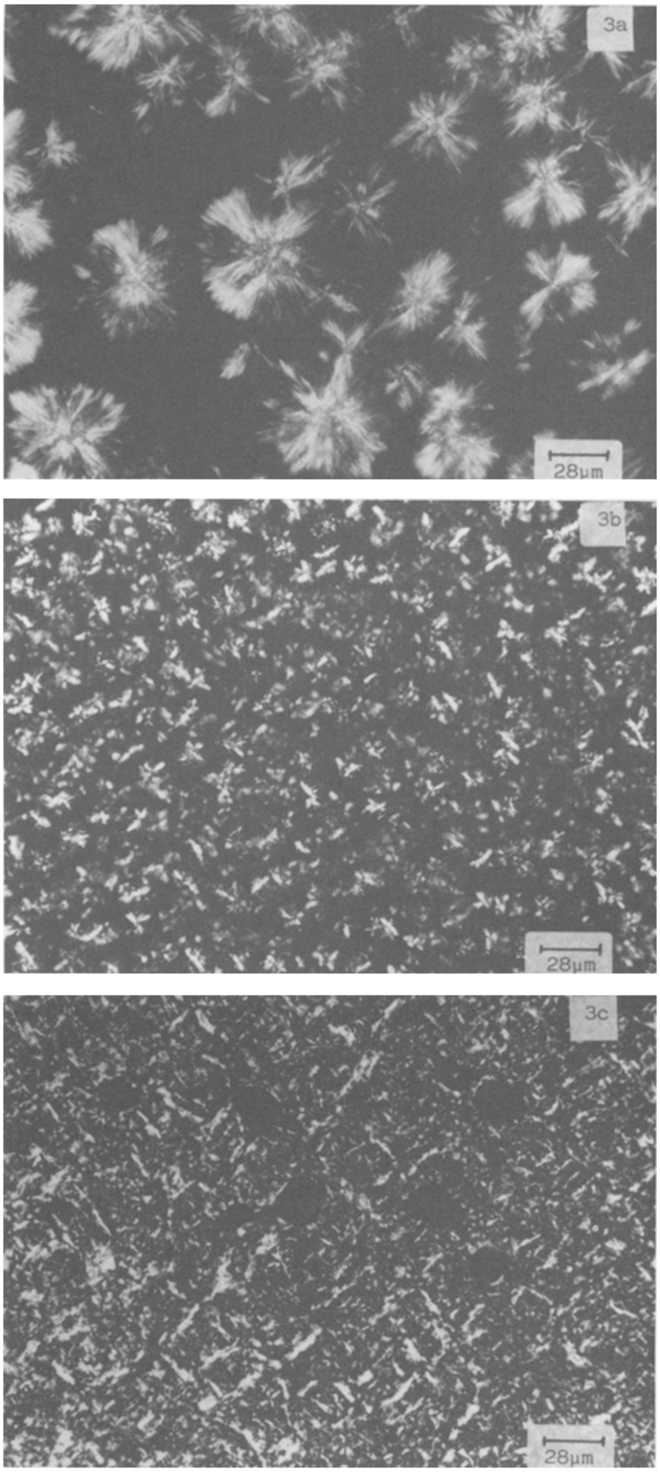

FIG. 3. Micrograph of crystalline forms of hydrogenated sunflowerseed oil crystallized either A, slowly ($K=3\times10^{-4}$ sec^{-1}; $T_f=20$ C), or B, quickly ($K=1.2\times10^{-2}$ sec^{-1}; $T_f=$C), primary structures.

obtained from both samples at 0 C. A spectrum corresponding to the β′ form was obtained in both cases, thus evidencing that the peak of DSC at low temperatures corresponds to a solid solution of crystalline structure similar to that corresponding to the high temperature peak. The formation of two solid solutions with different melting ranges is then evidenced. The solution corresponding to low temperature melting crystallizes in β′ form regardless of the cooling rate, whereas that of high temperature melting crystallizes as either β′ or (β+β′) mixes, according to a high or low rate of cooling, respectively.

Figures 3a and 3b show the crystalline morphologies obtained with slow or fast crystallization of hydrogenated sunflowerseed oil by polarized light microscopy. Regardless of the differences in crystal size produced by different cooling rates, formation of type A spherulites (12) is observed in the sample corresponding to slow cooling (Fig. 3a). These crystalline morphologies are characterized by long needles which leave from a central point and which can attain sizes of 20-30 μm. This morphology has been associated with the β crystalline form (12,13). Conversely, the rapidly cooled sample (Fig. 3b) shows clusters of small, thin needles 1 to 10 μm long. The high retention capacity of oil by margarines has been attributed to interactions among these needles (1). These β′ type crystals have many aggregates of lobular or elongated particles, and growth takes place from them forming type B spherulites, constituted by randomly oriented crystalline aggregates (12). Once in contact with each other, type B spherulites tend to form a network structure reinforced by the presence of perimetrically arranged crystals (Fig. 3c). It is very likely that these crystals play an important role with regard to the consistency of this type of product (i.e., having primary bonds).

Polymorphism, hydrogenated cottonseed oil (HCSO). Regardless of the cooling rate, the β′ X-ray diffraction spectrum was always obtained, in agreement with the well known β′ tendency of hydrogenated cottonseed oil. DSC does not show any differences with the different cooling rates, and peaks near 4 C and 35 C corresponded to melting of the respective β′ structure solid solutions. As far as morphology is concerned, cottonseed oil solidifies as small, numerous crystalline clusters, which then grow and branch with no preferential direction, forming B type spherulites.

Polymorphism, sunflower/cotton blends. In all cases the DSC thermograms exhibited peaks caused by melting of low temperature (peak 4-6 C) and high temperature (peak between 25.5 and 35 C) solid solutions. The latter was dependent on the hyrogenated cottonseed oil content of the sample. This behavior of the fatty phase, with formation of solid solutions with two melting ranges, is consistent with that seen in the original hydrogenated phases. The proportion of both solutions also depends on the cooling rate, i.e., the higher the cooling rate, the higher the proportion which crystallizes at low temperature.

The results of X-ray diffraction under conditions of slow and quick cooling of the fatty phase of a margarine are shown in Figure 4. It can be seen that in the quick crystallization, the β′ form, characterized by peaks d=4.22 and 3.85, has been obtained. On the other hand, in the slow crystallization there is a very small amount of crystals of the β form (peaks at d=4.54 and 3.85) besides those of the β′ form, together with two peaks at d=4.35 and 4.05, which have not been characterized. This behavior also occurs in hydrogenated oil blends (20% and 40% hydrogenated cottonseed oil); the β′ form is obtained at quick cooling rates, and the β′

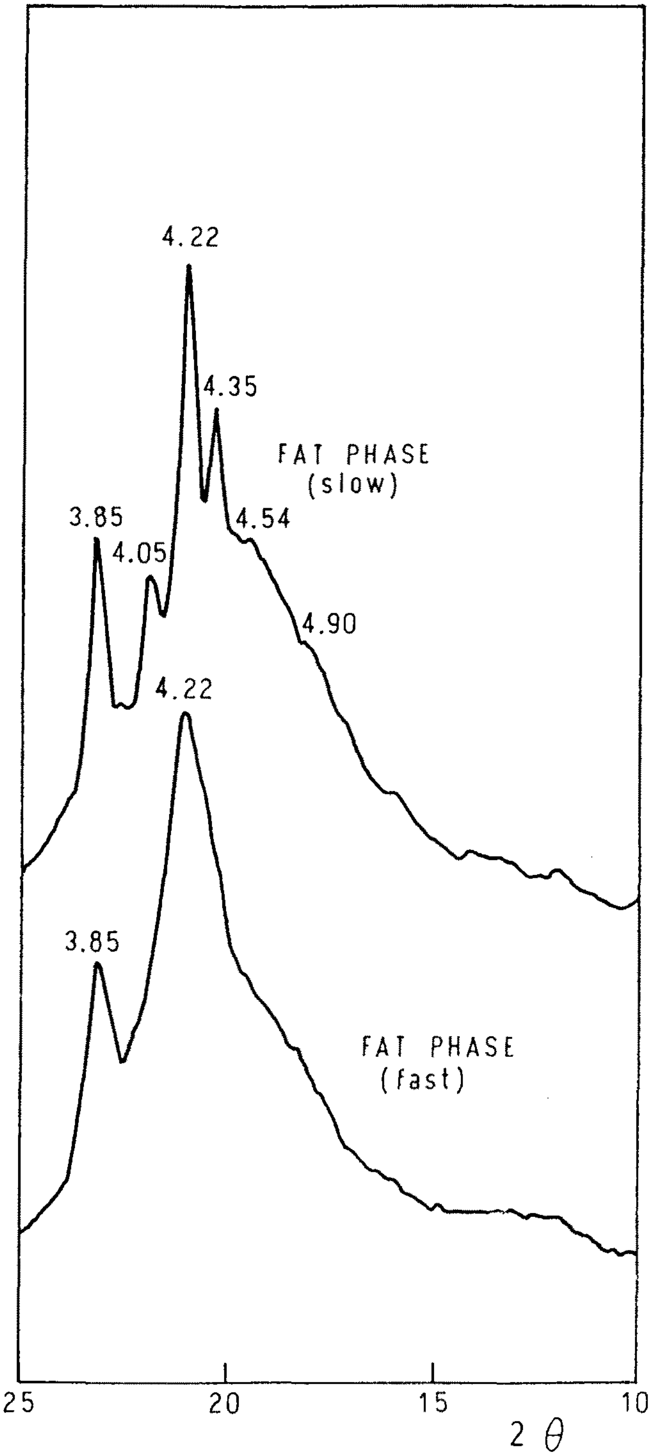

FIG. 4. X-ray diffraction spectra of fatty phase of margarine crystallized either slowly ($K=3\times10^{-4}$ sec^{-1}; $T_f=20$ C) or quickly ($K=2\times10^{-2}$ sec^{-1}; $T_f=-25$ C).

form together, with peaks at 4.35 and 4.05 at slow cooling rates.

In order to confirm the presence of the latter peaks, in some cases attributed to the β' form (4,14), samples of the quickly-crystallized and slowly-crystallized fatty phase were heated to 0, 10 and 27 C, and X-ray studies were performed at each temperature on the remaining solids. As the temperature increased, the β' peaks disappeared, but peaks at 4.05 and 4.35 remained, as did those of β form. Even in the rapidly cooled samples, in which only β' crystals could be seen at 5 C, small quantities of β' were observed at higher temperatures together with the peaks at 4.06 and 4.35. These results lead to the conclusion that even at quick cooling rates, small quantities of the β form are formed besides the solid solutions of low and high melting temperatures and that small crystals with high melting temperatures, which have diffraction peaks of 4.06 and 4.35, are segregated.

This effect of segregation of crystals of high melting point gives rise to discrepancies between the melting points obtained by microscopy and by the Wiley technique. Figure 5 shows the Wiley melting points of the different blends and those of the pure components. A continuous variation of the melting points of the blends can be observed upon changing the composition of the component oils. This is in agreement with the known capacity of triglycerides to form solid solutions (2).

However, melting points determined by microscopic observation of the disappearance of solids under slow heating were different for those obtained using the Wiley method. These melting points are also shown in Figure 5. At low contents of hydrogenated cottonseed oil (low melting point) the microscopic technique shows a trend toward a constant melting temperature around 40 C.

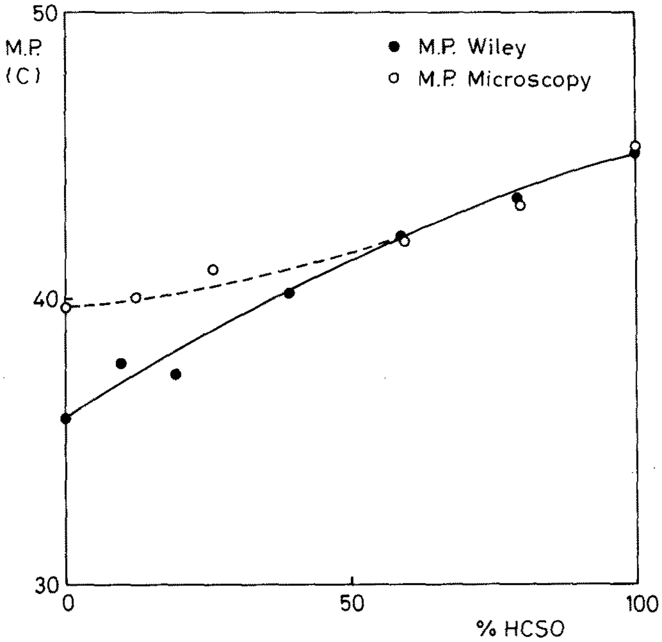

FIG. 5. Melting points of different blends and pure hydrogenated cottonseed oil and hydrogenated sunflowerseed oil obtained by microscopy and the Wiley technique.

In order to investigate this effect, the slowly-crystallized fat phase (28.7% hydrogenated cottonseed oil) was observed by polarized light microscopy ($K=9.9\times10^{-4}$ sec^{-1}; $T_f=17.5$ C). Figure 6 shows melting of the type B spherulites at different temperatures. Spherulites present at 22 C exhibit a partial melting of their central parts at 27 C, but the peripheral crystals are not yet melted; they are only slightly melted at 39 C. These

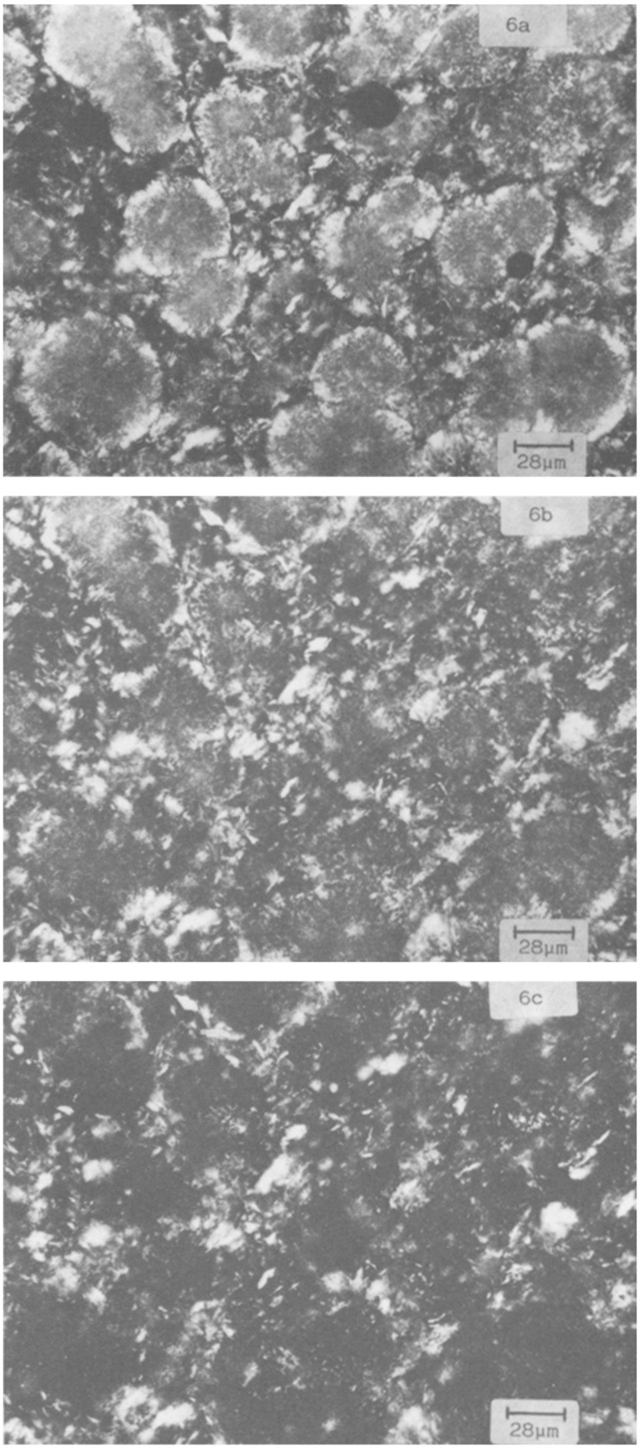

FIG. 6. Sequence of melting of the fat phase slowly crystallized ($K=9.9\times10^{-4}$ sec^{-1}; $T_f=17.5$ C) observed by polarized light microscopy: A, 22 C; B, 27 C; C, 39 C.

results suggest a segregation of two types of crystals. One is a β' solid solution which is completely melted at 37 C, leading to an important decrease of the solid phase that the Wiley technique considers as the final melting point. Crystals of higher melting point, which are located perimetrically to the B spherulites, melt at about 40 C. This segregation phenomenon, which is favored by slow cooling, does not manifest itself so clearly in quickly cooled samples, although it may occur.

Differential scanning calorimetry of the fat phase cooled either slowly ($K=3.0\times10^{-4}$ sec^{-1}; $T_f=20$ C) or quickly ($K=2.9\times10^{-2}$ sec^{-1}; $T_f=-25$ C) (Fig. 7) also show this behavior (notice should be taken of the numerous melting peaks of the slowly cooled fat phase showing the segregation of crystals of different melting points). Small crystals can be observed when the sequence of crystallization of the fat phase at slow cooling rate ($K=0.9\times10^{-3}$ sec^{-1}; $T_f=17.5$ C) is analyzed. These crystals arrange themselves as clusters during the cooling process ending up as type B spherulites. When cooling is fast ($K=1.2\times10^{-2}$ sec^{-1}; $T_f=12$ C) small crystalline clusters form rapidly; they are scarcely branched and exhibit a close, compact arrangement.

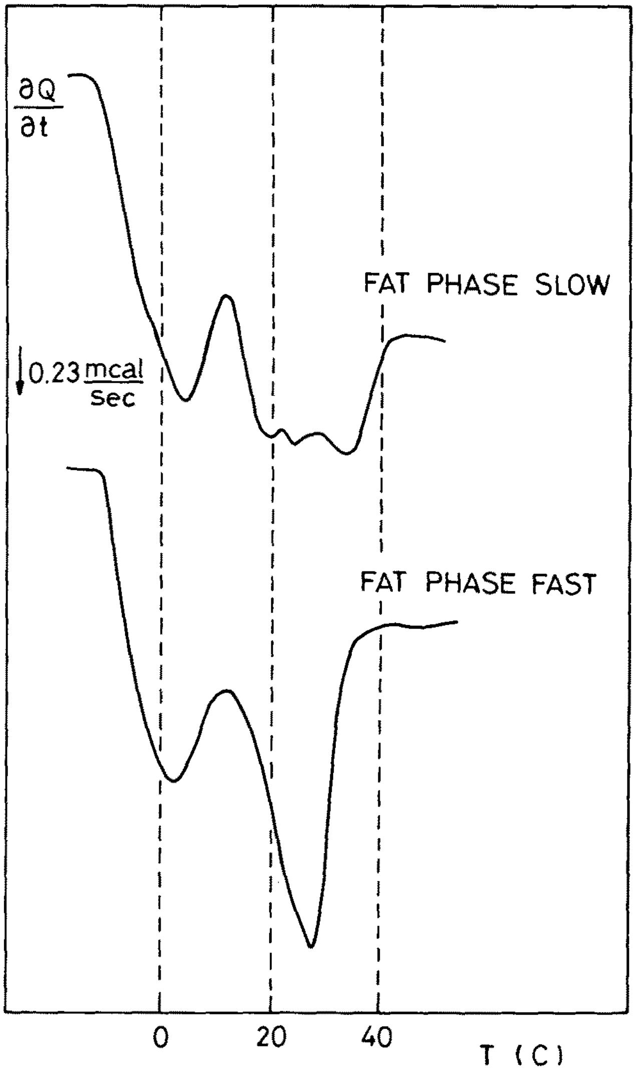

FIG. 7. DSC thermogram of fat phase cooled either slowly ($K=3.0\times10^{-4}$ sec^{-1}; $T_f=20$ C) or quickly ($K=2\times10^{-2}$ sec^{-1}; $T_f=-25$ C).

TEMPERATURE AND TIME CRYSTALLIZATION

Effect of cooling rate. Cooling rates can be changed by means of T_f and/or K. However, in an exponential cooling curve of the types represented by Eqn. (1) the cooling rate is not constant and decreases continuously until it becomes asymptotically nil. Once the exponential way of cooling has been adopted, the magnitude of supercooling reached and the length of time that the sample remains supercooled are more important than the cooling rate from the point of view of the nucleation phenomenon. Thus, in slowly cooled samples, which are kept supercooled for along time, nucleation will take place at higher temperatures than in those quickly cooled. This effect can be seen in Figure 8 for hydrogenated cottonseed oil of melting point (equilibrium temperature) $T_e=44.7$ C. The degree of supercooling needed for the appearance of crystals $\Delta T=(T_e-T_n)$ is lower the longer the time t_s that the sample has been kept supercooled. Both the increase of T_f and the decrease of K, which result in lower cooling rates, should lead to a higher temperature for the appearance of crystals. Both effects can be seen in Figure 9, which shows the temperature of appearance of crystals for hydrogenated cottonseed and sunflowerseed oils as a function of T_f for different K values. As can be seen, nucleation requires both time and supercooling; therefore, with high cooling rates, the shorter time should be compensated for because crystallization is taking place at a lower temperature.

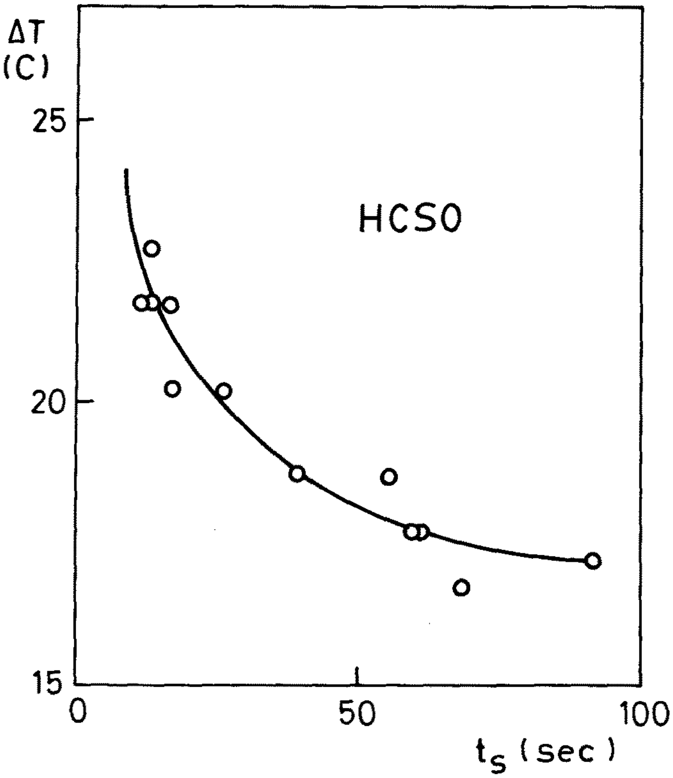

FIG. 8. Degree of supercooling, ΔT, for different supercooling times, t_s.

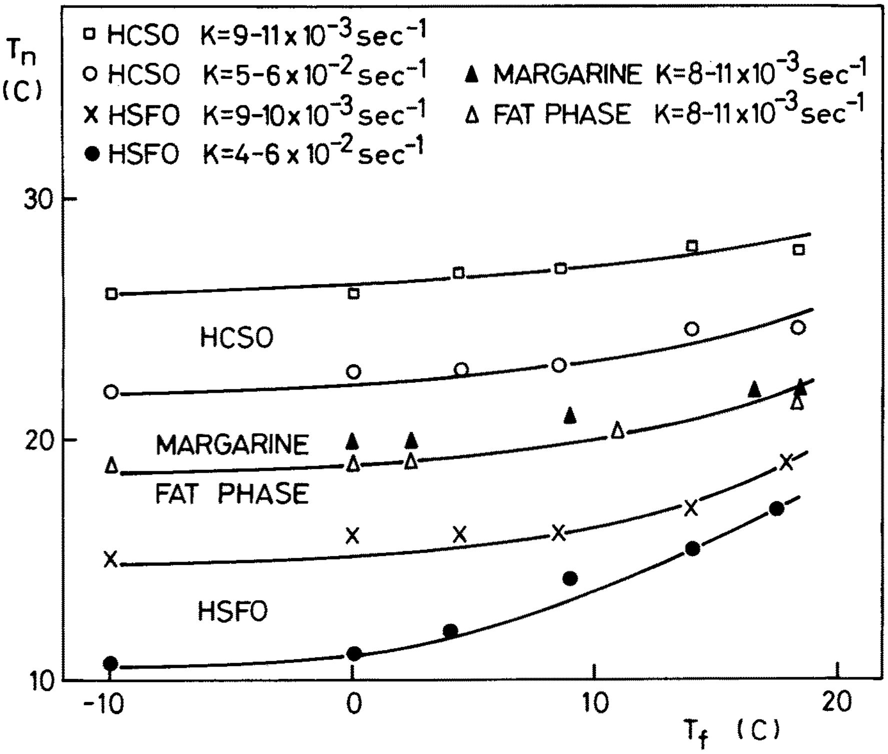

FIG. 9. Crystal formation temperature, T_n, for different coolant temperatures, T_f, maintaining K as a parameter.

The asymptotic tendency of the temperature of formation of crystals T_n for low temperatures of the refrigerating fluid T_f can also be observed in Figure 9. For $K=4\text{-}6\times10^{-2}$ sec^{-1} and $T_f \leqslant 0$ C, the supercooling necessary for the appearance of crystals is ΔT (HCSO)=22.7 C and ΔT (HSFO)=25.3 C, which allows that hydrogenated cottonseed oil crystallizes more easily. The times needed for the appearance of crystals can readily be calculated from the values of T_n, K and T_f of Figure 9 and Eqn. (1) written as follows:

$$t_n = \frac{1}{K} \ln \frac{T_i - T_f}{T_n - T_f} \qquad (2)$$

Effect of the composition. Figure 9 also allows the comparison of the temperatures at which crystals appear in hydrogenated cottonseed and sunflowerseed oils. For all the T_f and K values included in the figure, cooling rates are fast enough to lead to the β' form in all the cases. Cottonseed oil crystallizes at a higher temperature than sunflowerseed oil. This effect is sought in the formulation by means of hydrogenation of cottonseed oil to values higher than the Wiley melting point. It is claimed that this induces the crystallization of the rest of the fats in the β' form. Probably, the effect arises because with a higher melting point of the blend, a greater degree of supercooling is reached, and therefore, a faster crystallization of the solid solution in the β' form. The lower degree of supercooling needed by hydrogenated cottonseed oil to crystallize also contributes to the effect.

Temperatures of crystallization of the fat phase and the corresponding margarine also can be seen in Figure 9. The agreement between the fat phase and margarine shows that the disperse aqueous phase does not affect the conditions at which the crystals appear. Similar conclusions can be drawn for the temperatures at which crystals appear in the blends of HCSO/HSFO. It can be seen that lower degrees of supercooling are needed when the percentage of hydrogenated cottonseed oil increases because of its greater ease of crystallization.

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