Differential Scanning Calorimetry of Palm Kernel Oil Products [1]

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ABSTRACT

A variety of fractionated and hydrogenated fats were derived from a commercial sample of Malayan palm kernel oil. These were studied by differential scanning calorimetry at different rates of cooling and heating. The resulting thermograms, and latent heats derived from them, were compared with one another and with underlying triglyceride compositions. This enabled three potential interpretations of the thermograms to be compared. The shapes of the cooling thermograms were most complicated, and dependent on the influence of the spontaneous crystallization, which followed supercooling when cooling rates of 8 C per min or more were imposed. Triglyceride composition had a less significant influence on the shapes of the curves, while polymorphism had almost no influence. The cooling thermograms, thus, are more complicated than heating thermograms, a conclusion at variance with one expressed elsewhere. The dynamic nature of the differential scanning calorimetry method is highlighted by the results of this work, and it is concluded that there are dangers in conducting differential scanning calorimetry studies at a single rate of temperature change.

INTRODUCTION

Palm kernel oil is an important item in world trade, and the oil and its processed fat derivatives are used in a wide variety of foodstuffs. Its properties include a capability for rapid crystallization from the melt together with a useful melting profile. The natural oil is reasonably firm at ambient temperatures, and yet it melts quickly and cleanly at body temperature. The physical properties of palm kernel oil can be modified by industrial techniques such as hydrogenation, fractionation, and interesterification to give a wide variety of fats tailor made for specific applications in the food industry, such as the formulation of biscuit filling creams or substitute chocolate. The influence of these techniques on the corresponding differential scanning calorimetry (DSC) thermograms was studied to provide information for the evaluation of raw materials and finished products. Palm kernel oil, therefore, was hydrogenated in the laboratory to provide a series of samples with iodine values (IV) ranging from 0 to 18, while in a second set of experiments, palm kernel oil was solvent fractionated to provide stearines with similar IVs. One of these stearine samples was also hydrogenated. DSC thermograms of these samples were measured, and comparisons made between them, and with the underlying molecular compositions.

A surprising feature of this work was that while melting curves are simple and easily understood, the shapes of the cooling curves are variable and highly dependent on the speed of cooling.

Two possible explanations of these varying peak shapes are considered, namely crystallization of separate glyceride groups and polymorphic transformations. These potential explanations are discounted, however, and a third is developed in which the observed effects are attributed to rapid crystallization of supercooled oil. These deductions were substantiated by measurements of latent heats at several rates of cooling, and by the influence on the curves of interesterification.

Lauric oils have been studied (1-4) by differential thermal analysis (DTA) and DSC, but the very dependent nature of the crystallization thermograms on the rate of cooling has not been reported so far. On the other hand, Haighton and Vermaas (5) did suggest that some cooling curves may be unreliable due to supercooling effects.

The conclusions reached here contrast with those of Berger and Akehurst (6) who claimed that cooling curves are simpler and easier to interpret than heating curves. The difference between these two conclusions is due probably to the fact that Berger and Akehurst confined their attention to non-lauric oils, which do not display the rapid crystallization found in this work.

EXPERIMENTAL PROCEDURES

Fully refined and deodorized Malayan palm kernel (PK) oil, the properties and analytical composition of which are shown in the Tables I, II, and III, was used. Hydrogenations were conducted in a Parr 4501 autoclave (Parr Instrument Company, Moline, IL) in the presence of 1% of a supported active nickel catalyst containing 18% nickel. The hydrogenations were conducted at a temperature of 180 C and at a hydrogen pressure of 20 psi. Oil was removed during the

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TABLE I

Fatty Acid Analyses

Fatty Acid	Malayan palm kernel oil (% by wt)	Bezard's palm kernel oil (% by wt)	Palm kernel stearine (IV = 8.3)[a] (% by wt)	Palm kernel stearine (IV = 1.8)[a] (% by wt)
C6 saturated	0.2	0.2	0.1	trace
C8 saturated	3.6	4.1	2.2	1.0
C10 saturated	3.4	3.9	2.8	2.2
C12 saturated	47.4	48.6	55.2	49.6
C14 saturated	15.6	16.5	22.4	30.4
C16 saturated	8.9	7.5	8.1	11.5
C16 mono unsaturated	-	-	-	-
C18 saturated	2.1	2.4	1.5	2.8
C18 mono unsaturated	16.7	13.4	7.4	2.4
C18 di unsaturated	2.0	2.0	0.6	
C18 tri unsaturated	-	0.3		
C20 saturated	-	0.3		

[a]N = Iodine value.

TABLE II

Physical Properties of Palm Kernel Fats

	Malayan palm kernel oil	Fully hydrogenated palm kernel oil	Interesterified palm kernel oil	Unhydrogenated palm kernel stearine	Partly hydrogenated palm kernel stearine	Fully hydrogenated palm kernel stearine
Iodine value	18.5	0.4	18.5	8.3	4.4	0.4
Slip mp	27.0 C	42.8 C	26.2 C	32.0 C	32.1 C	34.7 C
SCI[a]						
20 C	38.2	71.6	27.2	68.2	74.9	77.5
25 C	17.6	-	9.7	60.3	67.8	75.2
30 C	12.0	38.2	1.4	33.2	33.2	46.2
35 C	8.0	18.8	1.0	1.2	1.2	7.0
40 C	4.0	11.2	0.2	-	-	1.4

[a]*SCI* = Solid content index by dilatometry (mm^3 per g).

course of the hydrogenation to give a series of samples of intermediate IVs. The oil was also solvent fractionated at suitable temperatures between -2 and +20 C, depending on the IV of the stearine required from dry acetone at a solvent to oil ratio of 5:1 by wt. The crystals were filtered off and washed 3 times, each with a volume of acetone comprising 10% of the oil in acetone solution and at the fractionation temperature.

Interesterification was carried out by heating the neutral dry oil with 0.4% sodium methoxide catalyst at 100 C for 15 min in an evacuated flask. Nitrogen was purged through the oil to remove volatile methyl esters. After the reaction, the oil was washed, dried, and filtered. Triglyceride carbon number analyses were measured by gas liquid chromatography (GLC) on a 60 cm column of 3% OVl supported on silica, at temperatures programmed from 250 to 350 C. The results were used to confirm that the interesterification reaction was complete (Table III).

DSC thermograms were measured on 7-9 mg fat samples with a Perkin-Elmer DSC-1B instrument. This was calibrated regularly against standards of pure indium and diphenylamine. The normal method of operation was to heat each sample to 80 C and hold it at this temperature for 10 min to destroy any persistent crystal nuclei. The sample then was cooled at 8 C per min using liquid nitrogen as refrigerant to obtain the cooling or crystallization thermogram. After crystallization was complete, each sample was held at -20 C for 10 min and then heated at 8 C per min to provide a heating or melting thermogram. The DSC thermograms resulting from these runs are presented in Figures 1 to 6. In these illustrations, the thermograms have been plotted in a manner corresponding to that often used for DTA curves so that correlation with related work (5,6) could be made more easily. In a few cases, different rates of cooling were used. This is illustrated in Figure 6.

Latent heats were determined by measuring the area under the peak by planimetry, and comparing the area per unit sample wt with the corresponding value for pure indium, which has a latent heat of fusion of 6.79 calories/g.

Peak shapes were reproducible on repeat runs with the same sample. Repeat samples of the same oil or fat gave minor variations, e.g., fully hydrogenated oil of IV = 0.5 in Figures 1 and 2. Temperatures were reproduced to within ± 0.5 C and latent heats to ± 3%. Samples taken from different batches of PK oil of nominally the same IV gave larger variations, as illustrated in the thermograms for unhydrogenated PK oils in Figures 1 and 2, or in Figure 4 (curve IV = 4.4) and Figure 6 (curve 8 C per min) where duplicate stearines were evaluated.

RESULTS AND DISCUSSION

Crystallization or cooling thermograms of hydrogenated palm kernel oil are shown in Figure 1. During hydrogenation of the oil, low melting point glycerides based on oleic acid are converted into higher melting point stearic acid counterparts, whereas, low melting point glycerides based on short chain acids are left unchanged. The appearance of a new peak at 25 C with the fully hydrogenated oil, therefore, is due to the formation of such stearic rich glycerides. The area under this peak is ca. 13% of the total area, a value which compares very closely with the known proportion of glycerides of carbon number 48, i.e., 12.18.18, and over, shown in Table III. The low mol wt glycerides do not form a separate peak, but their continued presence in the fully hydrogenated oil accounts for some low temperature tailing of the peak.

PK oil has been analyzed in considerable detail by Bezard (7), and recalculated results based on this information are presented in Tables I and III. As the fatty acid and triglyceride carbon number analyses of this oil were similar to those obtained in our study, we drew on his detailed

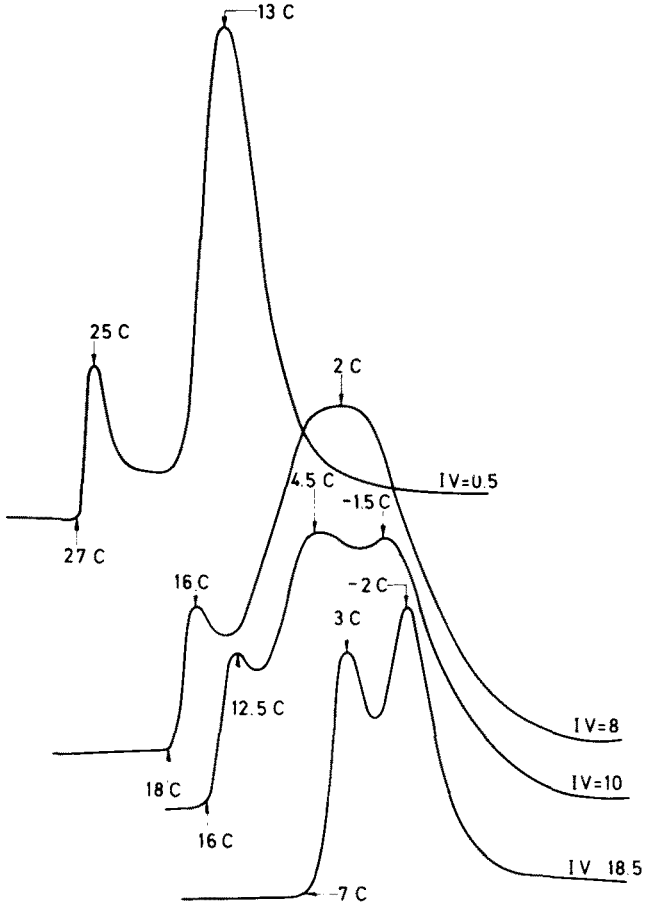

FIG. 1. Crystallization curves of palm kernel (PK) oil hydrogenated to various iodine values temperature scan rate 8 C per min.

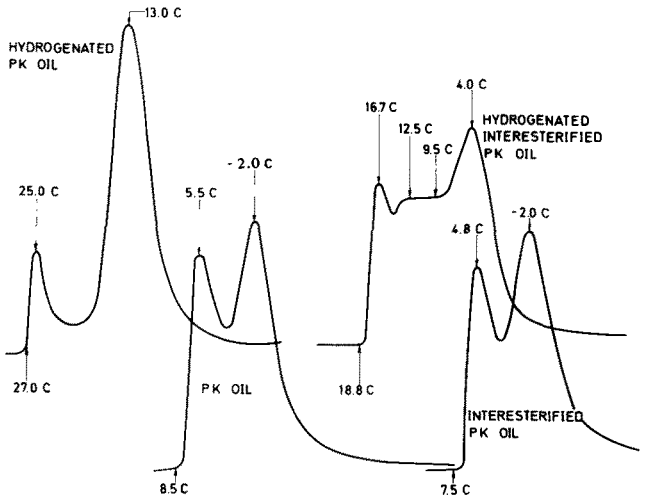

FIG. 2. Crystallization curves of palm kernel (PK) oil and hydrogenated oil (iodine value [IV] = 0.5) before and after interesterification, temperature scan rate 8 C per min.

results for the interpretation of our DSC thermograms. There is no clear division of glycerides which could give rise to the double peak of the unhydrogenated oil, the unsaturated group alone being insufficient for this purpose. In addition, it was noted that the melting thermograms of unhydrogenated and intermediate samples all showed single peaks. These observations caused us to question our initial view that the double crystallization peak of unhydrogenated oil is caused by the solidification of two discrete glyceride groups, although we remained confident that the high

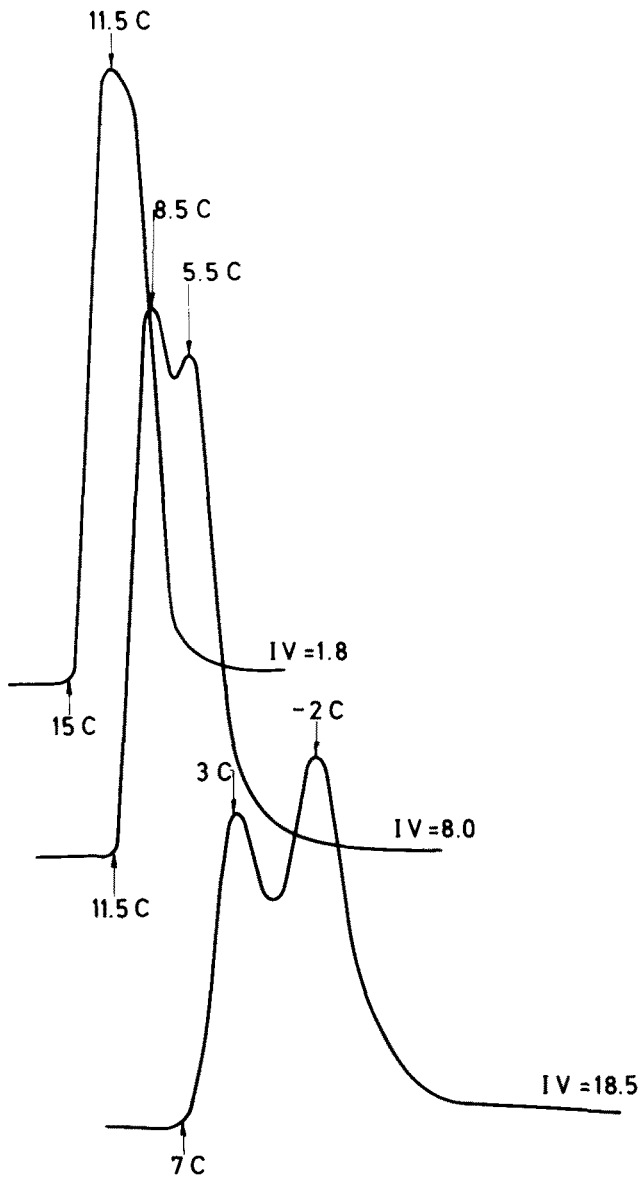

FIG. 3. Crystallization curves of solvent fractionated palm kernel stearines, temperature scan rate 8 C per min.

melting peak of the fully hardened oil is caused by such a group.

This doubt was strengthened by experiments in which a separate sample of PK oil was interesterified. The cooling thermogram of the unhardened oil (Fig. 2) remains a doublet and does not change in character, although peak temperatures do change slightly as a result of randomization.

The thermograms of the fully hydrogenated oils show more varied behavior, partly as a result of the changed level of high mp, stearic acid rich, glycerides (Table III). The final return to the base line is at a lower temperature with the interesterified and hydrogenated oil, in spite of the reduced amount of short chain glycerides of low mp, and eutectic interactions probably are involved.

In Figure 3, the crystallization thermograms of two solvent fractionated PK stearines are shown in comparison with that of the starting oil. Fractionation removes low mp glycerides based on both unsaturated and short chain acids, as illustrated by the triglyceride carbon number analyses in Table III. Therefore, these thermograms provided a contrast with the ones obtained during hydrogenation. There is, of course, no appearance of a new high temperature peak because there is no conversion of oleic acid to stearic acid.

The two peak shape of the starting oil changes to single

TABLE III

Triglyceride Carbon Number Analyses

Triglyceride carbon no.	Malayan palm kernel oil (% by wt)	Interesterified palm kernel oil (% by wt)	Bezard's[a] palm kernel oil (% by wt)	Palm kernel stearine (IV = 8)[b] (% by wt)	Calculated composition of randomized palm kernel oil (% by wt)
30	--	--	1.1	--	0.06
32	6.6	5.2[c]	7.4	3.2	1.1
34	8.6	5.9	8.8	6.0	6.7
36	21.1	16.4	24.2	24.4	16.8
38	16.2	16.2	16.5	24.7	14.7
40	9.6	12.7	9.7	15.7	14.9
42	9.2	18.6	8.3	9.9	19.3
44	6.8	10.4	6.4	5.6	10.5
46	5.5	5.8	4.6	3.6	6.7
48	6.5	5.7	5.2	3.2	6.2
50	3.0	1.8	2.7	1.6	1.8
52	3.2	0.8	2.8	1.3	0.8
54	3.6	0.6	2.4	0.9	0.5
56	--	--	--	0.3	--
48 and over	14.6	8.0	13.1	6.4	

[a]Recalculated from Reference 7.

[b]IV = Iodine value.

[c]This peak may contain some diglyceride.

peak behavior only with stearines of IV < ca. 8. It is tempting to attribute this to removal of low mp glycerides, but more detailed examination does not support this. At an IV of 8, the level of unsaturation is reduced by about half. The level of short chain glycerides has also been reduced considerably as shown by the carbon number analyses in Table III. Nevertheless, the area under the lower temperature peak with stearines of IV 8 or more is still quite considerable, showing no progressive change in line with the known change in composition. In addition, all the heating thermograms of these samples were single peak in shape. Hydrogenation of a stearine with an IV of 8.3 also supported this conclusion, as shown in Figure 4, the stearine hydrogenated to an IV of 4.4 being still double peak in character. The double peak nature of the crystallization thermogram is converted into a single peak at IVs below 4, but this cannot be attributed directly to a compositional change as the reduction in IV is so small. This view is substantiated by the shapes of the heating curves shown in Figure 5. The possibility that polymorphic transformations lead to these various peak profiles caused us to study a partly hydrogenated stearine of IV = 4.4 by recording the cyrstallization thermograms shown in Figure 6 at different rates of cooling.

At slow rates of cooling, i.e., 2 C per minute or less, a singlet peak is obtained. A singlet peak is also obtained at the highest rates of cooling, i.e., 32 C per min or more. At the intermediate, and incidentally most convenient and widely used rate of cooling of 8 C per min, however, a twin peak is obtained. This behavior cannot be due to crystallization of separate glyceride groups, although it could be due to polymorphic transformations, forms of lower stability being produced at the highest rates of cooling. However, this explanation was also shown to be untenable. It is known that palm kernel fats do not form a beta modification, being instead stable in the beta prime form (1,3,4). The two forms which come into consideration are therefore the alpha and beta prime modifications. Cooling at the fastest rates, 32 or 64 C per min, gives a singlet peak, and if this is due to crystallization of a large proportion of a single polymorphic form of lower stability, then this will be the alpha form. In contrast, the singlet peak obtained when cooling at the slowest scan rates could be attributed to a preponderance of the beta prime modification.

The inadmissibility of a polymorphic explanation is shown by the general shape and appearance of the curves in Figure 6. In comparison with the singlet peak obtained at a scan rate of 2 C per min, that at 4 C per min has a shoulder on the high temperature side. If the complex peaks at 4, 8 and 16 C per min are due to initial solidification in an alpha form quickly followed by a transformation into a beta-prime form, then the shoulder recorded at 4 C per min should be on the low temperature side of the peak. Again, at a scan rate of 16 C per min a shoulder appears on the low temperature side of the peak, contrary to the expected disposition if polymorphic transformations are the cause of the observed changes in peak shapes. Alpha forms do not generally supercool, and yet there is a variation in the initial cyrstallization temperatures, even when these are corrected for instrumental lag (Table IV). These corrections were carried out in accordance with procedures developed elsewhere (L.F. Vermaas, private communication, 1974), and in which repeated heating runs, carried out at different speeds on pure calibrant materials, e.g., palmitic acid, were compared with each other and with the corresponding capillary melting points.

Latent heats were calculated from the peak areas as explained earlier. These results, shown in Table IV, are all very close to one another, within experimental error, the slightly lower values at the fastest scan rates being perhaps due to the formation of imperfect cyrstals. These stabilize during the holding period at -20 C, thus giving normal values (35.8) on subsequent heating. The similarity of the results shows that the same polymorphic state is involved in each case, as any forms of lower stability must have appreciably lower latent heats of crystallization if they are to be held responsible for the observed peak shapes, e.g., for the curves obtained when cooling at 8 C per min.

Although these latent heat results show that the same polymorphic state is involved in each of the varied crystallization and melting runs, they do not prove that this form is a β-prime form. In view of the large number of component glycerides known to be present (Table III), it is also possible that there may be a mixture of polymorphic forms. Neither do the results obtained prove that crystallization is not first into an α form, followed by a rapid transformation into a β-prime form. What the results do show is that if solidification is by this route, then the polymorphic transformation is so rapid that it has no influence on the shape of the DSC thermograms. In fact, a comparison of Figures 5 and 6 shows that crystallization can take place at a temperature ca. 20 C lower than the mp, and it may be held that this crystallization is unlikely to be directly into the β-prime form without any prior formation of an α phase, however fleeting.

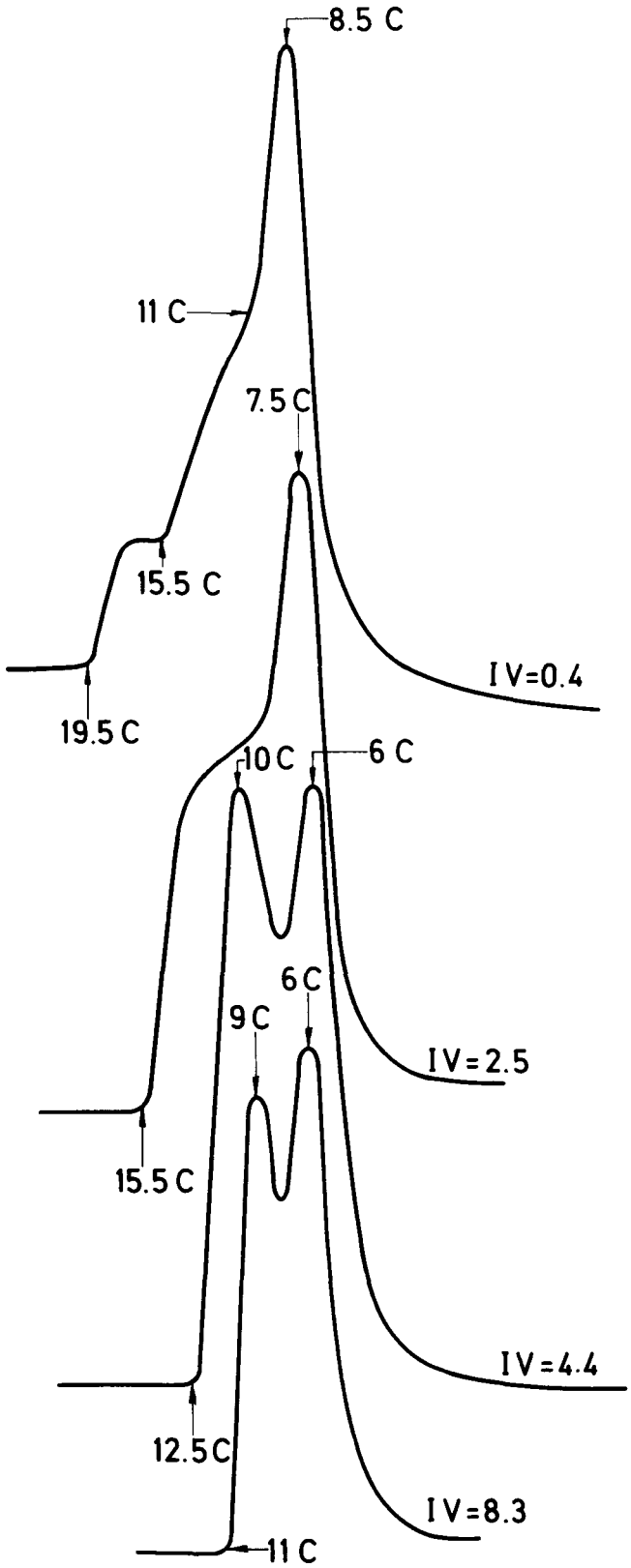

FIG. 4. Crystallization curves of solvent fractionated palm kernel stearine of iodine value (IV) = 8.3 hydrogenated to lower IVs, temperature scan rate 8 C per min.

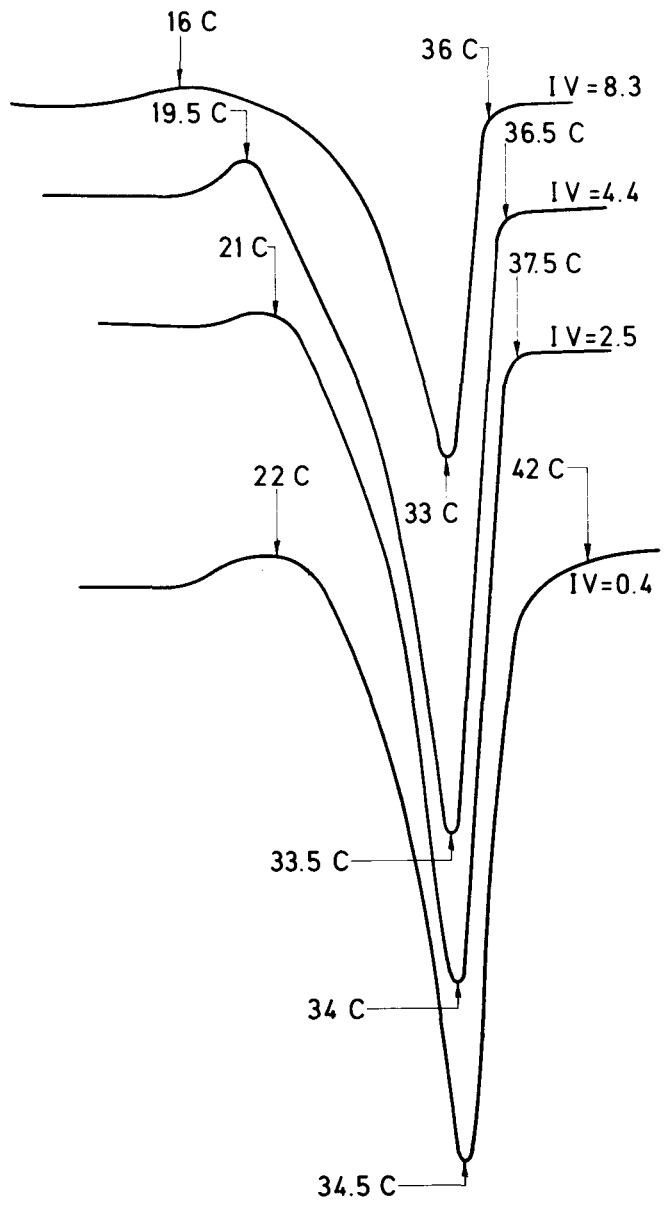

FIG. 5. Melting curves of the hydrogenated palm kernel stearines in Figure 4, temperature scan rate 8 C per min.

The values obtained for the latent heats are all ca. 36 calories per g, lower than that of 46 reported by Hampson (8) for the β form of trilaurin. This difference is due to the combined effects of the complex glyceride mixture, trilaurin comprising only about 24% of the stearine (Table III), and to the fact that Hampson studied the β modification, whereas this stearine is of lower polymorphic stability (1,3,4) probably β-prime. Therefore, further explanation of the peak shapes, based on the ramification of supercooling was considered, and found to explain satisfactorily all of the curves obtained in this work.

Figure 7 shows an equilibrium crystallization curve in diagramatic form. It corresponds to the mirror image of a dilatation curve. At low rates of cooling, the oil corresponding to the shaded area in the temperature interval AB crystallizes. The latent heat released during this crystallization gives rise to a deflection on the DSC thermogram. Similarly, in the temperature interval BC, oil crystallizes, but because the shaded area in the interval BC is larger than that in AB, a larger DSC deflection is recorded. This is repeated in the succeeding temperature intervals until an interval JK, for example, is reached, at which only a small amount of oil cyrstallizes. The resulting DSC curve therefore is a conventional single peak thermogram corresponding closely to the differential derivative of the crystallization curve. At higher rates of cooling, there is some supercooling, and the temperature falls to E, for example, before any crystallization takes place. When crystallization commences, however, the supercooled oil may crystallize spontaneously, giving rise to a sudden departure from the base-

TABLE IV

Crystallization of Palm Kernel Stearine Hydrogenated to Iodine Value (IV) = 4.4[a]

	Differential scanning calorimetry scan rate					
Uncorrected values	2 C/min	4 C/min	8 C/min	16 C/min	32 C/min	Cooled at 32 C/min to -20 C, held 10 min at -20 C, heated 8 C/min
Peak apex temperature(s)	11.7 C	12.2 C 10.2 C	10.0 C 7.0 C	6.5 C 3.0 C	3.0 C	--
Initial crystallization	16.7 C	16.4 C	12.6 C	11.0 C	8.0 C	--
Corrected values[a]						
Peak apex temperature(s)	12.2 C	13.2 C 11.2C	11.5 C 8.5 C	10.0 C 6.5 C	9.5 C	-- --
Initial crystallization	16.7 C	16.9 C	13.6 C	12.5 C	11.5 C	--
Latent heats of crystallization (cal/g)	36.3	37.4	37.6	35.2	33.7	--
Latent heats of fusion on heating at 8 C/min	35.6		36.1		35.8	35.6

[a]Temperatures corrected for instrumental lag.

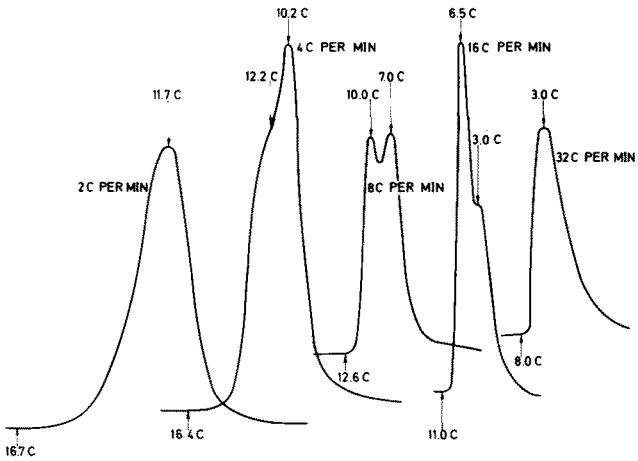

FIG. 6. Crystallization curves of solvent fractionated palm kernel stearine of iodine values (IV) = 8.3 subsequently hydrogenated to an IV = 4.4; various rates of cooling were used as shown alongside the curves.

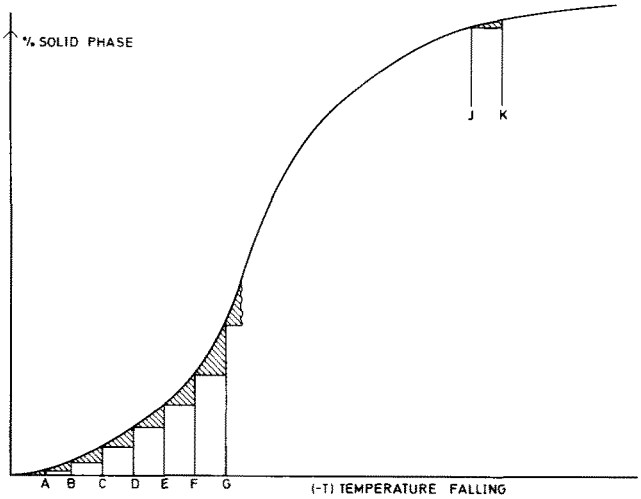

FIG. 7. Diagramatic illustration of an equilibrium crystallization curve.

line. The oil corresponding to the total area under the curve up to the temperature E solidifies, giving a large deflection. The area in the temperature interval EF is smaller than the total area A to E, and the DSC signal, therefore, falls only to rise again, because the area in the interval FG is larger than that in EF. A double peak, therefore, results, the second of these more or less corresponding to the single peak observed at lower cooling rates. At the highest cooling rates, the oil supercools to a temperature J, for example, and there then is no second peak. This single peak corresponds to the first of the two peaks in the thermograms obtained at intermediate scan speeds. This corresponds to the disposition of the shoulders seen when some of the intermediate cooling speeds were used.

It was found that this theory could be used to explain all of the DSC thermograms obtained with palm kernel oil, when used in conjunction with a knowledge of the glyceride composition. DSC cooling thermograms of coconut oil also showed single-double-single peak transformation as the cooling rate was varied, and in these cases also the present theory provided a convincing explanation.

In Figure 1, for instance, the unhydrogenated oil has a thermogram comprising a peak at 3 C due to spontaneous crystallization of supercooled oil, followed by a peak at -2 C caused by steady cyrstallization of the remaining oil. The fully hydrogenated oil, on the other hand, has an initial peak at 25 C caused by the crystallization of high mp glycerides containing on average two stearic acid radicals per molecule. The crystallinity of this glyceride group is so pronounced that it crystallizes uniformly and does not form a doublet peak at cooling speeds up to 64 C per min. This group also seeds the bulk of the fat, which then crystallizes without the pronounced supercooling effects found in the unhydrogenated oil.

The partly hydrogenated oil shown an intermediate behavior between these two extremes, giving rise to 3 peaks. An initial peak at 12.5 C is due to crystallization of a small amount of high mp material. This small amount is insufficient to seed the bulk of the fat, however, and some supercooling takes place. Supercooled fat then crystallizes spontaneously, giving rise to a peak at 4.5 C, after which the remaining glycerides crystallize uniformly as a peak at -1.5 C. This interpretation of the thermograms shown in Figure 1 was substantiated by additional experiments at both faster and slower cooling rates, and with oils hydrogenated to different IVs.

In Figure 2, the unhydrogenated interesterified oil has an initial peak at 4.8 C due to rapid crystallization of supercooled fat, and a second peak at -2.0 C due to steady solidification of the remaining fat. The interesterified hydrogenated oil is more complicated however, having a thermogram with a profile similar to that of the partly hydrogenated, but nonrandom, oil. The interpretation is also similar, as this fully hydrogenated oil also has a reduced amount of high mp glycerides containing two stearic acids, due this time not to incomplete hydrogenation, but

instead to randomization. This is illustrated by the values given in Table III.

In Figure 3 the stearine fractionated to an IV of 8.0 has an initial peak at 8.5 C due to spontaneous crystallization of supercooled material, whereas, the stearine of IV 1.8 gives a thermogram with a single peak. This is due to spontaneous crystallization of supercooled oil, a conclusion reached by consideration of the temperature at which crystallization commenced (15 C) in comparison with the mp (34 C). Experiments at other scan speeds gave sharp single peaks, showing spontaneous crystallization of supercooled oil, until the cooling rate was reduced to 2 C per min, when a broad peak, with shoulders, was obtained.

The remaining thermograms are straightforward, and are interpreted easily in terms of supercooling and spontaneous crystallization.

This work has shown that DSC cooling thermograms of lauric fats are complicated and at times difficult to understand and explain.

In contrast, Berger and Akehurst (6) claimed that cooling curves are simpler than melting curves. The difference between these two conclusions probably lies in the fact that lauric fats have a simple polymorphic behavior, coupled with a capability for rapid crystallization, these two aspects setting them apart from the non-lauric vegetable oils studied by Berger and Akehurst.

The conclusion that lauric fats have simple polymorphic behavior in which transformations play a minor role is in conformity with the work of Riiner (4), who observed no alpha phase during X-ray diffraction with programmed temperature (DPT) work with 4 lauric fats cooled at 0.3 C per min.

The work also has shown that DTA and DSC investigations should include studies at different rates of temperature change. The great power of both DTA and DSC is that they study fats under dynamic conditions, supplementing measurements made at equilibrium, e.g., dilatometry. The advantages of this dynamic nature can be lost if studies are confined to a single rate of temperature change.

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