Phase Behavior of Tristearin/Trioctanoin Mixtures

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ABSTRACT

The thermal behavior of mixtures of two monoacid, saturated triglycerides, tristearin (TS) and trioctanoin (TOC), was investigated with the intent of determining the liquid-solid and solid-solid solubility relationships. A Differential Scanning Calorimeter (Perkin-Elmer Model DSC-1) was used for the thermal analysis. Two different high purity grades of each component triglyceride were used. No large deviations from the ideal liquidus curve were exhibited by either system studied, regardless of purity. Polymorphism was not exhibited in TS/TOC binary mixtures. Polymorphic transitions were observed during the heating curve when the individual components were analyzed under the same conditions of analysis as the mixtures. In mixtures less than 73-86% TS, the TOC melted at a constant temperature that was 0.9 K lower than when TOC was melted alone. At higher TS concentrations, no TOC peak was seen in the thermograms. Solid solutions of TS and TOC were indicated at weight percent TS compositions greater than 73-86%. If a TS/TOC eutectic mixture existed, it would contain less than 3% (w/w) TS.

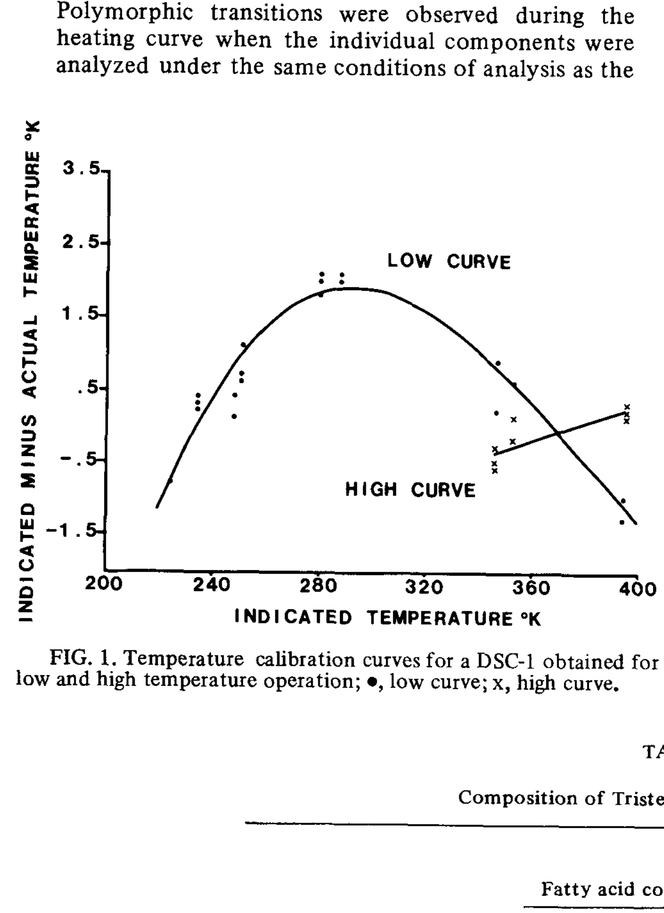

FIG. 1. Temperature calibration curves for a DSC-1 obtained for low and high temperature operation; •, low curve; x, high curve.

INTRODUCTION

Naturally occurring fats, composed of a wide variety of glycerides, melt over a wide range of temperatures. Solubility relations (1) and solid solution formation influence the melting and crystallization characteristics of a complex fat. The melting range of a complex fat does not simply reflect the melting range of the constituent triglycerides. Polymorphism may be evidant in a natural fat when it consists of predominately one particular glyceride or glyceride type.

The study of phase behavior of binary mixtures of mono and mixed acid triglycerides has contributed to the understanding of solid-liquid and solid-solid solubility relationships in natural fat systems of complex triglyceride composition (2). Lutton used a capillary melting point method to determine liquidus points of tristearin/tripalmitin and tristearin/trilaurin mixtures (3). The tristearin/tripalmitin system was of the eutectic type with partially miscible solid solutions when the tristearin in the mixtures was of the β_L polymorphic form. In the tristearin/trilaurin system, where the chain length and melting point differences are large, Lutton observed negligible solid solution formation. The phase behavior of binary mixtures of tristearin and a monoacid saturated triglyceride of very short chain length have not been previously reported.

The thermal behavior of mixtures of two monoacid saturated triglycerides, tristearin (TS) and trioctanoin (TOC), was investigated with the intent of determining the liquid-solid and solid-solid solubility relationships. Two

TABLE I

Composition of Tristearin and Trioctanoin Used

	Fatty acid composition		Triglyceride molecular weight distribution	
	Fatty acid	% by area	Total fatty acid carbons	% by area
Low purity				
Tristearin Eastman Lot 711-1	C 16:0 C 17:0 C 18:0 C 20:0	2.0 1.6 95.7 0.6	C 54 C 52	91.2 8.4
Trioctanoin Eastman Lot 712-AA	C 8:0	99.9+	C 24	99.1[a]
High purity				
Tristearin Applied Science Labs No. 21283 Lot 0011	C 18:0	99.9+	C 54 C 52	99.2 0.4
Trioctanoin Sigma Chemicals Lot 53C00860	C 8:0	99.9+	C 24	99.9+

[a] 0.9% Was C 22 and C 26.

different high purity grades of each component triglyceride were used in the study to determine the effect if any on the solubility relationships. The solubility of solid TS in liquid TOC was compared to the ideal as predicted by the Hildebrand Solubility Equation (1). Each pure triglyceride under certain conditions of analysis may exhibit polymorphism. It was of interest to determine if polymorphism would be exhibited in binary mixtures analyzed under conditions which did allow unstable polymorphic forms to crystallize when the pure components were analyzed individually.

EXPERIMENTAL PROCEDURES

A Perkin-Elmer Model DSC-1 Differential Scanning Calorimeter (DSC), low temperature mode, was used for thermal analysis. The most sensitive range setting of 2 was used in conjunction with small sample size to minimize thermal lag. Analyses were carried out within a dry box to minimize the problem of water condensation when liquid nitrogen was used as a coolant. A dry nitrogen flow rate of 37 ml/min continuously flushed the area around the sample and reference pan holders. Temperature calibration curves were separately determined for the temperature ranges 320 K to 395 K (high temperature scan) and 175 K to 395 K (low temperature scan). Separate temperature calibrations were necessary because the ambient environmental conditions of the instrument were changed due to the evaporating liquid nitrogen within the dry box. The change in ambient conditions for low temperature scans altered the temperature calibration of the DSC in the temperature range from 320 K to 395 K.

A low temperature calibration curve was determined using the following standards; m-xylene (Eastman Kodak), o-oxylene (Eastman Kodak), p-xylene (Eastman Kodak), mercury (Metal Salts Corp. triple distilled), carbon tetrachloride (Fisher Spectroanalyzed Certified A.C.S.), benzene (Baker Analyzed), napthalene (Fisher Thermetric Standards), tristearin (Applied Science Laboratories), and benzoic acid (Fisher Thermetric Standards). The resultant temperature calibration curve was nonlinear over the temperature range of 225 K to 396 K. The average standard deviation of the melting points was ± 0.2 K.

All weighings were done using an electrobalance (Cahn Model RTL). The tare control was used to compensate for the 26-27 mg sample pans, therefore, it was possible to weigh up to 10 mg samples to the nearest .01 mg. All calibration standards were sealed in aluminum sample pans and put in the DSC when sample and reference pan holders were at 320 K. Samples were cooled at the programmed rate of 5 K/min to 175 K, then heated at the same rate to a temperature 10 K above the melting point of the standard. A particular low temperature calibration cruve was only valid for specific instrument settings and conditions of analysis. Changes in scan rates, starting temperatures, and other parameters changed the temperature calibration curve. A typical low temperature calibration curve is illustrated in Figure 1.

Two different grades of each triglyceride were used in the mixtures. The fatty acid composition and the triglyceride molecular weight distribution of each purity grade of tristearin (TS) and trioctanoin (TOC) were determined by gas liquid chromatography (GLC). Methyl esters of the fatty acids were prepared by the transmethylation procedure of van Wijngaarden (4) and were analyzed with a dual column, dual flame ionization detector equipped Hewlett-Packard 5830A gas chromatograph. The colums were 2.16 mm x 3.6 m stainless steel, packed with 10% SILAR 10C on Gas Chrom Q (Applied Science Labs). Column oven temperature was programmed from 205 to 250 C at 5 C/min with a nitrogen carrier gas flow rate of 20 ml/min. Triglycerides were analyzed directly on 2.16 mm x 0.6 m columns packed with 3% OV-1 on 100/120 mesh Gas Chrom Q (Applied Science Labs). Column oven temperature was programmed from 200 to 340 C at 5 C/min with a nitrogen carrier gas flow rate of 185 ml/min. The results of the fatty acid and triglyceride analysis are presented in Table I.

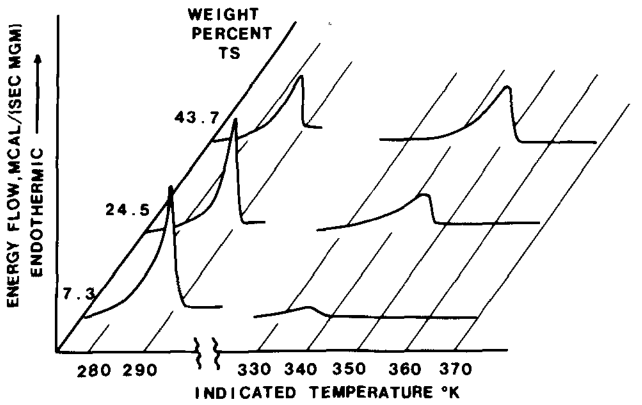

FIG. 2. Selected DSC thermograms of low purity TS/TOC mixtures.

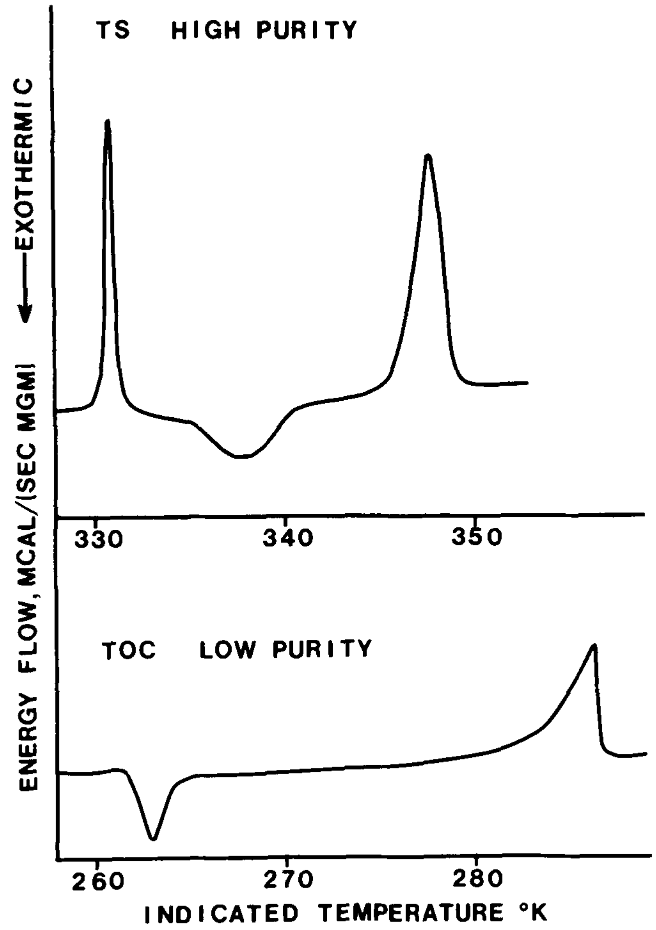

FIG. 3. DSC thermograms of TS and TOC.

The mixtures of TS and TOC were prepared directly in the DSC pan, and the sealed pan was placed in the DSC when the sample and reference pan holders were at 320 K. The sample was heated at the rate of 5 K/min to 353 K. The sample was held at 353 K for 30 min to remove any persistent crystal nuclei and to mix the two components. The sample was cooled at 5 K/min to 175 K, then heated at the same rate after a variable holding period of 5 to 20 min

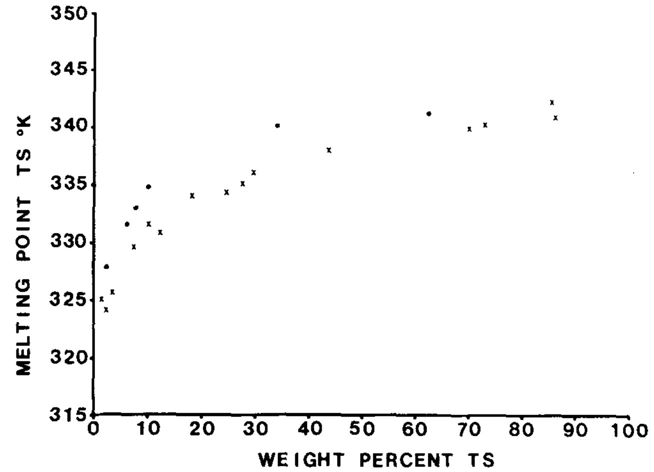

FIG. 4. Melting point of TS in TS/TOC mixtures; x, low purity; •, high purity.

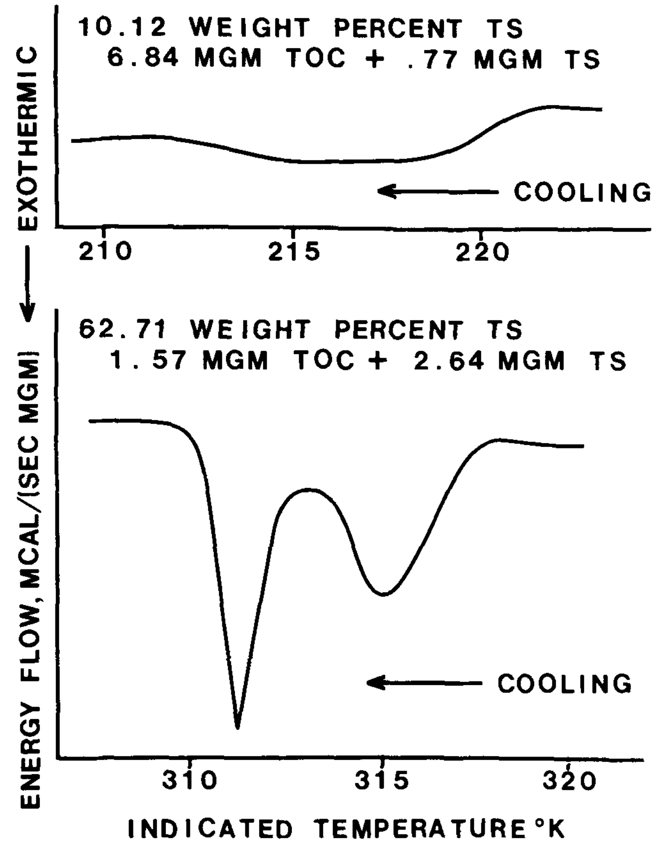

FIG. 5. Effect of composition on shape of freezing exotherms of pure TS in TS/TOC mixtures.

at 175 K to allow all the liquid nitrogen to evaporate from the Dewar flask. The heating program was discontinued at 353 K, and the sample was removed after the temperature of the holders had been adjusted to 320 K.

After 23 months of storage, the same samples still in the same aluminum pans, were reanalyzed. Heating curves were recorded from 320 K to 353 K at a heating rate of 5 K/min. An above ambient calibration curve was determined using naphthalene (Fisher Thermetric Standard), tristearin (Applied Science Labs) and benzoic acid (Fisher Thermetric Standard) as thermetric standards (Fig. 1, "high" curve).

Melting points of calibration standards were determined by drawing a line tangent to the most linear portion of the leading leg of the peak and extending it to the baseline. A line through this point on the baseline and normal to the chart paper temperature scale indicates the melting point. In the TS/TOC mixtures, the melting points were determined at the center of the peak summit, even if the summit was a plateau spanning a temperature range of as much as 2 K. This method was used to obtain a more precise temperature measurement due to the broad nature of the TS peak.

RESULTS

The shape of the TS peak is characteristic of the weight percent TS in the mixture, regardless of the purity of tristearin used. Small weight percent TS mixtures exhibit a very broad TS peak. The size and shape of the peak made it essential to maintain a flat baseline throughout the scan. Higher weight percent mixtures exhibit a long premelt, a peak, and a sharp termination of the endotherm. Selected thermograms of the mixtures, modified to express the output on a per milligram basis, are given in Figure 2. Thermograms of the component triglycerides showing evidence for their polymorphic behavior are presented in Figure 3. The α_L polymorphic form of the high purity tristearin sample melted at 326.4 K. The exothermic transition at 334.8 K represents the recrystallization of all or a portion of the α_L melt into the β_L form which melted at 344.8 K. Trioctanoin exhibits an exothermic transition at 261.0 K representing either the recrystallization into the β_L form from either the α_L or β_L' melt, or a direct solid-solid transformation of an unstable form to the β_L form which melts at 283.8 K.

In Figure 4, the temperature corrected melting point of TS in the two sets of mixtures is plotted against the weight percent composition of the TS/TOC mixture. No TS peak was observed for the 4.2% (w/w) mixture containing 0.2 mg of the less pure TS. No TOC peak was observed for a 86.0% (w/w) of the less pure TS mixture containing 0.6 mg TOC. A 2.9 K average increase in the melting point of TS in the TS/TOC mixtures was observed for the samples which had been stored for 23 months.

The melting point of pure TOC was compared to the melting point it exhibited in the presence of high purity TS. The melting point of the TOC was 0.9 K lower when the TOC was a component in the mixtures. This difference was significant at the 0.05 level using a one-tailed t-test.

The cooling curve of the 62.71% (w/w) highly pure TS mixture exhibits two close exotherms for the recrystallization of the TS, as shown in Figure 5. The peak occurring at the lower temperature is shaper. The same two-peak recrystallization for TS was observed in the cooling curve of the 34.29% (w/w) TS, but the recrystallization occurred at a lower temperature. In Figure 5 the cooling curve of TS in a 10.12% (w/w) TS is shown to be more symmetrical and rounded.

INTERPRETATION AND DISCUSSION

The Hildebrand Solubility Equation may be used to calculate the melting point of a component in a binary mixture. When either purity of TS was melted and recrystallized by the same methods as applied to the mixtures, the β_L melting point observed was lower than the first melt, or solvent crystallized β_L melting point. This lower or second melt melting point of TS was used as melting point of pure TS in the Hildebrand Solubility Equation. At the same weight percent of TS, mixtures containing the purer TS showed higher TS melting points than did the mixtures containing the less pure TS. A heat of fusion value of 54.6 cal/g (6) yielded a Hildebrand Solubility Equation which agreed well with experimental data for the pure TS. The less pure of the systems studied more closely corresponds with the Hildebrand Solubility Equation if the heat of fusion of 50 cal/g determined by Lutton in a study of the tristearin/trilaurin system (3) was used. No large deviations from the Hildebrand Solubility Relationship were exhibited by either purity of TS in the presence of TOC, indicating that the presence of C16 fatty acid residues did not materially affect the results.

The higher melting point exhibited by the less pure TS in TOC mixtures after 23 months of storage at room temperature indicates that cooling the mixtures at 5 K/min to 173 K, and heating at the rate of 5 K/min from 173 K to 353 K did not produce the β_L form crystals in their most stablilized state. Small inperfections which initially existed in the crystal lattice may have disappeared during long term storage.

Cooling curves of the 62.71 and 34.29% (w/w) pure TS in TOC showed two exothermic peaks for the TS crystallization. The first peak of the doublet, as seen in Figure 5, may represent the heat evolved as the first flash of nuclei appears. The second peak, following in quick succession, may be that representing the growth of these nuclei. Rossell observed a similar effect in a DSC study of palm kernel oil (7).

The liquidus curve of the TS/TOC phase diagram at low weight percentages of TS was defined to the limits of instrument sensitivity and sample pan capacity. It was evident from the temperature of the TS melt that a eutectic, if one existed, would be composed of less than 3% (w/w) TS. If the peak that has been labeled as the melting peak for pure TOC in the mixtures were in fact the melting peak of eutectic composition, the melt would be expected to be displaced to a lower temperature than the melt of pure TOC. The data may indicate the existence of a TS/TOC eutectic of low weight percent TS in TOC since the melting point of the pure TOC was higher than the melting point it exhibited as a component in a TS/TOC mixture. This was not taken as conclusive evidence for the existence of a eutectic of low weight percent TS since other factors could explain the higher melting point when TOC melted alone. In monoacid saturated tryglycerides, the variation in melting point with phase preparation and temperature treatment is a consideration which cannot be overstressed in the interpretation of thermal behavior (5). Both TS and TOC exhibited polymorphic transformations when they were the sole component in the sample pan, but only the β_L form, by analogy of melting points, was observed in the TS/TOC mixtues analyzed by the same procedures. It is feasible that the crystal structure of β_L form of TOC as the sole component in the pan was more stabilized because a portion of the crystals were formed either from the melt of the $\beta_L{}'$ form or by direct transformation from the $\beta_L{}'$ form. This difference in β_L form preparation may account for the 0.9 K higher melting point of TOC when it is the sole component in the pan versus its melting point as a component in the mixture.

A mixture of composition 73.33% (w/w) TS, containing 0.4 mg of TOC, showed a small but discernible TOC melt. No TOC melt was observed for a 86.1% (w/w) TS mixture containing 0.6 mg of TOC analyzed at range 2. A sample of 0.6 mg of pure TOC analyzed under the same conditions would exhibit an appreciable melt. This behavior is evidence for TS/TOC solid solution formation. The composition above which solid TS is intersoluble with solid TOC was between 73.3 and 86.1% (w/w) TS. Above this minimum weight percent of TS, the solidus line is defined by the initial melting point of the series of solid solutions, the composition of which varies with the weight percent TS composition of mixture. The complete phase diagram of the tristearin/trioctanoin system is plotted in Figure 6. The results confirm the lack of impact of the palmitate and other contaminates in the one preparation of TS on the TS/TOC phase diagram. The solidus line is unaffected within the precision of the techniques used. Sample size and instrumental factors precluded a detailed investigation of the 0-3% TS in TOC region.

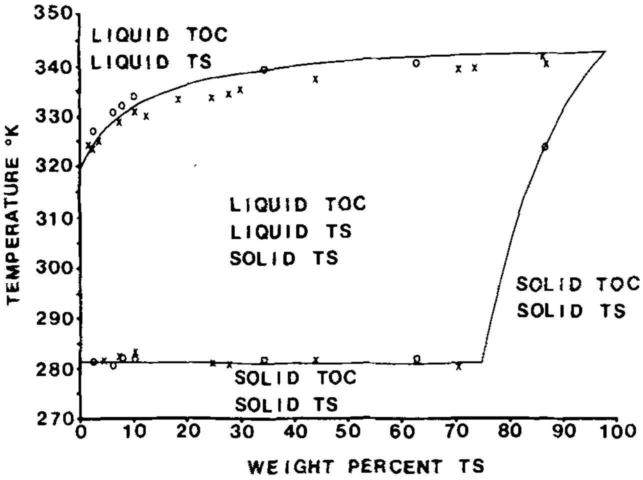

FIG. 6. Phase diagrams of TS and TOC binary mixtures; x, low purity; o, high purity.

ACKNOWLEDGMENT

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