

Binary Systems from Palmitic-Stearic Triglycerides

E. S. LUTTON, Miami Valley Laboratories,
The Procter and Gamble Company, Cincinnati, Ohio

Abstract

Melting-point and limited diffraction data are presented for the 13 hitherto unreported binary systems of the 15 obtainable from the six palmitic-stearic triglycerides. Data are presented for metastable α and stabilized states. These and earlier data on the other two systems show continuous solid solution formation and nearly linear melting-point variation for α states. Stabilized state behavior depends on many factors, such as molecular weight, molecular symmetry, phase tendency. In general, β tending components produce β phase systems and β' tending components produce β' systems; β predominates in systems of mixed β and β' tending components.

Introduction

THE SATURATED TRIGLYCERIDES possible from palmitic and stearic acids are six in number if optical isomerism is disregarded. Various ones of these occur in mixture in plastic shortenings. Preliminary to a thorough understanding of the effect of mixtures of saturated triglycerides upon shortenings is an understanding of the solidification behavior of the mixtures themselves. The problem is complex and detailed, but a beginning can be made with binary systems. There are 15 of these as listed in Table I. Of this imposing number, two have been previously reported from this laboratory in some detail, namely PPP-SSS (tripalmitin-tristearin) and PSP-SSS (1). Now a somewhat less detailed melting-point and diffraction study is reported on metastable (α) and stabilized states of the 13 other systems. Many of these systems are of practical significance, certainly those comprised largely of combinations of SSS (predominant in many saturated oils), PSP and PSS (important in saturated cotton oils), and SPS (the principal triglyceride of saturated lard). The other systems are of interest since PPP is easily obtained synthetically and since randomly interesterified P,S triglycerides contain all possibilities including SPP. All 15 of the systems are of academic interest for their indication of interactions among members of this family of closely related long-chain compounds.

Experimental

The preparations used for these binary systems were the same as reported in previous studies on

TABLE I
Binary Systems Possible with P,S Triglycerides

Stabilization conditions			
System	Conditions	System	Conditions
SPS-SSS	b, c	PSP-PSS	b, c
PSS-SSS	b, c	SPP-PSS	c
PSP-SSS ^a		PPP-PSS	d
SPP-SSS	c		
PPP-SSS ^a		SPP-PSP	b, c
		PPP-PSP	c
PSS-SPS	b, c		
PSP-SPS	c	PPP-SPP	c
SPP-SPS	c		
PPP-SPS	c		

^a Previously reported (1).
^b 1 week 49C.
^c 1 week 49C, 1 week 60C.
^d 1 week 49C, 1 week 57C.

triglyceride polymorphism (1,2) or of comparable quality; in some instances, different preparations of a given triglyceride were used in different systems. Procedures were as previously described (1,2) for the thermal studies and for x-ray diffraction. Metastable (α) states were obtained by melting samples to 80C and quickly chilling. Stabilized states were obtained by melting, chilling, and storing (with some systems for two different periods) as indicated in Table I. It was intended that all samples be 100% solid at all times during storage. Only data for the more strenuous storage systems are reported. It is not possible always to be certain, but it is believed that thermodynamic equilibrium was closely approached in storage.

Melting points for stabilized states appear in Figure 1. Diffraction data for selected samples appear in Table II. Melting points for metastable (α) states appear in Figure 2.

Discussion

For all the individuality of the various binary systems it is possible to make a number of generalizations.

All P,S triglyceride pairs in the metastable α state show a type of melting-point curve that indicates solid solution formation (3). The maximum departure from linear variation with concentration is 1C. Where tests by x-ray diffraction have been made, as in the PPP-SSS case (1), only a single set of long spacings has been encountered, signifying a single solid phase composition.

In the stabilized state (Figure 1) the degree of solid solution formation or "compatibility" of components, as evidenced by linearity or limited dips in melting-point curves, depends mainly on proximity in molecular weight and similarity in stabilized phase from melt. Before discussion of these points in greater

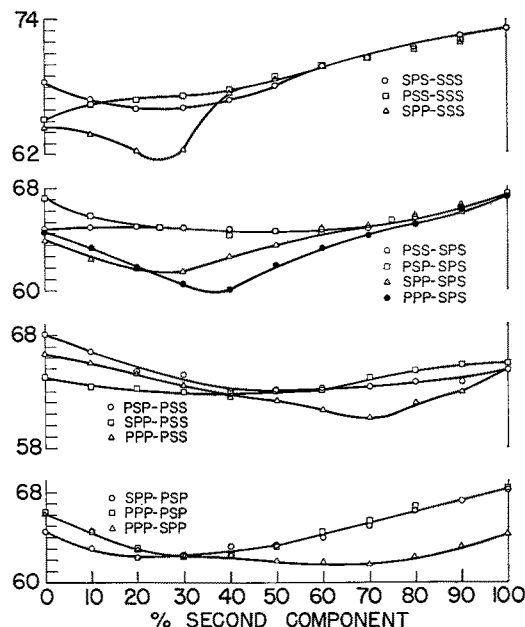


FIG. 1. Melting points of stabilized binary mixtures of P-S triglycerides.

TABLE II
 Phase (% β^a) of Stabilized Samples (Most Strenuous Condition)

%	PSS-SSS	PSS-SPS	PSP-SPS	PPP-SPS	PSP-PSS	SPP-PSS	PPP-PSS	SPP-PSP	PPP-PSP
0	0	0	0	100	0	100	100	100	100
10		0	0						
20	60	85		100	0	100	70	90	100
25			15						
30		90							
50	100	100	75	50	0	100	0	0	0
75			95						
80	100	100	100	100	0	0	0	0	0
100	100	100	100	100	0	0	0	0	0

SPS-SSS, SPP-SSS, SPP-SPS, PPP-SPP all 100% β at all compositions

^a % β estimated from short spacings according to intensity of 4.2 Å (β') line and 4.6 Å (β) line as compared with a set of patterns of standards obtained from mechanical mixtures of β' and β samples.

detail it is well to distinguish three molecular types: single acid, symmetrical diacid, and unsymmetrical diacid triglycerides and perhaps three phase types in stabilized systems (from melt): β , with strong 4.6 Å spacing as shown by SSS, PPP, and SPP; β , slightly modified from (SSS) β by having a closer pair of spacings in the 3.8 Å region; and β' as shown by PSP with strong 4.2 and 3.8 Å spacings. PSS has nearly equal β' and β tendencies, but only β' is obtained from melt. [From melt SPS does not show its stable β' form (4,5).]

Pairs of triglycerides, each of β (or SPS β) type, form systems of β (or SPS β) type on stabilization. The one exception is PPP-SPS, which is still 50% β' at the 50% SPS level after stabilization (Table II). (Since the lower melting 20% SPS sample was 100%

β , it seems unlikely that the low β percentage in 50% SPS was attributable to incomplete solidification on account of high storage temperature.) The pair of triglycerides in which each is β' tending, PSP-PSS, forms a system of β' type on stabilization. Systems of components of different phase types, e.g., PSP-SPS, show mainly β , but usually a significant region of both β' and β content.

As judged by high mp level, an uncertain criterion, SSS accommodates or takes into solid solution PSS and SPP (the latter remarkably well, considering its low MW) rather better than it does SPS or PSP. SPS accommodates PPP less well than it does PSP, SPP, or PSS. Thus the greatest incompatibility or limitation to solid solution formation seems to be between single acid and symmetrical (mixed) triglycerides.

PSS, of nearly equal β' and β tendency (β' from melt), accommodates β -tending SSS and SPS remarkably well, better than it accommodates SPP and considerably better than it accommodates PSP or PPP (where the MW factor is significant).

PSP, normally β' -tending, better accommodates β -tending SPS and even PPP than it does PSS.

SPP and PPP, of short average chain-length and low MW, have difficulty accommodating any of the other glycerides; SPP does best perhaps with PSS.

It is to be expected that one will be better able to interpret these effects on melting point and the diffraction pattern of mixing one triglyceride with another when the detailed crystalline structure of each pure component is known.

REFERENCES

- Lutton, E. S., JAOCS 32, 49 (1955).
- Lutton, E. S., F. L. Jackson and O. T. Quimby, J. Am. Chem. Soc. 70, 2441 (1948).
- Ricci, J. E., "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Inc., New York, 1951, p. 99.
- Lutton, E. S., and F. R. Hugenberg, J. Chem. Eng. Data 5, 489 (1960).
- Hugenberg, F. R., and E. S. Lutton, J. Chem. Eng. Data 8, 606 (1963).

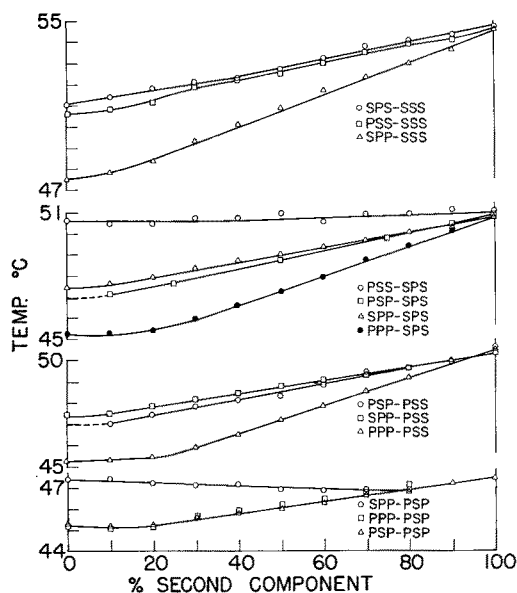


FIG. 2. Melting points of metastable (α) binary mixtures of P-S triglycerides.

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