Binary Systems with Monoglycerides

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Abstract

A number of binary systems have been studied, each involving a 1-monoglyceride. Included was the binary system of 1-monopalmitin (1P)-1-monostearin (1S). Other systems involved 2-monoglycerides, 1,3-diglycerides and triglycerides as follows: 2P-1P, 2S-1S, PP-1P, SS-1S, PPP-1P, SSS-1S. A general principle running through the observed behavior is that the more chemically similar the components, the greater is the interaction or solid solution formation. Thus 1P-1S showed continuous solid solution in both stable and metastable states with "compound formation" in the stable state. The systems 2P-1P and 2S-1S showed α (sub α) stability in a single solid solution phase for the range 20–80% 1-monoglyceride. The system PP-1P and SS-1S showed extensive solid solution formation in an α state but little or none in the stable state. There was essentially no solid solution formation observed for stable states of PPP-1P and SSS-1S; experimental limitations made it difficult to draw certain conclusions about the metastable state, but here, too, it is believed, solid solution formation was negligible.

Introduction

SATURATED MONOGLYCERIDES play a role in the consistency as well as in the interfacial activity of many commercial shortenings. These monoglycerides, mainly monopalmitin and monostearin, occur in mixtures with each other and with other glycerides, especially saturated di- and triglycerides. A study of selected binary systems is valuable for a sound understanding of the factors which operate to influence the phase behavior, hence the consistency, of materials containing these monoglycerides.

Experimental

Studies were carried out with the following materials: 1-monopalmitin (1P), 1-monostearin (1S), 2-monopalmitin (2P), 2-monostearin (2S), 1,3-dipalmitin (PP), 1,3 distearin (SS), tripalmitin (PPP), and tristearin (SSS).

The following systems were studied: 1P-1S, 2P-1P, 2S-1S, PP-1P, SS-1S, PPP-1P, and SSS-1S. Mixes were made in 10% intervals across the binary diagrams.

Thermal behavior was followed in 1-mm glass capillaries after the manner previously described (1,2). Rapid complete melting-points on metastable states after melting and chilling and regular complete melting-points on stabilized states after the storage times indicated in Table I were determined to characterize the lowest and highest melting forms.

TABLE I

System	Stabilization procedures for various systems
1P-1S	1 week 49C, 1 week 60C
2P-1P	1 week 49C
2S-1S	1 week 60C
PP-1P	1 week 49C, 1 week 60C
SS-1S	1 week 49C, 1 week 60C
PPP-1P	5 weeks 60C
SSS-1S	5 weeks 60C

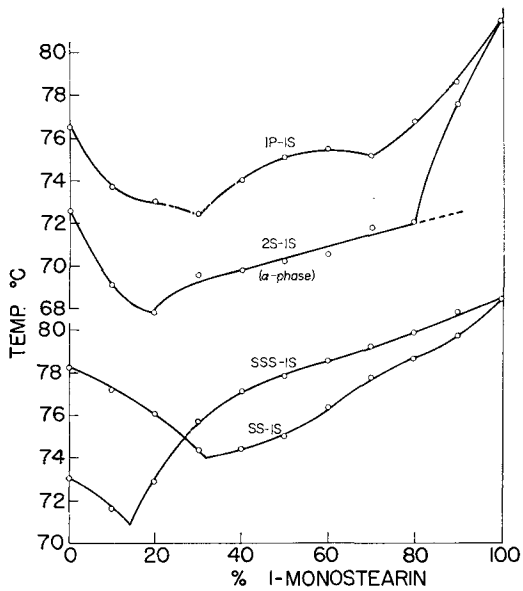

FIG. 1. Binary systems with 1-monostearin (1S), stabilized states.

It is believed that the stabilized states were close to thermodynamic equilibrium. No major exploration of intermediate melting forms was attempted, but slow transitions frequently made evident the occurrence of such forms. With 2-monoglyceride there was some indication of isomerism of 2- to 1-monoglyceride by a minor drop in the melting point from a maximum with increasing storage. This was most evident for samples with 90% 2-monoglyceride. Thus 90% 2S-10% 1S showed melting points of 64.8, 70.9, 70.5 and 69.1C upon increasing storage. Melting-point data are recorded in Figures 1–4.

In a sufficient number of cases to characterize a system as to diffraction behavior, flat film patterns were taken on capillary (thin-walled Pyrex) samples with a General Electric XRD-1 unit, employing CuKα radiation (nickel-filtered) and a 0.025-in. pinhole system; sample to film distance was 5 cm for phase identification and 10 cm for determining long spacings.

An α phase is indicated by a strong spacing of about 4.2 Å with only weak additional spacings nearby, and these only in case of 1-monoglycerides. Sub α

TABLE II

Phase Behavior of Binary Systems with Monoglycerides

a) Stabilized systems

% 2nd Component	1P-1S	2P-1P	2S-1S	PP-1P	SS-1S	PPP-1P	SSS-1S
0	β	β	β	β-b	β-a[a]	β	β
20	β	β	β	β-b	β-b	β	β
40	β			β,β-b	β,β-a		
50		α (sub α)	sub α			β	β
60	β			β,β-b	β,β-b		
80	β	sub α	sub α	β,β-b	β (β-b)	β	β
100	β	β	β	β	β	β	β

b) Metastable systems

0	sub α	β (2P)	β	β-a	β-a	α	α
20	α	β	β	β-a (α)	β-a (α)	α, sub α	α, sub α
40	α			α	α		
50		α (sub α)	sub α			β, sub α	α, sub α
60	α			α	α		
80	sub α	α	sub α	α	sub α	α, sub α	α, sub α
100	sub α	sub α	sub α	sub α	sub α	sub α	sub α

[a] β-a from melt, β-b from solvent or melt after storage at 70C.

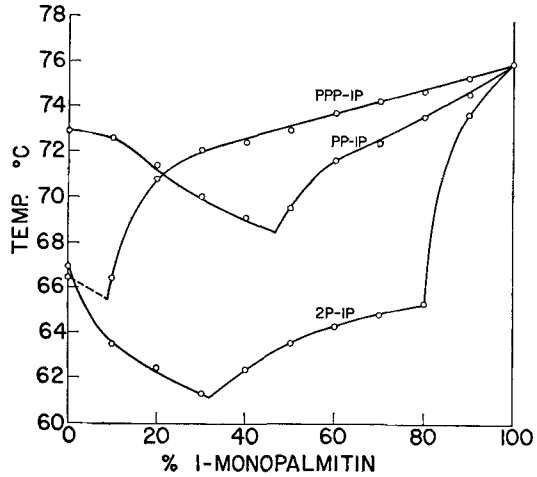

FIG. 2. Binary systems with 1-monopalmitin (1P), stabilized states.

is characterized by a 4.2 Å spacing with other smaller spacings of moderate strength. A β phase (including the 2-monoglyceride phase) is characterized by a strong spacing near 4.6 Å; β-b for diglycerides has a 2nd strong short spacing, β-a has two others. Characteristic long spacings are summarized by O'Connor (3). The high resolution necessary for separating long spacings, as in the SS-1S system, was accomplished with a 0.010-in. slit system. Phases observed are recorded in Table II.

The 1-monoglycerides, 1,3-diglycerides, and triglycerides were of comparable purity with those whose polymorphism has been previously reported from this laboratory and were similarly prepared (4).

The 2-monoglycerides were prepared by recognized methods (4) and were of high monoglyceride content but contained some 1-monoglycerides: 2P had an HV of 343 (Theory 340) and 1P content of 2.4%; 2S had an HV of 316 (Theory 314) and a 1S content of 10.0%.

Discussion

The individual character of the several binary systems can be realized by consulting Figures 1–4. One principle runs throughout: the more similar two compounds are, the more interaction, solid solution in most cases, is evident in their phase behavior.

1P-1S System. The two components, most alike of any pairs, show continuous solid solution formation in both metastable (α or sub α) and stable (β) states

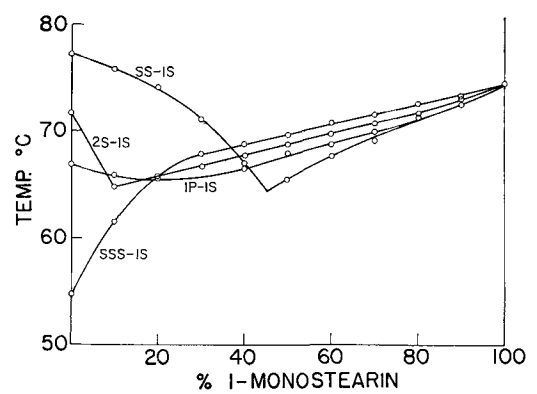

FIG. 3. Binary systems with 1-monostearin (1S), metastable states.

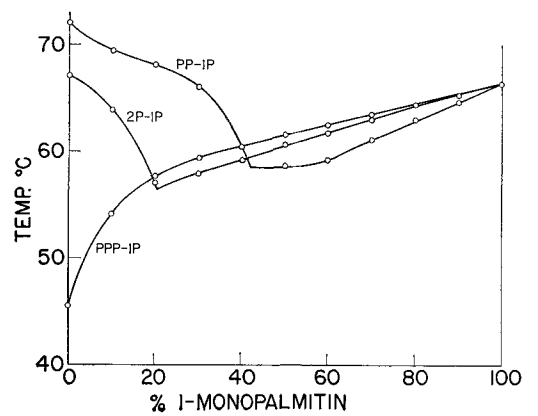

FIG. 4. Binary systems with 1-monopalmitin (1P), metastable states.

since no composition showed more than one set of long spacings. Near the 50–50 range, "compound formation," as in the palmitic-stearic acid system, was strongly indicated. This none-too-simple phenomenon is probably to be accounted for by similar features of crystallization behavior in the fatty acid and monoglyceride cases. The nature of the phenomenon is perhaps best discussed by Degerman and von Sydow (5).

2S-S (and 2P-1P). The β-phase-stable 1S and "β-like"-stable 2S produce α (and sub α) stable mixtures in the range 20–80% 1S. This is the more remarkable since 2S is monomorphic but will show an α melting point with as little as 10% 1S. The 2P-1P system behaves similarly; transformation occurs a little faster; the α phase exists a little lower in temperature. It would be interesting to explore the sub α-α transition in both systems as a function of composition.

SS-1S (PP-1P) System. In the SS-1S system there is continuous solid solution formation in the metastable state from 30 to 70% 1S, but limited solid solution formation in the stable (β) state, since two sets of long spacings are discernible over most of the composition range. Although α does not occur for SS, 100% α can be obtained with 70% SS. SS causes the tilted α of 1S to form a presumably perpendicular α as evidenced by the increase in long spacing from 50 to 54.5 Å on the addition of 50% SS to 1S. Apparently 1S has the effect of promoting β-a to β-b transformation in SS. This is contrary to the usual experience that admixture slows up phase transformation. The PP-1P system is similar except for faster transformation.

SSS-1S (PPP-1P) System. With these components, so unlike, no solid solution seems to occur in the stable state. Two sets of long spacings are obtained. Probably the same situation holds for the metastable state, but unfortunately it is difficult to prove because the identity in long spacings of the two α components, SSS and 1S, prevents distinction. The PPP-1P system appears to behave identically.

REFERENCES

1. Lutton, E. S., F. L. Jackson and O. T. Quimby, J. Am. Chem. Soc., *70*, 2441 (1948).
2. Lutton, E. S., JAOCS *32*, 49 (1955).
3. R. T. O'Connor, in "Fatty Acids," Second Edition, Part I, by K. S. Markley, Interscience Publishers Inc., Division of John Wiley and Sons Inc., New York, p. 285 (1960).
4. Mattson, F. H., and R. A. Volpenhein, J. Lipid Res. *3*, 281 (1962).
5. Degerman, G., and E. von Sydow, Acta Chem. Scand. *12*, 1176 (1958).

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