Solidification Points of Some Binary Mixtures of Derivatives of Stearic Acid[1]

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THE PURPOSE of this investigation was to make a study of the solidification points of some binary systems of compounds of equal chain length and dissimilar functional groups. Previous to this study many binary systems were investigated, but these comprised different chain lengths and the same functional group (5, 6, 7, 8). The binary systems selected for study were stearic acid-stearamide, stearic acid-stearonitrile, stearic acid-1-octadecanol, and stearonitrile-stearamide. These compounds are either manufactured commercially or are of interest as intermediates, and a study of these binary mixtures would be useful for thermal analysis of mixtures.

Solidification points, rather than melting points, were determined because even though the solidification point curves give only a rough indication of the position and shape of the liquidus lines, they are nevertheless useful for estimating the composition of unknown mixtures inasmuch as they are quite reproducible. In a great many cases, too, it is simpler to run solidification points.

Experimental

Stearic Acid. Humko's commercial stearic acid (S-97) was crystallized twice from methanol and twice from acetone. The solidification point of the resulting product was 68.9°.

Stearamide. This compound was prepared from stearic acid by the method described by Aschan (1). Repeated crystallizations from acetone yielded a product which solidified at 108°.

Stearonitrile. This compound was prepared from stearic acid and urea by the method of Kaplan (3). After six crystallizations from acetone the compound solidified at 39.9°.

1-Octadecanol. After four crystallizations from ethanol Eastman's 1-octadecanol (m. pt. 56.5-58°) solidified at 57.6°.

Determination of Solidification Points. The solidification points of the mixtures were determined by a method similar to the A.S.T.M. titer procedure (2). Melts of from 5 to 10 g. were made up determinately by weighing the amounts of each component. These were placed in a test tube and cooled in a water bath maintained 3 to 4 degrees below the solidification point of the particular sample used. The molten mixture was stirred manually, and the temperature was read every 15 seconds on a Bureau of Standards Thermometer calibrated to 0.1 degree. In each determination a plot of time *vs.* temperature, corrected for exposed mercury column, was made, and from this curve the true solidification point was obtained, corrected for the degree of supercooling by extrapolation. In all cases the maximum degree of supercooling permitted was 0.3-0.4°. The data represent true solidification points in which the solid and liquid phases are in equilibrium. Each determination is the result of several readings, and the maximum error in reproduction of the solidification points was 0.1°. The precision of the determinations of the solidification points was within 0.1°.

Discussion

Figure 1, which shows the freezing points of mixtures of stearic acid and stearamide, indicates a eutectic temperature of 65.8° and corresponds to a composition of approximately 85 mole percentage of

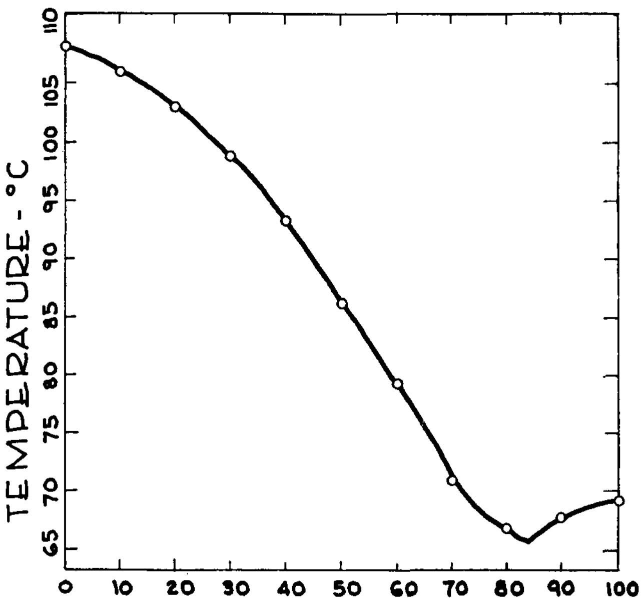

FIG. 1. Solidification Temperatures of Stearic acid—Stearamide.

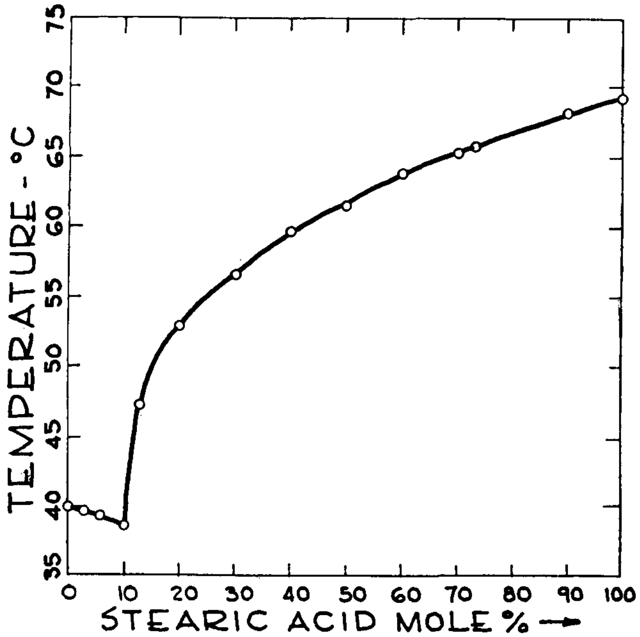

FIG. 2. Solidification Temperatures of Stearic acid—Stearonitrile.

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stearic acid. The time-temperature curves were carefully studied to see if a second transition temperature, indicating compound formation, could be found, but none could be observed. Slight changes in composition gave abrupt changes in the solidification points.

Figure 2 shows no indication of compound formation between stearic acid and stearonitrile. A definite eutectic halt occurred at 38.5°, which corresponds to a composition of about 89 mole percentage stearonitrile.

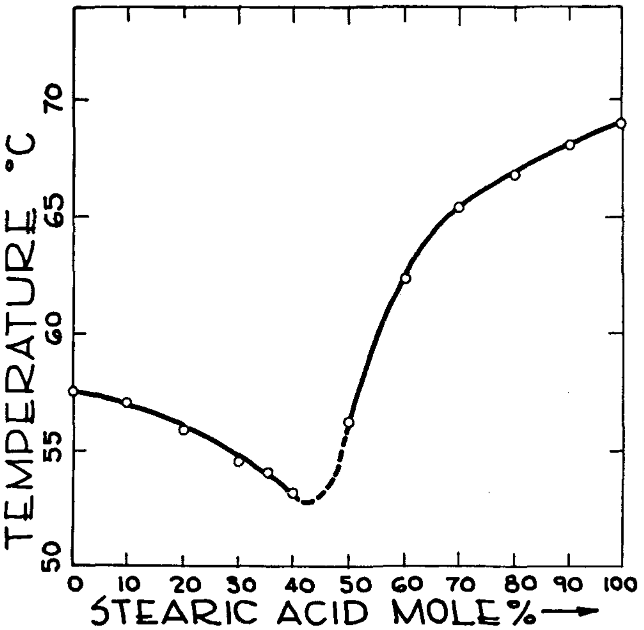

FIG. 3. Solidification Temperatures of Stearic acid—1-Octadecanol.

The solidification points of mixtures of stearic acid and 1-octadecanol are plotted in Figure 3. In this case there was no indication of compound formation or of a definite eutectic halt. Mixtures close to the indicated eutectic composition supercooled greatly, even when the melt was seeded. Ralston (4) reported that the difficulty in obtaining eutectic halts in mixtures of saturated acids could be considered as evidence of solid-solution formation.

Figure 4, which shows the solidification points of mixtures of stearonitrile and stearamide, indicates the eutectic temperature to be 39.6°. This temperature corresponds to a composition of 2 mole percentage stearonitrile. No evidence of compound formation could be observed.

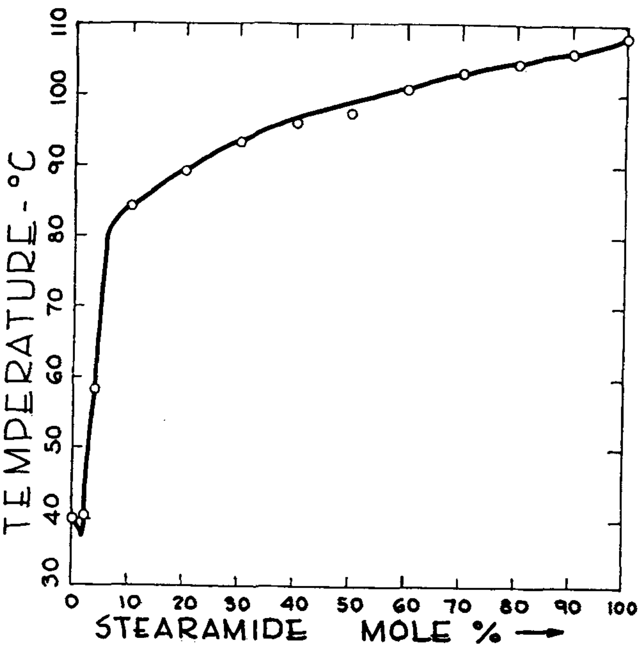

FIG. 4. Solidification Temperatures of Stearonitrile—Stearamide.

Summary

The solidification points of binary mixtures of stearic acid-stearamide, stearic acid-stearonitrile, stearic acid-1-octadecanol, and stearonitrile-stearamide were determined.

Acknowledgment

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REFERENCES

1. Aschan, O., Ber. *31*, 2349 (1898).
2. A.S.T.M. Standards, Part 7, 1952.
3. Kaplan, W., U. S. Patent 2,444,828 (July 6, 1948); Chem. Abs., *42*, 7315 (1948).
4. Ralston, A. W., "Fatty Acids and Their Derivatives," p. 373, John Wiley and Sons Inc., New York (1948).
5. Schuette, H. A., and Vogel, H. A., Oil and Soap, *22*, 238-240 (1945).
6. Schuette, H. A., and Vogel, H. A., *ibid.*, *16*, 209-212 (1939).
7. Shriner, R. L., Fulton, J. M., and Burks, D. Jr., J. Am. Chem. Soc., *55*, 1494-1499 (1933).
8. Smith, J. C., J. Chem. Soc., 974-980 (1939).

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Glyceride Structure of Vegetable Oils by Countercurrent Distribution. II. Soybean Oil[1]

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SOYBEAN OIL has been considered to conform to a general rule of even distribution although, as Eckey (5) has stated, some studies "indicate that the arrangement cannot be strictly that which would conform with pure even distribution." Hilditch, Meara, and Holmberg (9) fractionated soybean oil by crystallization from acetone, and their data indicate "that the individual fatty acids are distributed extremely widely or evenly throughout all the triglycerides in the oil." On the other hand, Hashi (6) has isolated oleo-dipalmitin from soybean oil, and Hashi (7) and Suzuki and Yokayama (12)

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