The Melting Point Behavior of Mixtures of the Solid Tetra- and Hexabromides of Linoleic and Linolenic Acids[*]

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BINARY mixtures of the saturated fatty acids have been studied for approximately a hundred years, probably beginning with the work of Heintz in 1854 (1). Schuette has reported solidification point diagrams of the "even" fatty acids from 8 to 36 carbon atoms (2). Similar studies on the unsaturated fatty acids proceeded when satisfactory methods for their purification were developed (3, 4, 5, 6). Smith reported the melting points of binary mixtures of oleic and of elaidic acid with palmitic and stearic acids in 1939 (7), and in 1941 Stewart and Wheeler published the melting points of binary mixtures of oleic, linoleic, and linolenic acids (8). This paper presents the melting point curve of mixtures of the solid tetrabromide of 9,12-cis,cis-linoleic acid with the solid hexabromide of 9,12,15-cis,cis,cis-linolenic acid. Although these solid bromostearic acids are probably racemic mixtures of the d,l- forms, they are usually treated as chemical entities and hence are so treated in this report.

Experimental

The acids were prepared essentially by the method of Rollett (3).

a) *Tetrabromostearic Acid*

Fatty acids were obtained from the saponification of 2 gallons of cottonseed oil (I.V. 114.8; % linoleic 57.0; apparent % linolenic 0.4%) and dissolved in approximately 14 liters of Skellysolve F. Solid acids were filtered off at —10°C. and the filtrate was brominated while the temperature was kept below 0°C. with dry ice. After 30 minutes the excess bromine was discharged with caprylene. The filtered, washed, and dried tetrabromides weighed 1987 g. Recrystallization from 2 gallons of Skellysolve C gave 1780 g. of pure tetrabromide melting at 115.0 to 115.7°C. (cor.). On remelt this was 115.2 to 115.6°C.

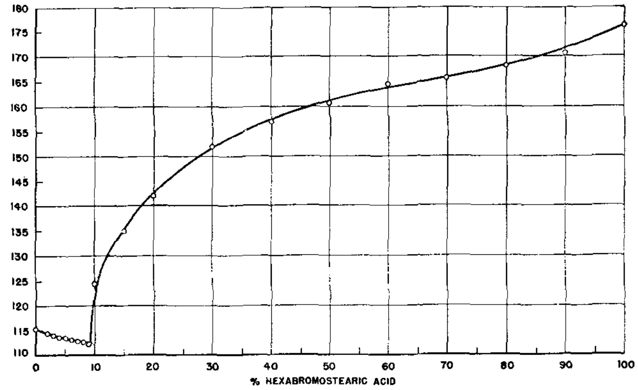
b) *Hexabromostearic Acid*

Commercial distilled linseed oil fatty acids (I.V. 186.1; % linoleic 18.9; % linolenic 50.9) were brominated in a 500-g. batch in 10 liters of U.S.P. ether. The temperature was kept below —10°C. with dry ice. After 30 minutes in contact with excess bromine, the precipitate was filtered and washed. The filter cake was immediately slurried in ether containing dissolved ethylene and allowed to stand overnight to discharge the excess bromine. Filtration and washing gave 195 g. of crude hexabromide. Three recrystallizations from 10 volumes of toluene gave 152 g. melting at 181.2 to 181.8°C. One hundred grams were dissolved in 1,000 ml. of toluene containing 5 g. filter-cel and 5 g. of Norite A and filtered hot. The pure white solid which crystallized from the water-white filtrate melted at 181.7 to 182.0°C. Two more recrystallizations from toluene gave 86 g. of the pure hexabromide melting at 181.7 to 182.4°C. Melting points are all corrected values.

The hexabromide is extremely heat sensitive at or near its melting point. In the above melting points the bath (9) was preheated to 175°C. before immersion of the capillary melting tube and heated at an approximate temperature rise of 1°C. per minute. Doubling of the rate of temperature rise was found to raise the melting point 3°C. This phenomenon probably accounts for the higher melting points reported by some investigators.

FIG. I

MELTING POINT CURVE OF BINARY MIXTURES OF TETRABROMOSTEARIC ACID AND HEXABROMOSTEARIC ACID



The data on mixtures as shown in Figure 1 were obtained on remelts previously fused by dipping the capillary tube for a few seconds in a bath at approximately 10° above the melting point in the manner previously described (10) with the exception that mixtures melting above 175°C. were fused at 185° to minimize the rapid decomposition of the hexabromide. (As in the previous work, the melting point was taken to be the point of disappearance of the last trace of solid.) All mixtures appeared to decompose in the liquid state however. A 10% sample originally remelting at 129.9° showed a second remelt at 125.2°, a third remelt at 120, a fourth remelt at 112.4, and a fifth remelt at 111.5°C. In obtaining the data of Figure 1, capillary tubes containing the resolidified mixtures were immersed in the bath at approximately 10°C. below the melting point, and the bath temperature was raised 1°C. per minute. Compositions reported are per cent by weight.

The remelt curve shows a eutectic point between 9 and 10% hexabromide. Excess hexabromide is almost insoluble in the eutectic mixture. Melting points of the original powdered mixtures were in all cases higher than the remelts, and the eutectic point appeared between 4 and 5% hexabromide. Data are shown in Table I.

It was difficult to obtain reproducible results on the original powdered mixtures since the melting point varied inversely with the amount of mixing and grindings. After fusion and resolidification however additional grinding had no effect on the melting point. This was shown by fusing and resolidifying 1 gram of the 15% powder in a test tube and obtain-

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TABLE I

Melting Points of Mixtures

% Hexabromide	Original Powder	Remelt
100	180.0	176.1
90	174.7	170.5
80	170.1	168.0
70	167.0	165.6
60	165.3	164.4
50	160.7	160.7
40	159.6	157.0
30	154.0	152.2
20	149.3	142.2
15	136.0	135.0
10	129.4	124.4
9	129.8	112.3
8	126.0	112.7
7	122.2	112.9
6	119.3	113.1
5	115.5	113.6
4	114.0	113.6
3	114.3	114.0
2	115.0	114.6
0	115.6	115.3

ing identical remelts on a thoroughly reground powder and on a single chip.

Some evidence was obtained for a low melting form in the case of the 10 and 15% hexabromide mixtures. Upon immersion in the bath the samples appeared to melt almost completely at 10-20° below the final melting point but quickly recrystallized and then did not melt completely until the indicated temperature was reached.

Because of the thermal instability of the hexabromide, the data reported can only be considered rather approximate, but at least accurate enough to define the general nature of the melting point diagram of this system. In their present form the data are not of value for estimating fatty acid composition although with further study an empirical method could possibly be devised.

Summary

1. The melting points of binary mixtures of tetrabromostearic acid and hexabromostearic acid are reported.

2. The system shows a eutectic between 9 and 10% by weight of hexabromide and at a temperature of 112°C.

3. It has been shown that it is necessary to report heating time and rate as well as melting point for hexabromostearic acid because of its extreme sensitivity to heat.

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Report of the Committee on Analysis of Commercial Fats and Oils

Fall Meeting, November 1949

SUBCOMMITTEE ON F.A.C. COLOR STANDARDS, E. W. Blank, chairman: At the fall meeting of the subcommittee in New York (1948) R. C. Stillman offered to forward to the subcommittee data on the spectrophotometric analysis of the F.A.C. color standards. These data, obtained by the collaboration of R. C. Stillman and A. K. Presnell, have been received by the chairman of the subcommittee. They demonstrate in a striking manner that the standards are not uniform with respect either to chromaticity or to optical density. The conclusions to be drawn from these data will be discussed at the fall meeting in Chicago.

At the meeting of the subcommittee in New York (1948) the suggestion was made that possibly the F.A.C. standards could be read through colored filters and compared on a "gray" basis, ignoring chromaticity. On the basis of preliminary experience these suggestions do not appear feasible. Residual chromaticities appear through the filters. The only way to avoid this would be to rebuild the standards, which again is not a feasible project. Work will continue on this problem.

SUBCOMMITTEE ON ANALYSIS OF DRYING OILS, J. C. Konen, chairman: During the past year the subcommittee activities have included collaboration with A.S.T.M. on the determination of hydroxyl value and diene value, a collaborative study of the effect of temperatures on the determination of iodine value, and a check for ash on a group of samples submitted for analysis by the Smalley Foundation. In addition correspondence and discussion were carried out on methods which have been written up and are now being edited for subcommittee approval before submission to the Fat Analysis Committee. These include ash, iodine value, saponification value, and viscosity. A method written up for flash and fire point is being held in abeyance pending results of the subcommittee on Determination of Closed Cup Flash Point.

Although no new methods are being offered this year, it is anticipated that four and possibly five new methods will be submitted to the Fat Analysis Committee during the coming year.

SUBCOMMITTEE ON ANALYSIS OF LECITHIN, H. T. Iveson, chairman: During the period since this committee has last reported, the work has been confined to two projects.

1. *The Determination of the Acid Values of Lecithin.*

The original method which this committee submitted for the analysis for the acid value of lecithin was objected to by certain members because of the choice of the solvent used for the KOH, which was ethyl alcohol. Two other methods have been submitted for approval, one which uses water as the solvent and another which uses isopropyl alcohol as the solvent. The committee is still in the process of checking the