Pure Acid-Free Amides of C_{18} Fatty Acids

Their Preparation and Binary Freezing Point Behavior

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CONSIDERABLE fundamental information has been published on the freezing point behavior of binary and ternary systems of homologous long-chain saturated and unsaturated fatty acids (*4, 7*). This has proved useful in explaining and predicting the feasibility or nonfeasibility of separating the individual acids from their mixtures by crystallization. Except for the work of Guy and Smith (*3*) no data of this kind were found in the literature for the corresponding long-chain fatty acid amides. These authors showed that stearamide forms an equimolar compound with palmitamide. The present paper concerns the freezing point behavior of binary mixtures of stearamide, oleamide, elaidamide, and linoleamide with each other and with some of the corresponding fatty acids.

EXPERIMENTAL

Materials. Highly pure stearic acid, freezing point, 69.3° C.; oleic acid, freezing point, 16.3° C.; and elaidic acid, freezing point, 43.8° C., were prepared by procedures previously described (*5, 6*). Pure linoleic acid, iodine value (Wijs) 180.3, theoretical 181.0, was obtained from the fatty acids of safflower oil by the urea inclusion method of Swern and Parker (*10*) as modified by Fore, O'Connor, and Goldblatt (*1*). The formamide (Eastman Kodak White Label product) was used as such.

Synthesis and Purification of Amides. The pure amides were prepared from the pure acids by a modification of the formamide method of Roe, Scanlan, and Swern (*8*). With the exception of the oleamide, separation of the amide from the unreacted fatty acid by solvent crystallization, even at relatively low yields, proved to be very ineffective. After two crystallizations from chloroform and one from 2-propanol, the stearamide—25% over-all yield—still contained 2.5% of free acid. About 1.8% of free acid remained in the elaidamide after four crystallizations from 95% ethanol and about 2.4% in the linoleamide after four crystallizations from acetone. Removal of this residual acid in the linoleamide by washing with alcoholic potash resulted in marked discoloration.

The pure acid-free amides used for the freezing point measurements were obtained from the crude reaction products by the following procedures. The oleamide was prepared in 65% over-all yield by four crystallizations from acetone: freezing point, 75.9° C., iodine value 90.4, calculated 90.2; N = 4.97%, calculated 4.98%; free acid, 0.0%. The stearamide reaction mixture containing 13.2% of unreacted acid was dissolved in 20 parts by weight of warm cyclohexane and passed through a column of Alorco activated alumina (a mixture of equal parts of Grade F-1, 14- to 30-mesh, and Grade F-20, 80- to 200-mesh). The column was maintained at 65° to 70° C. by an electrically heated jacket to prevent crystallization. After removal of the solvent the product was acid-free. It was crystallized twice from carbon tetrachloride: freezing point 108.9° C., N = 4.96%, calculated 4.94%; free acid, 0.0%; over-all yield, 48%. Pure linoleamide was obtained by dissolving the reaction mixture in about 8 parts by weight of commercial hexane (Skellysolve B) and passing through a column of activated alumina at room temperature. The column had previously been flushed with nitrogen while heated. The product was finally crystallized three times from commercial hexane at about 0° C.: freezing point 60.0° C., N = 5.02%, calculated 5.01%; iodine value 180.4, calculated 181.6; free acid, 0.0%. The elaidamide preparation mentioned above, containing 1.8% of free acid, was dissolved in 30 parts by weight of cyclohexane, passed through a heated alumina column, and crystallized once from this solvent with a 90% recovery: freezing point 91.8° C., N = 4.80%, calculated 4.98%; iodine value 90.4, calculated 90.2; free acid, 0.0%. All crystallizations were performed by the centrifugal filtration method (*9*).

Procedure. The freezing point determinations were made by the thermostatic sealed-tube method (*5*), which involves finding two temperatures a few tenths of a degree apart at which, in one case, liquefaction is complete and, in the other, a few crystals persist after a long period of agitation at constant temperature. The sample tubes were flushed with nitrogen and evacuated before sealing. The technique for determining the equilibrium temperatures of the unstable (low-melting) form of oleic acid has been described (*6*). That no decomposition took place in the sealed samples during the measurements or on storage was proved by the duplicability of the freezing point determinations on the linoleamide and on a few of the oleamide-linoleamide mixtures after a year's storage in a refrigerator. The pure oleamide could be kept in a glass-stoppered bottle at room temperature. Under these conditions, however, the pure linoleamide turned to a brown stickly mass, even when the bottle was filled with nitrogen and stored at 0° C.

RESULTS AND DISCUSSION

Binary freezing point measurements were made for the various amide-amide and amide-acid combinations (Table I and Figure 1). It is apparent from these diagrams that the binary freezing point behavior of these amides varies widely, depending upon the second component. The freezing points of all compositions in the oleamide-linoleamide systems (curve 6) fall on an almost straight line—actually slightly concave downward— connecting the freezing points of the pure substances. This and the fact that all compositions crystallized completely within a very narrow temperature range show definitely that these compounds form an unbroken series of solid solutions. The diagrams for stearamide with oleamide and with linoleamide (curves 2 and 3) indicate in each case the existence of one invariant point, a peritectic representing the equilibrium between the liquid phase and two different solid solutions. The corresponding invariant point in the stearamide-elaidamide diagram (curve 1) is a eutectic lying a few tenths of a degree below the freezing point of the elaidamide, but the two solid phases involved here are also in all probability solid solutions. The system oleamide-elaidamide (curve 5) differs in that an incongruently melting 1 to 1 molecular compound crystallized from liquid compositions containing from 25.3 to 48.8 mole % of elaidamide. This is similar to the behavior of the palmitamide-stearamide system (*3*).

Because the tendency to form solid solutions usually persists in the presence of a solvent, the separation and purification of these amides by crystallization would be expected to be difficult, especially if a nonpolar solvent were used. The pure amides should therefore be prepared from the pure acids.

The diagrams also show that the freezing point is entirely

Table I. Binary Freezing Point Data[a]

A. Linoleamide, B. Oleamide

Mole % B	Freezing Point ° C.
0.00	60.0
9.50	61.7
19.39	63.5
29.90	65.0
39.73	66.6
49.28	68.2
58.99	69.5
70.94	71.4
79.59	72.8
87.98	74.1
100.00	75.9

A. Elaidamide, B. Stearamide

Mole % B	Freezing Point ° C.
0.00	91.8
10.90	91.6
(15.6)[b]	(91.4)[b]
20.85	92.7
31.45	94.7
39.91	97.0
50.88	99.8
61.97	101.8
71.36	103.3
81.21	105.7
91.57	107.5
100.00	108.9

A. Oleamide, B. Stearamide

Mole % B	Freezing Point ° C.
0.00	75.9
2.92	76.1
11.31	76.8
20.57	77.7
(23.8)[c]	(78.0)[c]
30.02	84.1
34.57	87.7
39.71	90.2
44.33	92.1
50.50	95.0
60.11	98.2
79.82	103.8
100.00	108.9

A. Stearic Acid, B. Stearamide

Mole % B	Freezing Point ° C.
0.00	69.3
5.54	68.8
10.31	68.2
(14.2)[b]	(67.7)[b]
20.65	71.8
30.21	77.7
39.89	83.5
49.34	88.9
63.06	96.5
67.34	98.3
69.23	99.2
78.15	102.5
88.93	105.9
100.00	108.9

A. Oleamide, B. Elaidamide

Mole % B	Freezing Point ° C.
0.00	75.9
10.31	74.2
19.52	72.8
(25.3)[b]	(71.7)[b]
30.03	72.5
39.80	73.6
(48.8)[d]	(74.0)[d]
49.93	74.9
60.07	80.3
69.97	83.5
80.09	86.8
89.40	89.2
100.00	91.8

A. Linoleamide, B. Stearamide

Mole % B	Freezing Point ° C.
0.00	60.0
4.95	61.9
7.25	62.8
9.86	61.4
11.43	64.5
(12.0)[c]	(64.6)[c]
29.49	85.7
39.83	90.6
44.57	92.4
51.33	95.2
58.10	97.6
78.55	103.2
88.02	105.6
100.00	108.9

A. Oleic Acid B. Oleamide

Mole % B	Freezing Point ° C.	Mole % B	Freezing Point ° C.
0.00	16.3[e]	43.15	43.1
3.16	15.9[e]	49.62	48.5
(8.0)[b]	(13.2)[b]	59.06	56.3
10.91	18.4	67.57	62.2
19.54	26.5	79.82	68.5
29.98	34.0	89.54	72.3
39.37	40.2	100.00	75.9
(41.3)[d]	(41.4)[d]		

[a] Values in parentheses obtained by graphical extrapolation.
[b] Eutectic. [c] Peritectic. [d] Incongruent melting point.
[e] Freezing point metastable form: 0.00%, 13.5° C.; 3.16%, 13.0° C.; metastable eutectic (by extrapolation) 5.8%, 11.8° C.

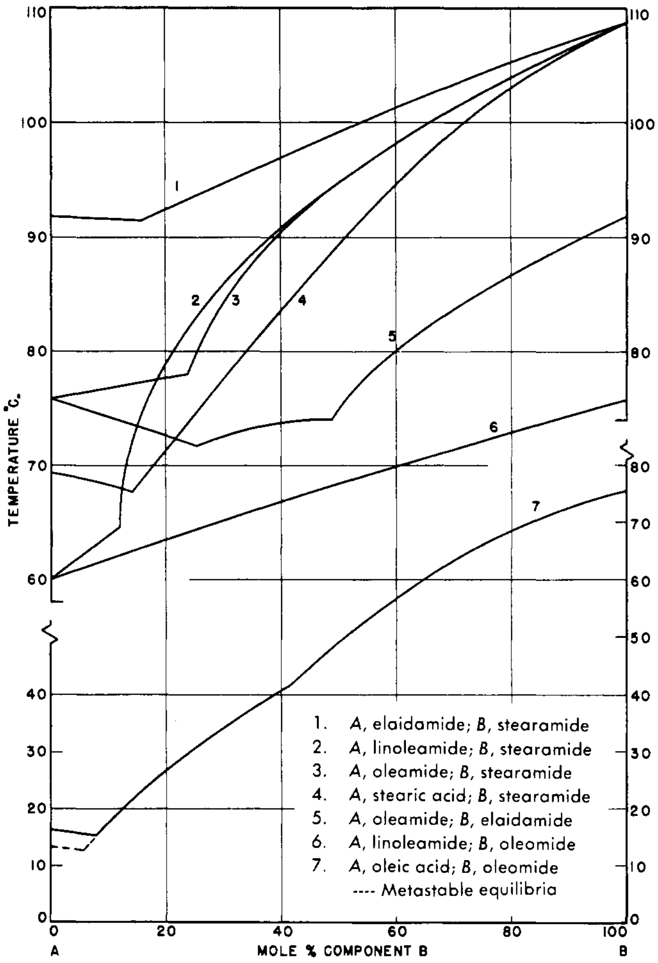

Figure 1. Binary freezing point diagrams

unreliable as a criterion of purity for these unsaturated amides. In fact, some of the expected impurities in oleamide and linoleamide tend to raise the freezing point, and the presence of even 15 mole % of stearamide lowers the freezing point of elaidamide by only a few tenths of a degree, hardly perceptible by the most precise capillary melting point technique.

From the oleamide-elaidamide diagram it is apparent that pure elaidamide cannot be prepared in good yield by the isomerization of oleamide, assuming that the percentage conversion to the trans form is the same (about 67%) as in the isomerization of oleic acid. The maximum theoretical yield of pure elaidamide would be about 50% of that present in the equilibrium mixture. The corresponding figure for the yield of elaidic acid from oleic acid, calculated on the basis of the binary freezing point diagram for these two acids (2), is about 95%.

The binary diagram for stearamide with stearic acid (curve 4) shows only one invariant point, a eutectic, in addition to those for the pure compounds. The system oleamide-oleic acid (curve 7), on the other hand, exhibits three invariant points. Two of these are eutectics, between oleamide and the stable and metastable modifications of oleic acid, respectively. The third represents the incongruent melting point of a 1 to 1 molecular compound which crystallizes from liquid compositions containing from 8.0 to 41.3 mole % oleamide. It has been shown that acetamide forms equimolecular compounds with both stearic and oleic acids (5, 6). The fact that oleamide forms an equimolecular compound with oleic acid, therefore, suggests the probability that a similar 1 to 1 compound exists in the liquid mixtures of stearic acid and stearamide, but that its concentration never exceeds its solubility.

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