mixture on a usable tie line, however, would have apparently required the use of a weight ratio in Equation 1 which would have caused an excessive extrapolation error. This difficulty was resolved by the use of working mixtures which placed the resultant mixtures in the other two-phase region of the system, where NaCl was the solid phase. The first addition of a working mixture to I_{lU4} appeared from visual observation to give a resultant mixture lying in the one-phase region, which was not usable for application of the method. To bring the latter into the two-phase region, however, it was necessary only to add a small additional measured amount of NaCl. Like considerations applied from I_{lU6} to I_{lU9}, only the first being located by resultant mixtures lying in the same two-phase region containing the former. This effect was caused by the shorter NaCl solubility curve.

When a resultant mixture lies in a two-phase region other than that containing the point located, a larger value of the weight ratio in Equation 1 may be tolerated than that recommended previously (*3*), because the slopes of the concerned tie lines may then be so different that errors of extrapolation are rendered relatively small. Thus in the present study weight ratios greater than 2 gave acceptable results under such circumstances.

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Binary Freezing Point Behavior of Some *N*-Substituted Amides of Palmitic, Stearic, Oleic, and Linoleic Acids

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THE FREEZING point behavior of long chain fatty amides and their binary mixtures is markedly affected by their high degree of association (*8*). The formation of a crystalline equimolar compound in the system stearamide-palmitamide, shown by the freezing point data of Guy and Smith (*2*) might, for example, be attributed to this strong tendency for hydrogen bonding between two amido groups. Association complexes are also involved in the solid-liquid equilibria of the oleamide-linoleamide system (*6*) which exhibits a continuous series of solid solutions.

Mascarelli and Benati (*4*) and Meldrum and Turner (*5*) observed that the substitution of both hydrogens in the amide group eliminated the tendency for association in solution, as indicated by the fact that such derivatives exhibited normal molecular weights. The present report deals with the freezing point data for the binary systems *N*-benzyloleamide–*N*-benzyllinoleamide, *N*-cyclohexyloleamide–*N*-cyclohexyllinoleamide, and *N*-benzylpalmitamide–*N*-benzylstearamide; i.e., for mixtures of compounds in which one of the amido hydrogens has been substituted, and also for the system *N*-stearoylmorpholine–*N*-palmitoylmorpholine, in which both of the amido hydrogens have been substituted.

EXPERIMENTAL

Materials. Highly pure palmitic acid, freezing point, 62.5° C., stearic acid, freezing point, 69.3° C., and oleic acid, freezing point, 16.3° C., were prepared by procedures previously described (*3, 7*). 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 (*9*) as modified by Fore, O'Connor, and Goldblatt (*1*). The benzylamine, morpholine, and cyclohexylamine were reagent grade or Eastman Kodak (White Label) products.

Synthesis and Purification of the Substituted Amides. The *N*-substituted amides were prepared by refluxing the pure fatty acid with a 50% excess of amine in the presence of a catalyst using benzene or toluene as an entraining liquid. The preparation of *N*-cyclohexyllinoleamide is typical of the general procedure. A mixture of 28.0 grams (0.1 mole) of linoleic acid, 14.8 grams of cyclohexylamine (0.15 moles), 3 grams of Amberlite IRA-400 resin, and 25 ml. of toluene was refluxed in an apparatus equipped with a stirrer and a Dean-Stark trap until water was no longer evolved. The resin was removed by filtration and the mixture stripped under a stream of nitrogen at reduced pressure. The crude product was dissolved in commercial hexane and passed through a column of Alorco activated alumina (equal parts of Grade F-1, 14- to 30-mesh, and Grade F-20, 80- to 200-mesh) at room temperature or at about 60° C. depending upon the solubilities. After removal of solvent, the product was crystallized six times from absolute methanol. The crude *N*-benzyloleamide and *N*-benzyllinoleamide reaction products were purified by solvent crystallization alone, omitting percolation through alumina.

The resulting *N*-substituted amides were shown by titration to be acid-free and had the following properties (calculated values in parentheses): *N*-Benzyloleamide, f.p., 58.8° C.; I.V. (Iodine Value, Wijs), 68.3 (68.3); C, 80.52% (80.80%); H, 10.90% (11.12%); N, 3.76% (3.77%). *N*-Benzyllinoleamide, f.p., 35.8° C.; I.V., 137.0 (137.3); C, 81.17% (81.24%); H, 10.64% (10.64%); N, 3.73% (3.79%). *N*-Cyclohexyloleamide, f.p., 48.7° C.; I.V., 70.0 (69.8); C, 79.61% (79.28%); H, 12.54% (12.47%); N, 3.84%

(3.85%). *N*-Cyclohexyllinoleamide, f.p., 32.2° C.; I.V., 140.4 (140.4); C, 79.69% (79.71%); H, 12.05% (11.99%); N, 3.84% (3.87%). *N*-Benzylpalmitamide, f.p., 95.1° C.; C, 79.32% (79.93%); H, 10.90% (11.39%); N, 4.02% (4.05%). *N*-Benzylstearamide, f.p., 99.2° C.; C, 80.61% (80.37%); H, 11.61% (11.51%); N, 3.74% (3.75%). *N*-Palmitoylmorpholine, f.p., 43.8° C.; C, 74.10% (73.79%); H, 12.30% (12.08%); N, 4.31% (4.31%). *N*-Stearoylmorpholine, f.p., 52.3° C.; C, 74.67% (74.72); H, 12.36% (12.26%); N, 3.96% (3.99%).

Procedure. The freezing point determinations were made by the thermostatic sealed tube method (*3*) 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.

RESULTS AND DISCUSSION

The results are given in Table I and represented graphically in Figure 1. Binary diagrams (II and IV) for *N*-monosubstituted systems *N*-benzyloleamide–*N*-benzyllinoleamide and *N*-cyclohexyloleamide–*N*-cyclohexyllinoleamide are both of the simple eutectic type and thus differ from that for the oleamide-linoleamide system (*6*), which is represented by an almost straight line connecting the freezing points of the two pure components. The binary freezing point behavior for the *N*-monosubstituted system *N*-benzylpalmitamide–*N*-benzylstearamide (Diagram I), on the other hand, is very similar to that for the palmitamide-stearamide system, showing equimolar compound formation with the eutectics at 33.0 and 56.9 mole % (89.1° and 90.4° C.) as compared to about 33 and 56 mole % for the unsubstituted amide system (*2*). The binary system *N*-stearoylmorpholine–*N*-palmitoylmorpholine (Diagram III) also exhibits a 1:1 molecular compound, melting incongruently with a eutectic at 18.8% stearoylmorpholine (40.3° C.) and a peritectic at 46.8% (41.6° C.) in spite of the fact that both of the amido hydrogens are substituted.

A knowledge of the freezing point behavior of such binary systems is often useful in selecting the best procedure for preparing the highly pure substances when purification is by crystallization. The formation of solid solutions or of molecular compounds usually persists in the presence of a solvent. The separation and purification of oleamide and linoleamide would be expected to be very difficult, since they form a continuous series of mixed crystals (*6*). Thus, the pure amides could be prepared to best advantage from the pure acids. It would be expected from the results above, on the other hand, that the *N*-benzyl and the *N*-cyclohexyl derivatives of oleamide and linoleamide could be prepared from less pure acids and purified satisfactorily at the final stage.

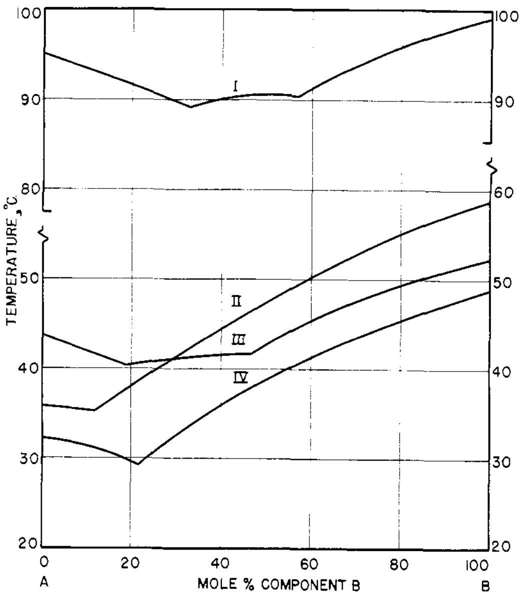

Figure 1. Binary freezing point diagrams

I. A,*N*-benzylpalmitamide; B,*N*-benzylstearamide
II. A,*N*-benzyllinoleamide; B,*N*-benzyloleamide
III. A,*N*-palmitoylmorpholine; B,*N*-stearoylmorpholine
IV. A,*N*-cyclohexyllinoleomide; B,*N*-cyclohexyloleamide

Table I. Binary Freezing Point Data[a]

B, Mole %	Freezing Point, ° C.	*B*, Mole %	Freezing Point, ° C.
A. *N*-Benzyllinoleamide *B*. *N*-Benzyloleamide		*A*. *N*-Cyclohexyllinoleamide *B*. *N*-Cyclohexyloleamide	
0.00	35.8	0.00	32.2
9.76	35.3	10.71	31.3
(11.8)[b]	(35.2)[b]	15.96	30.4
15.12	36.5	(21.4)[b]	(29.2)[b]
19.50	37.6	22.53	29.8
29.77	41.3	30.45	32.7
40.08	44.6	37.34	35.2
50.68	47.8	50.89	38.7
61.61	50.7	60.55	41.4
69.55	52.8	70.61	43.7
80.33	55.0	80.26	45.6
90.52	56.9	90.94	47.5
100.00	58.8	100.00	48.7
A. *N*-Benzylpalmitamide *B*. *N*-Benzylstearamide		*A*. *N*-Palmitoylmorpholine *B*. *N*-Stearoylmorpholine	
0.00	95.1	0.00	43.8
11.32	92.8	9.97	41.7
21.90	91.4	13.91	41.4
31.69	89.4	(18.8)[b]	(40.3)[b]
(33.0)[b]	(89.1)[b]	20.36	40.5
40.43	90.1	30.57	41.0
50.00	90.6	40.03	41.6
(56.9)[b]	(90.4)[b]	(46.8)[c]	(41.6)[c]
59.25	91.1	50.17	42.8
70.55	94.0	60.02	45.2
79.55	95.8	70.28	47.7
88.91	97.4	80.44	49.6
100.00	99.2	90.01	51.0
		100.00	52.3

[a] Values in parentheses obtained by graphical extrapolation.
[b] Eutectic.
[c] Incongruent melting point.

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