# Binary Freezing-Point Diagrams for Palmitic Acid With Various Amines and With 2,6-Dimethyl-Gamma-Pyrone

ROBERT R. MOD, FRANK C. MAGNE, and EVALD L. SKAU, Southern Regional Research Laboratory,[1] New Orleans, Louisiana

RECENT PUBLICATIONS from this laboratory describe the purification of long-chain fatty acids by recrystallization of their molecular compounds with acetamide (1) or with certain amines (2). In the course of the development of these methods considerable information was obtained by binary freezing-point measurements and solvent crystallization on the tendency of long-chain fatty acids to form molecular compounds with a number of amides (3, 4) and amines (5, 6, 7). The present communication deals with binary freezing-point data for palmitic acid with benzylamine, morpholine, 3-aminopyridine, 4-aminopyridine, 2-aminothiazole, 4-amino-2,6-dimethylpyrimidine, ortho-phenylenediamine, and alpha-picoline. The system with 2,6-dimethyl-gamma-pyrone was also included since this is known to form molecular compounds with a number of organic acids (8).

## Experimental

The pure palmitic acid was prepared by the method previously described (3). The alpha-picoline was purified by shaking with sodium hydroxide pellets and fractionally distilling through a 30-plate Oldershaw column protected from moisture and carbon dioxide. Only the middle portion of the distillate was used. The pure benzylamine and morpholine salts of palmitic acid were obtained by repeated recrystallization of equimolar acid-amine mixtures from benzene and acetone, respectively (7). The 2,6-dimethyl-gamma-pyrone and the remaining amines were purified by fractional solvent crystallization. However the 3-aminopyridine, 4-aminopyridine, and ortho-phenylenediamine were first vacuum-sublimed.

The freezing points were determined by the thermostatic sealed-tube method previously described (3), which gives the true equilibrium temperature between the crystals and the liquid of the given composition with a precision of ± 0.2°C. after correction for thermometer calibration and emergent stem. For each composition weighed amounts of palmitic acid and the amine were sealed in a glass tube under vacuum. The compositions up to 50% of amine in the benzylamine and morpholine systems were prepared from palmitic acid and the pure 1:1 amine salt. For the higher concentrations of amine in the morpholine system and for all the concentrations in the alpha-picoline system, appropriate amounts of palmitic acid were weighed into the tubes, and the amine was then added by means of an automatic micro-burette. All precautions were taken to exclude moisture and carbon dioxide. The tubes were then chilled to −78°C., evacuated, and sealed.

## Results and Discussion

The freezing-point data for the various binary systems with palmitic acid are given in Table I. The systems involving compound formation are represented graphically in Figure 1.

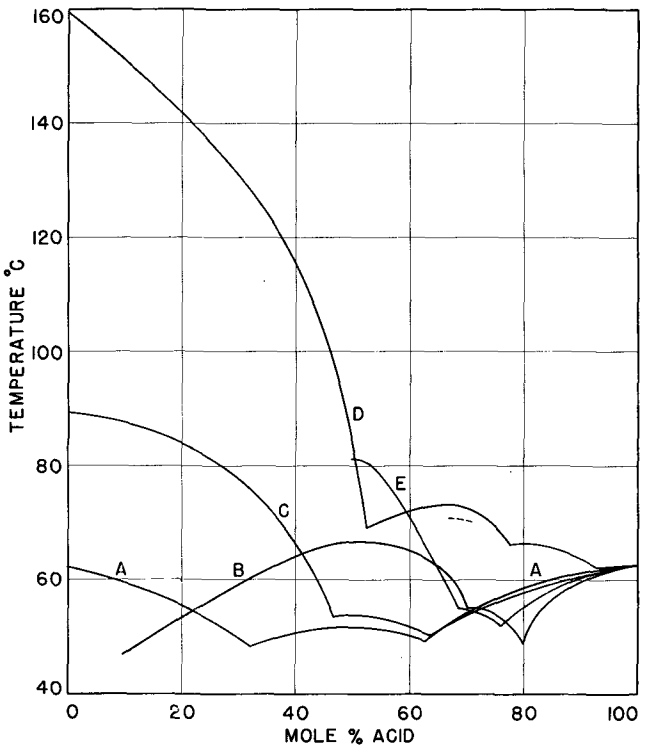


FIG. 1. Binary freezing-point diagrams for palmitic acid with A, 3-aminopyridine; B, morpholine; C, 2-aminothiazole; D, 4-aminopyridine; E, benzylamine.

The position of the amino group in the pyridine ring has a marked effect on the binary freezing-point behavior of the aminopyridines. As previously reported (5), 2-aminopyridine forms two crystalline molecular compounds with palmitic and other saturated fatty acids, one being an equimolar compound and the other containing 4 moles of acid to one of amine. It is apparent from Figure 1 that 3-aminopyridine forms only a 1:1 crystalline molecular compound (f.p. 51.8°C.) with palmitic acid. 4-Aminopyridine, on the other hand, forms a 4:1 compound (f.p. 66.5°C.), also a 2:1 compound which exists in two polymorphic forms (f.p. 73.2°C. and 70.8°C., respectively). Both polymorphic forms were obtained in the binary compositions containing 68.31 and 70.62 mole % of acid (see curve D and broken line in Figure 1). The low-melting form crystallized directly from the melt, and the high-melting form was obtained by chilling the melt suddenly to −78°C. All of the above molecular compounds have congruent melting points.

The absence of a crystalline 1:1 compound in the 4-aminopyridine system does not, of course, imply that this compound does not exist in liquid binary mixtures. The fact that 4-aminopyridine rather than the 1:1 compound crystallizes from an equimolar acid-amine mixture can be explained either by the relatively high freezing-point and therefore the relatively low solubility of 4-aminopyridine or by a low concentration of the 1:1 compound in the liquid

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

TABLE I
Binary Freezing Point Data for Various Palmitic Acid Systems [a]

| Mole % acid | Freezing point, °C. | Mole % acid | Freezing point, °C. | Mole % acid | Freezing point, °C. |
|---|---|---|---|---|---|
| Morpholine | | 4-Aminopyridine | | 3-Aminopyridine | |
| 9.77 | 47.2 | 0.00 | 159.6 | 0.00 | 62.3 |
| 15.09 | 50.8 | 10.41 | 150.1 | 9.99 | 59.2 |
| 19.94 | 53.9 | 19.97 | 142.7 | 19.38 | 56.2 |
| 26.88 | 57.1 | 30.35 | 130.3 | 29.88 | 49.7 |
| 33.67 | 61.2 | 35.23 | 123.9 | (31.9)[b] | (48.3)[b] |
| 50.00[c] | 66.7[c] | 40.08 | 114.9 | 35.10 | 49.6 |
| 55.12 | 66.5 | 44.74 | 104.2 | 40.43 | 50.9 |
| 64.15 | 62.9 | 47.47 | 94.2 | 47.38 | 51.7 |
| 65.41 | 62.5 | (52.5)[b] | (69.4)[b] | 48.73 | 51.7 |
| 69.24 | 57.3 | 53.38 | 69.5 | (50.00)[c] | (51.8)[c] |
| 69.95 | 55.7 | 55.88 | 70.4 | 55.07 | 51.4 |
| (70.0)[d] | (55.3)[d] | 59.53 | 71.7 | 58.72 | 50.6 |
| 71.81 | 55.1 | 64.98 | 73.0 | (62.6)[b] | (49.5)[b] |
| 73.77 | 54.5 | (66.66)[e] | (73.2)[e, f] | 65.67 | 51.9 |
| 75.28 | 53.9 | 68.31 | 73.1[g] | 71.51 | 55.3 |
| 77.85 | 51.8 | 69.84 | .....[h] | 78.37 | 58.2 |
| (79.9)[b] | (49.1)[b] | 70.62 | 72.5[i] | 85.72 | 60.4 |
| 80.12 | 50.0 | 74.40 | 70.0 | 100.00 | 62.5 |
| 82.18 | 53.7 | (77.8)[b] | (66.1)[b] | | |
| 87.12 | 58.1 | (80.00)[j] | (66.5)[j] | | |
| 90.61 | 59.9 | 80.19 | 66.5 | | |
| 100.00 | 62.5 | 85.31 | 65.2 | | |
| | | 88.23 | 64.4 | | |
| | | (93.1)[b] | (62.1)[b] | | |
| | | 94.84 | 62.3 | | |
| | | 96.94 | 62.4 | | |
| 4-Amino-2,6-dimethylpyrimidine | | o-Phenylenediamine | | Alpha-picoline | |
| 0.00 | 183.5[k] | 0.00 | 101.2 | 41.67 | 32.9 |
| 20.39 | 174.0[l] | 9.97 | 98.6 | 50.08 | 43.4 |
| 40.55 | 149.3 | 19.99 | 96.6 | 56.66 | 47.7 |
| 49.73 | 131.9 | 29.96 | 94.3 | 70.69 | 55.0 |
| 53.52 | 122.5 | 40.00 | 90.8 | 82.10 | 58.5 |
| 62.14 | 88.6 | 49.98 | 85.5 | 100.00 | 62.5 |
| 67.89 | 66.2 | 59.84 | 77.0 | | |
| (70.9)[b] | (51.2)[b] | 70.03 | 63.1 | | |
| 76.93 | 55.2 | (72.8)[b] | (58.6)[b] | | |
| 86.98 | 60.2 | 80.02 | 60.0 | | |
| 100.00 | 62.5 | 89.94 | 61.3 | | |
| Benzylamine | | 2-Aminothiazole | | 2,6-Dimethyl-gamma-pyrone | |
| 50.00[c] | 81.2[c] | 0.00 | 89.4 | 0.00 | 133.3 |
| 55.12 | 77.4 | 19.82 | 83.8 | 10.18 | 127.7 |
| 60.51 | 69.8 | 30.13 | 77.9 | 19.50 | 121.8 |
| 65.26 | 61.6 | 39.27 | 67.2 | 30.18 | 112.9 |
| 67.03 | 58.1 | 44.88 | 57.7 | 39.33 | 102.2 |
| (68.4)[d] | (55.4)[d] | (46.6)[b] | (53.6)[b] | 45.12 | 93.9 |
| 69.90 | 55.3 | 48.96 | 53.7 | 49.12 | 87.3 |
| 71.54 | 54.5 | (50.00)[c] | (53.8)[c] | 55.65 | 76.3 |
| 74.81 | 53.1 | 54.15 | 53.3 | 60.69 | 67.0 |
| (76.0)[b] | (52.1)[b] | 58.81 | 52.3 | (66.1)[b] | (54.9)[b] |
| 79.97 | 55.0 | (63.5)[b] | (50.4)[b] | 68.53 | 56.2 |
| 84.90 | 58.2 | 68.63 | 53.2 | 75.27 | 57.7 |
| 89.89 | 60.2 | 73.18 | 55.4 | 80.10 | 59.3 |
| 100.00 | 62.5 | 79.06 | 57.3 | 83.11 | 59.9 |
| | | 82.58 | 58.7 | 100.00 | 62.5 |
| | | 88.03 | 60.3 | | |

[a] The values in parentheses were obtained by graphical interpolation or extrapolation.
[b] Eutectic.
[c] Equimolar compound.
[d] Incongruent melting point of 2:1 compound.
[e] 2:1 compound.
[f, g, h, i] Equilibrium temperatures with low melting modification of 2:1 compound were 70.8°, 70.7°, 70.5°, and 70.3°C., respectively.
[j] 4:1 compound.
[k] Capillary melting point 183.4–183.7°C.
[l] Capillary melting point, completely melted at 174°C.

mixture. It seems likely that in the liquid phase of any of these acid-aminopyridine compositions 1:1, 2:1, and 4:1 compounds may all be present in equilibrium with the free acid and amine. That the composition of the crystals formed depends upon the specific acid as well as the specific amine used is shown by the fact (5) that 2-aminopyridine gives a crystalline 2:1 compound instead of the 4:1 compound, with mono- and polyunsaturated $C_{18}$ fatty acids.

A 2:1 compound, in addition to the equimolar compound, is formed in the benzylamine and morpholine systems. Both these 2:1 compounds have incongruent melting points (55.4° and 55.3°C., respectively) and therefore cannot be prepared by the simple method of mixing the components in the stoichiometric proportions. The 2-aminothiazole diagram shows no indication of any but the 1:1 compound (f.p. 53.8°C.). 4-Amino-2,6-dimethylpyrimidine, ortho-phenylenediamine, alpha-picoline, and 2,6-dimethyl-gamma-pyrone give simple eutectic diagrams.

If all the substances investigated formed ideal solutions with palmitic acid, the freezing point in the range where palmitic acid is the solid phase would be a function only of the mole fraction of palmitic acid present in the mixture and would be independent of the added component, i.e., the palmitic acid branches of the diagrams in Figure 1 would all coincide. The fact that they do not coincide can be attributed mainly to two counteracting effects: a) the presence in the liquid of molecular compounds, particularly those containing greater than equimolar parts of acid, which tend to cause freezing points lower than the ideal and b) the molecular association of the second component, which tends to cause higher freezing points. Since these effects vary with concentration and since the degrees of association and the amount of compound formed are unknown, no quantitative deductions can be made. However it is apparent that morpholine and benzylamine, which are both relatively strong bases and form 2:1 as well as 1:1 compounds, cause the greatest lowering of the palmitic acid freezing-point as would be expected. On the other hand, the fact that 4-aminopyridine causes only a slight lowering in spite of the fact that it forms both 4:1 and 2:1 molecular compounds with the acid probably indicates that association of the amine may be the predominating factor in this system and that the molecular compounds here are more highly dissociated.

## Summary

In connection with the search for molecular compounds which might prove applicable in the purification of long-chain fatty acids, freezing-point data have been obtained for binary systems between palmitic acid and the following: ortho-phenylenediamine, alpha-picoline, 4-amino-2,6-dimethylpyrimidine, 2,6-dimethyl-gamma-pyrone, 2-aminothiazole, benzylamine, morpholine, 3-aminopyridine, and 4-aminopyridine. The freezing-point diagrams for the first four of these binary systems are of the simple eutectic type. All the others indicate the existence of at least one crystalline molecular compound containing one or more moles of palmitic acid to one of amine. 2-Aminothiazole forms an equimolar compound. Both benzylamine and morpholine form an equimolar and an incongruently melting 2:1 compound. The position of the amino group in the pyridine ring has a marked effect on the behavior of the aminopyridines. Unlike 2-aminopyridine, which forms a 1:1 and a 4:1 compound with palmitic acid, 3-aminopyridine forms only an equimolar compound and 4-aminopyridine forms only 4:1 and 2:1 compounds. The latter exists in two polymorphic modifications.

REFERENCES

1. Magne, F. C., Mod, R. R., and Skau, E. L., J. Am. Oil Chemists' Soc., *34*, 127–129 (1957); Skau, E. L. (to Secretary of Agriculture), U. S. Patent 2,816,903 (1957).
2. Magne, F. C., Skau, E. L., and Mod, R. R. (to Secretary of Agriculture), U. S. Patent 2,791,596 (1957); Magne, F. C., Mod, R. R., and Skau, E. L., J. Am. Oil Chemists' Soc., *35*, 477–479 (1958).
3. Magne, F. C., and Skau, E. L., J. Am. Chem. Soc., *74*, 2628–2630 (1952).
4. Magne, F. C., Hughes, E. J., Mod, R. R., and Skau, E. L., J. Am. Chem. Soc., *74*, 2793–2795 (1952); Mod, R. R., and Skau, E. L., J. Phys. Chem., *56*, 1016–1017 (1952); Mod, R. R., Skau, E. L., and Planck, R. W., J. Am. Oil Chemists' Soc., *30*, 368–371 (1953).
5. Mod, R. R., and Skau, E. L., J. Phys. Chem., *60*, 963–965 (1956).
6. Mod, R. R., Magne, F. C., and Skau, E. L., J. Phys. Chem., *60*, 1651–1654 (1956).
7. Mod, R. R., Magne, F. C., and Skau, E. L. (in manuscript).
8. Kendall, J., J. Am. Chem. Soc., *36*, 1222–1243 (1914)

[Received September 4, 1958]