# Binary Freezing Point Behavior of Some Saturated and Unsaturated Fatty Acid Methyl Esters With Methyl Heptadecanoate

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## ABSTRACT

The binary freezing point behavior of methyl heptadecanoate with methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl elaidate and methyl petroselaidate have been determined. Both stable and metastable polymorphic forms were observed. Methyl laurate formed a simple eutectic with a region of metastable equilibrium. Methyl myristate formed a simple eutectic of stable equilibrium and a solid solution of metastable equilibrium. Methyl palmitate exhibited a solid solution of metastable equilibrium terminating in a eutectic and a region of discontinuous stable equilibrium. Methyl stearate formed a solid solution of metastable equilibrium and also continuous stable equilibrium which formed an incongruently melting molecular compound that terminated in a eutectic point. Methyl heptadecanonate with the unsaturated eighteen carbon atom acid methyl esters exhibited only simple eutectic points and a small region of metastable equilibrium. The binary freezing point behavior of the methyl esters in general resemble that of the corresponding ethyl esters. The limited results of mixtures of methyl esters of an odd carbon acid with unsaturated acids indicate an induced stabilizing effect caused by unsaturation in the carbon chain.

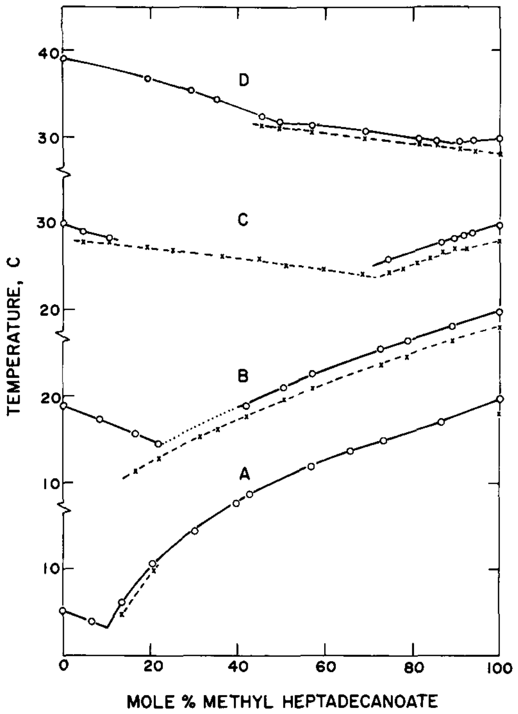

FIG. 1. Binary freezing point diagrams for methyl heptadecanoate with A, methyl laurate; B, methyl myristate; C, methyl palmitate; and D, methyl stearate. Broken lines represent metastable form.

## INTRODUCTION

Binary mixtures of the long chain fatty acids have been extensively investigated, particularly with regard to freezing point (1). Mutual solubility data have also been reported for the methyl and ethyl esters, but only for a selected few of the most common higher melting acids (2). Of the ester systems investigated, the ethyl esters have received the most attention due in part to their obvious dimorphic character. Binary freezing point data have been reported for ethyl esters of both odd and even carbon numbered saturated acids. The methyl esters, on the other hand, have received almost no attention. Methyl palmitate-methyl stearate, methyl laurate-methyl myristate and methyl stearate-methyl behenate to date are the only methyl ester systems to have been investigated (3-5). Since the methyl esters of the saturated acids are also reported to be dimorphic (6) their binary mixture should be expected to exhibit some of the characteristics of the corresponding ethyl ester systems. The present report concerns the mutual solubility behavior of methyl heptadecanoate with methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl elaidate and methyl petroselaidate.

## EXPERIMENTAL PROCEDURES

Methyl stearate, methyl heptadecanoate, methyl palmitate, methyl myristate and methyl laurate were recrystallized materials obtained by fractional distillation. The methyl elaidate and methyl petroselaidate were recrystallized materials prepared from the highly pure acids. The freezing points of the saturated esters, determined by the thermostatic sealed tube method (7), were as follows: methyl stearate, 38.9 C; methyl heptadecanoate, 28.1 and 29.8 C; methyl palmitate, 29.8 C; methyl myristate, 19.0 C;

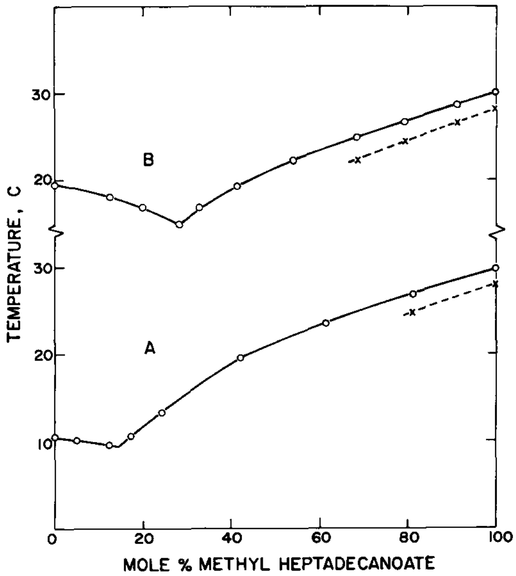

FIG. 2. Binary freezing point diagrams for methyl heptadecanoate with A, methyl elaidate and B, methyl petroselaidate. Broken lines represent metastable form.

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and methyl laurate, 5.2 C. The freezing points for methyl elaidate, 10.27 C, and methyl petroselaidate, 19.06 C, were determined by the method of heating curves (8) with a calibrated thermocouple.

Binary freezing points, obtained by the thermostatic sealed tube method, represent the true equilibrium temperature between the crystals and the melt to within ±0.2. The apparatus used has been previously described (7).

The metastable forms were obtained by slowly lowering the temperature of the completely melted sample until crystals first appear and then raising the temperature in approximately 0.2 C increments, allowing sufficient time for the mixture to come to equilibrium, until the last crystal disappears. The metastable form (transparent crystals) at certain concentrations would only partially melt and then begin to convert over to the higher melting stable form (opaque crystals). This conversion was influenced greatly by concentrations and in many instances was too rapid to allow for the determination of an equilibrium temperature. Shock chilling of the sample in a dry ice-acetone mixture, followed by a slow rise in temperature, almost always resulted in the formation of the stable modification.

## RESULTS AND DISCUSSION

In Table I are tabulated the freezing point data for the binary systems of methyl heptadecanoate and the methyl esters of the even carbon-numbered saturated acids. The data are shown graphically in Figure 1. The full lines represent the temperature at which the various liquid compositions are in equilibrium with the stable polymorphic modification. The broken lines represent the corresponding metastable equilibria. The tendency toward compound formation increases as the chain length of the even numbered carbon ester increases. Methyl laurate (Figure 1, A) forms a simple eutectic whereas methyl stearate (Figure 1, D) exhibits compound formation. In the methyl laurate system a eutectic is formed at 3.1 C and 10.1% methyl heptadecanoate. The metastable form of methyl heptadecanoate was obtained only in the concentration range between 13% and 21% adjacent to the eutectic composition. An increase in chain length of two $-CH_2-$ groups, the methyl myristate-methyl heptadecanoate system (Figure 1, B) results in the formation of a solid solution of the metastable form of methyl heptadecanoate with the methyl myristate extending from about 11.0 C and 16.5% to the melting point of methyl heptadecanoate. It should be noted that the curve for the stable modification is discontinuous from about the eutectic point (14.5 C, 21%) to approximately 40% methyl heptadecanoate. For the methyl palmitate system the stable forms of methyl palmitate and methyl heptadecanoate were obtained only for compositions between 0% and 10% and between 75% and 100% methyl heptadecanoate, respectively. The metastable (low melting) forms of the two esters exhibited a eutectic at 23.8 C and 71.5% methyl heptadecanoate. The freezing point of the low melting form of pure methyl palmitate was not realized. In the methyl stearate-methyl heptadecanoate system (Fig. 1, D) in which the even ester has the longer chain length (18 vs. 17 carbon atoms) a series of solid solutions are formed between the metastable forms of the methyl heptadecanoate and the methyl stearate. This solid solution range extends from about 31.5 C and 45% methyl heptadecanoate to the freezing point of the metastable form of methyl heptadecanoate. Unlike the methyl palmitate system, a 1:1 molecular compound is formed, melting congruently at about 31.6 C to form a eutectic at 29.4 C and 89% methyl heptadecanoate. In the latter case, the eutectic is formed with the stable forms of methyl heptadecanoate and methyl stearate.

TABLE I

Binary Freezing Point Data

| Mole % $C_{17}$ | $C_{17}$-$C_{12}$, Temperature C | | Mole % $C_{17}$ | $C_{17}$-$C_{14}$, Temperature C | | Mole % $C_{17}$ | $C_{17}$-$C_{16}$ Temperature C | | Mole % $C_{17}$ | $C_{17}$-$C_{18}$ Temperature C | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Metastable | Stable | | Metastable | Stable | | Metastable | Stable | | Metastable | Stable |
| 0.00 | --- | 5.2 | 0.00 | --- | 19.0 | 0.00 | --- | 29.8 | 0.00 | --- | 38.9 |
| 6.47 | --- | 7.8 | 8.12 | --- | 17.4 | 4.18 | 28.0 | 29.0 | 19.47 | --- | 36.6 |
| 10.1[a] | --- | 3.1[a] | 16.52 | 11.3 | 15.7 | 10.52 | 27.8 | 28.5 | 29.42 | --- | 35.3 |
| 13.41 | 4.5 | 6.3 | 21.72 | 12.8 | 14.6 | 19.43 | 27.4 | --- | 35.33 | --- | 34.4 |
| 20.44 | 9.9 | 10.7 | 22.2[a] | --- | 14.5[a] | 25.30 | 26.9 | --- | 45.71 | 31.4 | 32.5 |
| 30.14 | --- | 14.4 | 31.45 | 15.3 | --- | 36.67 | 26.2 | --- | 49.71 | 31.1 | 31.7 |
| 39.76 | --- | 17.7 | 35.40 | 16.3 | --- | 45.10 | 25.8 | --- | 50.0[b] | --- | 31.6[b] |
| 42.98 | --- | 18.4 | 42.00 | 17.9 | 19.1 | 50.81 | 25.2 | --- | 57.35 | 30.6 | 31.4 |
| 56.95 | --- | 22.0 | 50.53 | 19.7 | 21.1 | 59.73 | 24.8 | --- | 69.15 | 29.9 | 30.7 |
| 65.56 | --- | 23.7 | 57.19 | 21.0 | 22.7 | 68.19 | 24.0 | --- | 81.43 | 29.2 | 29.8 |
| 73.18 | --- | 25.0 | 72.67 | 23.8 | 25.6 | 71.5[a] | 23.8[a] | --- | 85.44 | 29.0 | 29.5 |
| 86.62 | --- | 27.1 | 78.71 | 24.9 | 26.5 | 74.34 | 24.6 | 25.8 | 89.0[a] | --- | 29.4[a] |
| 100.00 | 28.1 | 29.8 | 89.05 | 26.6 | 28.3 | 77.63 | 25.0 | --- | 90.45 | 28.7 | 29.6 |
| | | | 100.00 | 28.1 | 29.8 | 80.91 | 25.4 | 26.2 | 93.94 | 28.4 | 29.7 |
| | | | | | | 83.98 | 26.6 | --- | 100.00 | 28.1 | 29.8 |
| | | | | | | 86.77 | 26.9 | 28.0 | | | |
| | | | | | | 89.62 | 27.0 | 28.3 | | | |
| | | | | | | 91.65 | 27.2 | 28.7 | | | |
| | | | | | | 93.64 | --- | 29.0 | | | |
| | | | | | | 100.00 | 28.1 | 29.8 | | | |

[a] Eutectic point by extrapolation.

[b] Congruently melting 1:1 molecular compound.

TABLE II

Binary Freezing Point Data

| | $C_{17}$-$C_{18}\Delta^6$ Temperature C | | | $C_{17}$-$C_{18}\Delta^9$ Temperature C | |
|---|---|---|---|---|---|
| Mole % $C_{17}$ | Metastable | Stable | Mole % $C_{17}$ | Metastable | Stable |
| 0.00 | --- | 19.1 | 0.00 | --- | 10.3 |
| 12.27 | --- | 18.0 | 4.88 | --- | 10.1 |
| 19.89 | --- | 16.8 | 12.25 | --- | 9.7 |
| 27.8[a] | --- | 15.0[a] | 14.5[a] | --- | 9.4[a] |
| 28.37 | --- | 15.1 | 17.43 | --- | 10.6 |
| 32.73 | --- | 16.8 | 24.13 | --- | 13.4 |
| 41.46 | --- | 19.4 | 42.02 | --- | 19.5 |
| 54.30 | --- | 22.2 | 61.35 | --- | 23.6 |
| 68.49 | 22.3 | 24.9 | 81.09 | 24.8 | 27.0 |
| 79.05 | 24.4 | 26.5 | 100.00 | 28.1 | 29.8 |
| 91.08 | 26.6 | 28.5 | | | |
| 100.00 | 28.1 | 29.8 | | | |

[a] Eutectic point by extrapolation.

The freezing point data for the binary systems with the methyl esters of the unsaturated acids are tabulated in Table II and are shown graphically in Figure 2. Unlike their saturated counterpart, binary mixtures of methyl elaidate and methyl petroselaidate with methyl heptadecanoate formed only simple eutectics, 9.4 C and 14.5% and 27.8 C and 15.0%, respectively (Fig. 2). In these systems the metastable form of the methyl heptadecanoate crystallized only at the higher concentrations of the heptadecanoate (60% to 100%). At the lower concentrations only the stable form crystallized when the liquid sample was cooled. Since neither methyl elaidate nor methyl petroselaidate exhibited any dimorphic character on the basis of heating and cooling curve analyses, the ready conclusion is that the unsaturation in the fatty acid chain imparts preferred bimolecular crystalline orientation to odd-even unsaturated acid methyl ester mixtures. The saturated odd-even acid methyl ester mixtures seem to be influenced by the dimorphic character and chain lenth of the even acid ester. Whereas compound formation is evident among even and odd saturated fatty acid binary mixtures differing in carbon chain length by as many as six units (1), compound formation among the methyl ester systems herein investigated was limited to adjacent homologs testifying to the reduced bonding affinity of the methoxy group. The simple eutectics formed by the saturated-unsaturated ester systems parallel results reported for similar fatty acid binary mixtures (1).

Similar also to acid mixtures, the position of the site of unsaturation apparently is not a significant factor in the phase behavior of the methyl esters.

The behavior of saturated fatty acid methyl esters in binary mixtures resemble in many ways that of the corresponding ethyl esters. Whereas solid solutions are not the general rule, as in the case of the ethyl esters, they cannot be completely ruled out in the case of adjacent odd-even methyl esters.

## ACKNOWLEDGMENT

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