

# Mutual Solubilities of Some Fatty Acid Methyl Esters

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## ABSTRACT

Mutual solubility data have been obtained for methyl esters of the predominant fatty acids in vegetable oils. Binary freezing point diagrams are presented for systems exhibiting regions of metastable equilibria. Simple eutectic systems were obtained for both saturated-unsaturated and unsaturated-unsaturated methyl ester binary mixtures.

## INTRODUCTION

Crystallization procedures have been proposed on numerous occasions for the isolation and purification of unsaturated fatty acids from vegetable oils (1-3). The procedures involve solvent crystallization of the acids at very low temperature, often without prior knowledge of the mutual solubilizing effects of the acids involved. Although the procedures generally suggest that the acids be used, the methyl esters and sodium soaps also have been used. The methyl esters require lower temperatures but tend to extend the range of possible solvent selections, whereas the sodium soaps have limited solubility in most organic solvents. The present report presents mutual solubility data for the methyl esters of some of the more common fatty acids found in vegetable oils.

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## EXPERIMENTAL PROCEDURES

Methyl stearate and methyl palmitate were recrystallized products prepared from samples obtained by fractional distillation. The methyl oleate, methyl petroselinate, methyl palmitoleate, and methyl linoleate were purchased from the Hormel Institute, Austin, Minn. The purity was estimated to be greater than 99% by gas liquid chromatography and thin layer chromatographic analyses, and the materials were used without further purification. The final estimate of purity and the freezing points of the materials were determined by using the method of heating curves and apparatus described by Skau (4). Temperature measurements were made with a thermocouple calibrated at the freezing points of benzoic acid, naphthalene, and mercury using thermometric cells and with the sublimation temperature of carbon dioxide (5). The freezing points thus obtained were as follows: methyl stearate, 38.88 C; methyl palmitate, 29.97 C; methyl petroselinate, -0.42 C; methyl oleate, -19.69 C; methyl palmitoleate, -33.41 C; and methyl linoleate, -36.60 and -41.85 C. Solubility temperatures were determined by the thermostatic sealed tube method (6). Weighed amounts of the esters were enclosed in sealed glass tubes, along with glass beads to ensure good agitation. The tube then was rotated end-over-end in a constant temperature bath. Two temperatures were determined at which the last crystal either disappeared or remained undissolved after prolonged agitation. The mean of these two temperatures

TABLE I

Mutual Solubility Data for Fatty Acid Methyl Esters

Methyl palmitate in methyl palmitoleate		Methyl palmitate in methyl oleate		Methyl palmitate in methyl linoleate		Methyl stearate in methyl oleate	
Mole % palmitate	Temperature, C	Mole % palmitate	Temperature, C	Mole % palmitate	Temperature, C	Mole % stearate	Temperature, C
100.00	29.97	100.00	29.97	100.00	29.97	100.00	38.88
79.80	27.1	81.11	27.4	79.27	27.0	68.47	34.8, 33.9
59.34	23.6	60.81	23.7	60.81	23.9	61.01	32.2, ---
40.08	18.8	42.73	19.4	38.71	18.6	51.75	31.6, 31.1
19.55	10.8	20.99	11.5	19.90	11.1	37.71	28.2
9.76	3.4	9.57	2.8	9.70	3.6	13.37	17.1
4.92	-4.0	4.87	-4.5	4.88	-3.5	4.34	5.9
1.95	-13.0	2.20	-12.7	1.95	-13.0	1.69	-3.2
0.98	-19.4	1.24	-19.6	0.73	-22.1	<0.03 <sup>a</sup>	-20 <sup>a</sup>
0.092	-33.5	1.2 <sup>a</sup>	-20.0 <sup>a</sup>	0.094	-36.4	0.00	-19.69
0.02 <sup>a</sup>	-33.6 <sup>a</sup>	0.73	-19.8	<0.01 <sup>a</sup>	-36.7 <sup>a</sup>		
0.00	-33.41	0.00	-19.69	0.00	-36.60		
Methyl stearate in methyl linoleate		Methyl oleate in methyl linoleate		Methyl oleate in methyl palmitoleate		Methyl petroselinate in methyl palmitoleate	
Mole % stearate	Temperature, C	Mole % oleate	Temperature, C	Mole % oleate	Temperature, C	Mole % petroselinate	Temperature, C
100.00	38.88	100.00	-19.69	100.00	-19.69	100.00	-0.42
81.78	36.1	95.28	-20.3	78.27	-22.5	81.28	-2.6
59.63	32.8	80.25	-22.2	56.02	-26.3	57.90	-6.5
39.32	28.7	59.22	-25.4	37.81	-31.1, -41.7	37.03	-11.2
19.22	21.2	39.19	-29.7	32.69	-33.6, -42.6	18.57	-18.3
9.66	14.4	19.36	-37.1, -45.2	28.05	-37.0, -43.4	8.97	-25.6
5.83	9.3	16.5 <sup>a</sup>	-38.7 <sup>a</sup> , ---	23.86	--- -44.1	3.95	-33.0
1.91	-1.3	15.27	-38.4, -44.0	22.71	-36.6, -44.1	3.6 <sup>a</sup>	-34.0 <sup>a</sup>
0.88	-8.6	13.12	-38.0, -43.5	22.4 <sup>a</sup>	-36.8 <sup>a</sup> , ---	2.85	-33.8
0.10	-26.1	9.81	-37.5, -42.9	20.62	---, -44.8	1.21	-33.7
<0.02 <sup>a</sup>	-36.7 <sup>a</sup>	4.31	-36.8, -41.9	19.8 <sup>a</sup>	---, -45.0 <sup>a</sup>	0.00	-33.41
0.00	-36.69	0.00	-36.60, -41.85	18.24	-35.9, -44.9		
				14.11	-35.3, -44.3		
				8.93	-34.6, -43.6		
				0.00	-33.41		

<sup>a</sup>Eutectic point by interpolation.

is, therefore, the true equilibrium temperature between the last crystal and the liquid. The freezing point thus determined, corrected for thermometer calibration and emergent stem, is considered accurate to within  $\pm 0.2$  C.

### RESULTS AND DISCUSSION

Complete mutual solubility data were obtained for the following binary systems: methyl palmitate-methyl linoleate, methyl stearate-methyl linoleate, methyl palmitate-methyl oleate, methyl stearate-methyl oleate, methyl palmitate-methyl palmitoleate, methyl petroselinate-methyl palmitoleate, methyl oleate-methyl linoleate, and methyl oleate-methyl palmitoleate. These data are presented in Table I.

Because of the large difference in the freezing points of the two components, the eutectics of the saturated vs unsaturated ester systems are, as expected, very close to the unsaturated acid side of the binary freezing point diagram. In fact, in the extreme cases, namely, the stearate-oleate, stearate-linoleate, palmitate-palmitoleate, and palmitate-linoleate systems, more precise data would be necessary to estimate the eutectic composition accurately.

Some of the pure esters and their binary mixtures exhibited two freezing points, indicating the formation of a metastable polymorphic crystal modification. An example is the region between ca. 50-70 mole % methyl stearate in the stearate-oleate system in which a second, lower melting polymorphic modification of methyl stearate was observed. The lower melting modification was obtained by shock-chilling the melt in liquid nitrogen.

Binary freezing point diagrams for methyl oleate-methyl palmitoleate and methyl oleate-methyl linoleate are presented in Figure 1. Methyl linoleate, which exhibits two polymorphic modifications, formed a simple eutectic at ca.  $-38.7$  C and 16.5 mole % methyl oleate. A second, lower melting polymorph of methyl linoleate crystallized from compositions between 0-20 mole % methyl oleate. The methyl oleate-methyl palmitoleate system also exhibited a region of metastable equilibrium. The stable form of the esters formed a eutectic mixture at ca.  $-36.8$  C and 22.4 mole % methyl oleate. The lower melting polymorphic modifications of the two components appeared between 8-38 mole % methyl oleate and formed a simple eutectic at ca.  $-45.0$  C and 19.8 mole % methyl oleate. These results would indicate that the methyl esters of vegetable oil fatty

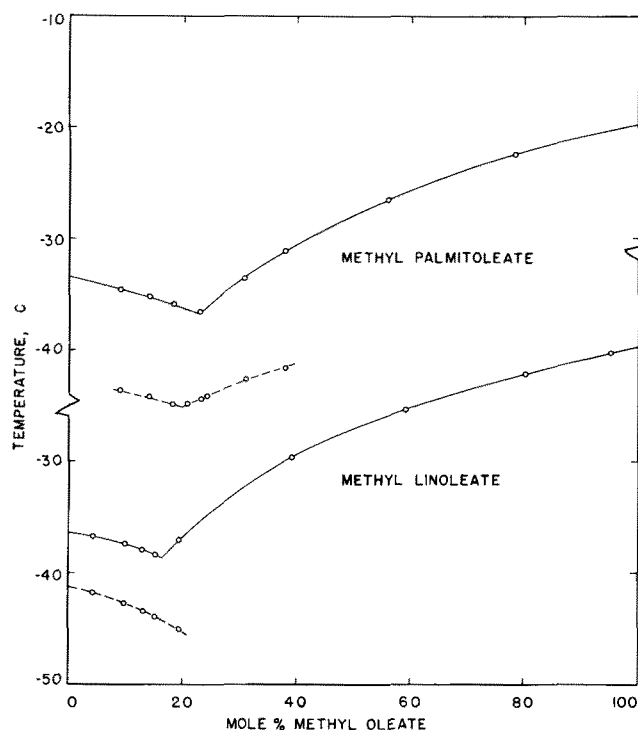


FIG. 1. Binary freezing point diagrams for methyl oleate-methyl palmitoleate and methyl oleate-methyl linoleate. Solid line represents stable equilibria and broken line represents metastable equilibria.

acids could be amenable to purification by low temperature crystallization.

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