Binary Freezing Point Determinations for Fatty Acid-Fatty Acid Ester Mixtures

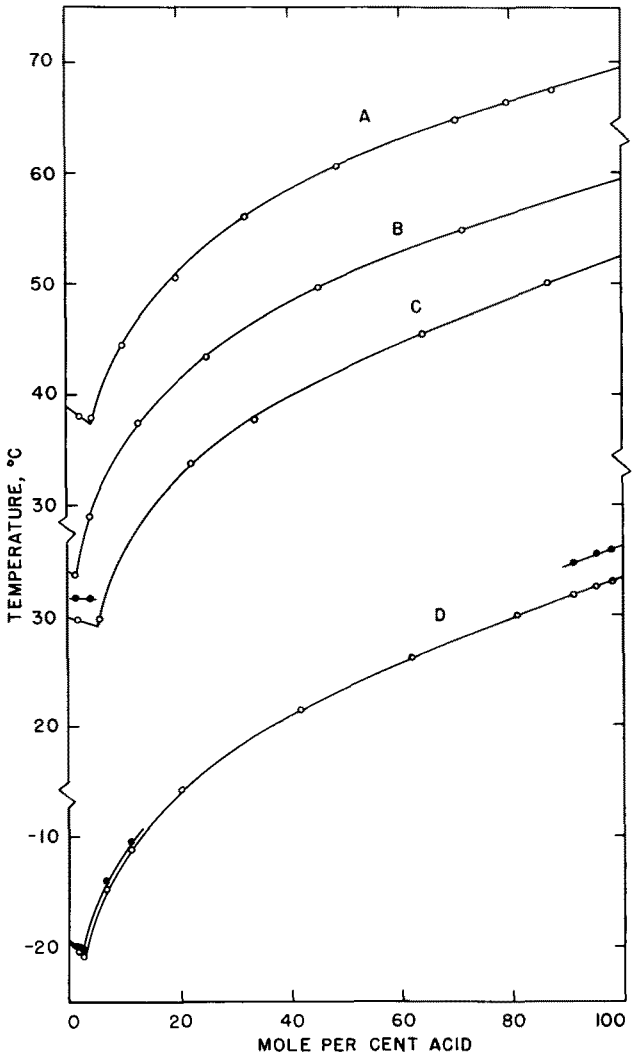

FIG. 1. Binary freezing point diagrams for stearic acid-methyl stearate, A; stearic acid-ethyl stearate, B; palmitic acid-methyl palmitate, C; and oleic acid–methyl oleate, D. Open circles, stable form, and closed circles, metastable form.

ABSTRACT

Binary freezing point data are presented for methyl and ethyl stearate with stearic acid, methyl palmitate with palmitic acid, and methyl oleate with oleic acid. Simple eutectic points were observed for each of the systems. Oleic acid crystallized only as the low melting polymorph between ca. 11 and 90%, whereas both the low and the high melting polymorphs of oleic acid could be obtained at concentrations between 0 and 11% and 90 and 100% oleic acid.

The mutual solubilities of the long chain fatty acids and many of their derivatives have been determined by numerous investigators and are well documented. Mutual solubility data between the fatty acid and fatty acid ester are overlooked and often required. The present paper concerns the mutual solubilities of stearic, palmitic and oleic acid and their methyl esters, and stearic acid and ethyl stearate.

The acids used were prepared by the usual fractional distillation of their methyl esters followed by solvent recrystallization. The esters were prepared from the pure acids followed by solvent recrystallization. The binary freezing points and freezing points of the pure materials were determined by the thermostatic sealed tube method which gives the true equilibrium temperature between the liquid and the crystal to within 0.2 C (1-3).

The binary freezing point curves are presented in Figure 1. It is interesting to note that oleic acid, which is known to exhibit two polymorphic modifications, crystallizes only as the lower melting polymorph in the presence of the methyl ester between 10 and 90 mole % oleic acid, while both polymorphs can be obtained between 0 and 11% and 90 and 100% acid (Fig. 1D). Two polymorphic forms of ethyl stearate were also observed in the presence of stearic acid in the immediate concentration range of the eutectic composition, 2.0%, (Fig. 1B). Simple eutectic systems were observed for the methyl stearate–stearic acid and methyl palmitate–palmitic acid systems. The binary freezing point data are presented in Table I.

A.V. BAILEY
J.A. HARRIS
E.L. SKAU

TABLE I

Binary Freezing Point Data for Fatty Acid-Fatty Acid Ester Systems

Methyl stearate-stearic acid		Ethyl stearate-stearic acid			Methyl palmitate-palmitic acid		Methyl oleate-oleic acid		
Mole % stearic acid	Temperature, C	Mole % stearic acid	Temperature, C		Mole % palmitic acid	Temperature, C	Mole % oleic acid	Temperature, C	
100.0	69.5	100.0	69.5		100.0	62.4	100.0	13.4	16.4
87.01	67.4	71.28	64.8		86.59	60.0	97.92	13.0	16.0
79.08	66.2	46.49	59.6		64.04	55.5	94.33	12.6	15.6
70.50	64.7	25.90	53.3		33.80	47.6	91.15	11.7	14.7
49.37	60.3	12.79	47.3		22.19	43.9	80.99	10.0	
32.12	56.0	4.23	31.3	38.8	6.06	29.8	61.86	6.2	
19.36	50.4	1.9 [a]	---	33.6[a]	5.8 [a]	29.0[a]	41.90	1.5	
10.03	44.4	1.69	31.3	33.6	0.91	29.7	20.24	-5.8	
5.05	37.8	0.00		33.9	0.0	29.7	10.68	-11.2,	-10.5
4.8 [a]	37.2[a]						6.91	-14.8,	-14.1
2.31	38.0						2.71	-20.8,	-20.2
0.00	38.9						2.8 [a]	-21.0[a]	-20.3
							2.27	-20.8	-20.2
							1.47	---	-20.2
							0.00	-19.7	

[a]Eutectic point by interpolation

Southern Regional Research Laboratory[1]
New Orleans, Louisiana 70179

[1]S. Market. Nutr. Res. Div., ARS, USDA.

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