Solid–Liquid Phase Equilibria of Mixtures of Methyl Myristate and Methyl Palmitate

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The solid–liquid phase equilibria of binary mixtures of methyl myristate (tetradecanoic acid methyl ester) and methyl palmitate (hexadecanoic acid methyl ester) were measured at ambient pressure. Both the initial and final melting points were determined visually. The mixture is of the eutectic type with complete miscibility in the liquid phase and partially miscible solid solutions. The eutectic temperature is 11.3 °C; the mole fraction of methyl myristate at the eutectic point is 0.74.

Introduction

Fatty acid methyl esters are important intermediates during the processing of fats. They may be hydrogenated in order to form fatty alcohols, the basic ingredients for manufacturing detergents. Since fatty acids are less stable than their corresponding methyl esters, the esters also play an important role during the synthesis of oil and fat products with specific properties (*1*).

As with other lipids, among the most significant physical properties of fatty acid methyl esters are those connected to the process of melting and solidification. This requires knowledge of the solid–liquid phase behavior. While phase equilibria of binary mixtures of some fatty acid methyl esters have been determined (*2*), those of mixtures of methyl myristate and methyl palmitate are not known to have been previously published.

The solidus and liquidus lines were determined by measuring the initial and final melting points of each mixture, a method recommended by Kerridge (*3*). While the solidification point in theory is the same as the final melting point, it is generally found to lie below the temperature at which melting occurs because of supercooling.

Experimental Method

Mixtures of methyl myristate and methyl palmitate were melted and thoroughly stirred. A small amount was filled into a capillary (inner diameter 0.720 mm) which was then sealed at both ends with two-component adhesive. Most of the mixture was filled into a vial (diameter 30 mm) which was capped afterward. The capillaries were supported by a small frame made of brass because of its good thermal conductivity. Both this frame and the vials were then submerged in a water bath that was placed in a refrigerator overnight. The mixtures were thus allowed to cool slowly and to solidify.

Both the capillary frame and the vials were held in a large 40-L water bath at a rate of approximately 1 K/h, shown to be sufficiently slow to ensure that the phase boundary had the same temperature as the water bath within ±0.1 K. The temperature of the water bath was measured with a platinum resistance thermometer, also with an accuracy of ±0.1 K.

The vials were utilized for determining initial melting points. They were carefully observed with the help of a cathetometer for first signs of melting. In most cases, several experiments were performed with each mixture. The mixture was then completely melted and resolidified following the method described above. The reproducibility was within ±0.2 K, except near the boundaries of the solid two-phase system.

The initial melting points could not be accurately determined in the capillaries through the cathetometer. However, being virtually isothermal, they allowed for a close following of the final stages of melting. The temperature at which the cloudiness of the liquid in the capillary disappeared was listed as the final melting point.

Again, the samples were afterward resolidified in the same manner as the vials in order to repeat the measurements. With some mixtures, freshly filled capillaries were used for repeating so as to show that resolidification had no effect on the results. Reproducibility usually also was within ±0.2 K.

Methyl myristate was obtained from Merck-Schuchardt at >99% purity, with traces of methyl laurate and methyl palmitate. Methyl palmitate (Roth, 95% pure) was found to contain about 4% methyl myristate and about 1% methyl stearate. Both substances were used without further treatment.

The mixtures contained a maximum of 1% of substances other than methyl myristate and methyl palmitate. However, as the addition of methyl laurate or methyl stearate to methyl myristate and methyl palmitate also reduces melting temperatures (*2*), both substances act in the same direction as the main components. These impurities were therefore not expected to affect the results beyond the limits of experimental accuracy.

The compositions of the mixtures were determined by using an HP 5890 gas chromatograph with a weakly polar packed column (Perkin-Elmer Dexsil 300 GC Chrom) and an FID detector. Helium was used as a carrier gas. The oven temperature was programmed from 100 to 220 °C. The chromatographic response factors were determined by analyzing standard mixtures prepared gravimetrically. The mole fractions of methyl myristate were related to the total amount of matter, including the trace impurities. The accuracy of this calibration was better than ±0.001.

Results

The binary mixture of methyl myristate (1) + methyl palmitate (2) is of the eutectic type with partially miscible solid solutions. Only mixtures with a methyl myristate mole fraction between $x_1 = 0.40$ and $x_1 = 0.90$ exhibit eutectic behavior. For this system, the eutectic point was shown to lie at $x_{1,e} = 0.74$ and $T_e = 11.3$ °C.

The results are given in full detail in Table I and in Figure 1. The melting points of the pure components were taken

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Table I. Measured Initial ($t_{m,i}$) and Final ($t_{m,f}$) Melting Temperatures of Methyl Myristate (1) + Methyl Palmitate (2)

x_1	$t_{m,i}$/°C	$t_{m,f}$/°C	x_1	$t_{m,i}$/°C	$t_{m,f}$/°C
0.996	18.1	18.6	0.706	11.4	12.1
	18.0				12.1
0.944	14.5	17.7			12.3
		17.5			12.3
0.913	12.3	17.1	0.625	11.3	14.2
	12.7	17.1		11.1	13.8
0.900	11.3	16.9			13.9
	11.7	16.9	0.539	11.3	19.8
0.801	11.3	13.4		11.2	19.7
	11.4	13.5	0.410	11.3	22.4
0.793	11.3	13.0		11.1	22.6
		13.2	0.396	11.7	22.7
		13.1		11.9	22.5
0.767	11.4	12.5	0.350	14.5	23.5
		12.7			23.2
0.745	11.3	11.8	0.307	15.8	24.7
		11.8		15.6	25.1
		11.7	0.210	18.8	26.0
		11.8		19.0	26.3
		11.8		18.9	25.9
0.721	11.2	12.0	0.141	21.1	27.3
		12.0		20.8	27.6
				21.0	
			0.045	26.9	29.1
				26.7	29.0

from Swern (*1*). They are given as 18.8 and 30.6 °C for the most stable, and therefore highest-melting, modifications of methyl myristate and methyl palmitate, respectively.

A problem encountered frequently (*4, 5*) when measuring solid–liquid phase diagrams of triglyceride mixtures is that, since these mixtures may form less stable crystals of varying composition, melting starts over a range of temperatures rather than at a clearly defined eutectic temperature. However, such a phenomenon was not observed in the system presented here. Crystals of reduced stability clearly are not formed during solidification with the technique employed here.

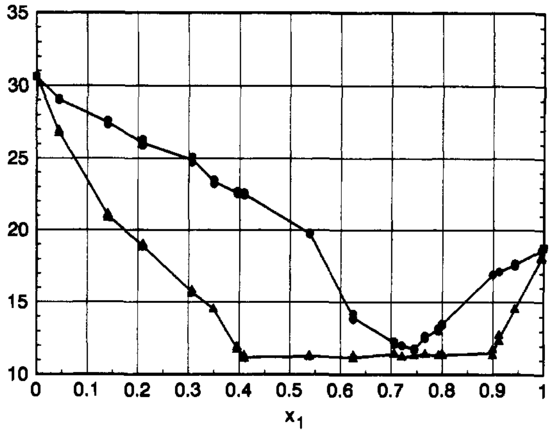

Figure 1. Solid–liquid phase diagram for methyl myristate (1) + methyl palmitate (2): ▲, initial melting points; ●, final melting points; ■, pure components (*1*).

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