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Solubilities of Some Normal Saturated and Unsaturated Long-Chain Fatty Acid Methyl Esters in Acetone, *n*-Hexane, Toluene, and 1,2-Dichloroethane

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Solubility data have been obtained for a number of highly pure long-chain fatty acid methyl esters: methyl stearate, methyl palmitate, methyl heptadecanoate, methyl petroselaidate, methyl elaidate, methyl petroselinate, methyl oleate, methyl palmitoleate, and methyl linoleate in acetone, *n*-hexane, toluene, and 1,2-dichloroethane. All methyl esters were completely miscible in the solvents used. Two polymorphic forms of methyl linoleate were observed.

In recent publications from this laboratory the solubility behavior of a number of normal long-chain saturated and unsaturated fatty acids were reported in isopropyl ether, methanol, acetone, and toluene (*1*), in dimethylsulfoxide (*2*), and in *N,N*-dimethylformamide and *N,N*-dimethylacetamide (*3*). Earlier, Ralston, Harwood, Hoerr *et al.* reported on a careful extensive study of the solubilities of a number of long-chain saturated and unsaturated fatty acids and saturated fatty acid esters in a wide variety of solvents (*5-8, 10, 12*). Privett *et al.* (*9*) reported the solubilities of a number of saturated fatty acids, their methyl esters, alcohols, and triglycerides in acetone in an attempt to fill in the gap in solubility data which existed at that time. Thus, the solubility behavior of the saturated fatty acids, the unsaturated fatty acids, and the saturated fatty acid esters has been investigated extensively in a wide variety of solvents. However, not a great deal has been reported concerning the solubility characteristics of the methyl esters of the unsaturated fatty acids, partly because of lack of suitable highly pure materials and a practical apparatus for accurately determining solubilities at the necessary low temperatures required for unsaturated fatty acid esters. With the advent of modern gas-liquid and thin-layer chromatographic techniques, materials with a certified high purity became available. A recent publication from this laboratory (*4*) described an apparatus for determining solubilities by the thermostatic sealed tube method at temperatures approaching that of dry ice. Thus, the present investigation into the solubility behavior of a number of low melting saturated and unsaturated fatty acid methyl esters was possible.

EXPERIMENTAL

Methyl stearate, methyl palmitate, and methyl heptadecanoate were recrystallized products prepared from samples obtained by fractional distillation. The methyl elaidate and methyl petroselaidate were recrystallized materials prepared from the highly pure acids. The methyl oleate, methyl petroselinate, methyl palmitoleate, and methyl linoleate, purchased from the Hormel Institute with purity estimated to be greater than 99% by GLC and thin-layer chromatographic analyses, were used with no further purification. The final estimate of purity and the freezing points of the materials were determined using the method of heating curves and apparatus described by Skau (*13*). Liquid nitrogen was used as the coolant. Temperature measurements were made using a thermocouple calibrated at the freezing points of benzoic acid, naphthalene, and mercury using thermometric cells and at the equilibrium sublimation temperature of solid carbon dioxide (*11*). The freezing points obtained are: methyl stearate, 38.24; methyl palmitate,

Table I. Solubility of Methyl Esters[a]

(Weight %)

Methyl Stearate		Methyl Palmitate		Methyl Heptadecanoate		Methyl Petroselaidate		Methyl Elaidate		Methyl Petroselinate		Methyl Oleate		Methyl Palmitoleate		Methyl Linoleate	
%	t, °C	%	t, °C	%	t, °C	%	t, °C	%	t, °C	%	t, °C	%	t, °C	%	t, °C	%	t, °C
In Acetone																	
(85.82)	(37.4)	82.3	22.7	83.0	22.1	83.6	12.7	83.6	4.2	83.6	−6.5	83.6	−24.9	82.2	−38.9	83.5	−42.2
(47.37)	(31.9)	60.8	18.1	62.0	18.1	63.0	8.5	63.0	0.1	63.0	−8.8	63.0	−28.2	60.6	−42.4	62.8	−45.8
(10.83)	(24.5)	(56.12)	(17.5)	(55.8)	(17.7)	(56.68)	(7.1)	(56.56)	(−0.7)	(56.91)	(−11.0)	(36.22)	(−31.4)	(54.09)	(−43.8)	(36.44)	(−48.5)
(2.77)	(18.6)	34.1	13.8	35.6	14.7	36.2	4.5	(21.67)	(−6.0)	36.2	−13.6	21.2	−33.6	33.9	−45.7	21.1	−51.6
(0.40)	(6.2)	(20.11)	(10.9)	(26.04)	(12.2)	(21.70)	(1.6)	11.6	−9.7	(21.99)	(−15.6)	11.6	−36.4	(19.43)	(−47.6)	11.5	−54.5
(0.06)	(−7.7)	10.7	6.9	11.2	8.9	11.6	−2.2	(4.82)	(−14.9)	11.6	−19.0	(4.94)	(−40.7)	10.6	−50.9	(5.15)	(−59.5)
		(4.53)	(0.7)	(4.95)	(4.1)	(5.04)	(−7.6)	2.5	−19.4	(4.04)	(−23.9)	2.5	−44.4	(4.38)	(−57.4)	2.5	−63.1
		0.5	−4.3	2.4	−0.7	2.5	−12.8	1.3	−24.2	2.5	−27.8	1.3	−48.4	2.3	−61.4	1.3	−67.3
		0.25	−9.8	1.0	−5.4	1.3	−22.0	0.5	−30.5	1.3	−32.0	0.5	−53.7	1.1	−66.9	0.5	−72.8
		0.1	−17.0	0.5	−11.5	0.5	−24.8			0.5	−37.4			0.5	−73.8		
In *n*-Hexane																	
(86.16)	(36.2)	75.8	20.7	76.7	20.4	77.5	11.3	77.5	3.3	77.5	−7.7	77.5	−26.4	75.7	−41.0	77.4	−42.3
(65.08)	(33.8)	51.1	14.8	52.4	14.1	53.5	4.6	53.5	−3.3	53.5	−13.9	53.5	−32.4	(57.55)	(45.3)	(59.56)	(−46.5, −47.4)
(18.87)	(21.0)	(44.62)	(12.3)	(46.06)	(12.4)	(47.44)	(2.6)	(47.25)	(−5.5)	(46.86)	(−15.9)	(47.50)	(−34.5)	50.9	−47.0	53.3	−47.5
(5.84)	(10.7)	25.9	4.9	27.1	6.2	27.7	−3.6	27.7	−11.0	27.7	−21.7	27.7	−39.7	25.7	−53.7	(28.46)	(−53.3)
(1.45)	(−1.1)	(14.51)	(−0.1)	(14.33)	(0.7)	(15.69)	(−8.9)	(14.83)	(−17.0)	(15.70)	(−26.7)	15.3	−44.9	(22.10)	(−54.1)	(28.42)	(−53.5)
(0.33)	(−13.5)	7.5	−7.3	7.8	−4.9	8.1	−15.0	8.1	−22.3	8.1	−32.4	8.1	−50.0	14.1	−58.3	15.2	−58.5
		(3.13)	(−14.6)	3.2	−11.7	(2.76)	(−22.2)	(3.39)	(−29.5)	(3.55)	(−38.3)	(6.63)	(−51.1)	7.4	−62.7	8.0	−62.8
		0.5	−20.3	1.6	−16.7	1.7	−27.2	1.7	−34.7	1.7	−43.6	3.4	−56.3	3.0	−68.3	1.7	−68.8
		0.25	−25.5	0.8	−21.5	0.9	−32.1	0.85	−39.8	0.9	−48.2	1.7	−61.2	1.5	−72.4	0.85	−73.1
		0.1	−32.1	0.3	−27.4	0.3	−35.5	0.34	−46.6	0.3	−54.0	0.85	−65.9	0.8	−80.1		−77.3
												0.34	−72.0	0.3	−81.4		−82.7
In Toluene																	
(77.11)	(35.9)	74.6	20.1	75.5	19.4	76.3	9.7	76.3	1.1	76.3	−9.3	76.3	−29.0	74.4	−42.9	(76.43)	(−45.3)
(32.29)	(23.5)	49.5	9.9	50.7	10.1	51.8	−0.2	51.8	−8.7	51.8	−18.8	51.8	−38.4	(67.41)	(−45.5)	51.6	−54.3
(16.36)	(14.4)	(43.08)	(7.2)	(44.47)	(7.5)	(45.38)	(−3.0)	(44.86)	(−11.4)	(45.30)	(−21.5)	(45.21)	(−41.0)	49.3	−51.7	(45.94)	(−56.4)
(4.04)	(−1.7)	24.6	−2.4	25.5	−1.4	26.3	−12.4	26.3	−20.6	26.3	−30.2	(24.46)	(−50.8)	(34.88)	(−57.7)	26.2	−65.2
(1.19)	(−13.0)	(13.58)	(−10.0)	(14.48)	(−9.0)	(14.80)	(−20.0)	14.3	−28.5	(14.59)	(−37.8)	14.5	−57.1	24.5	−61.9	14.4	−72.2
(0.12)	(−32.4)	7.0	−21.3	7.3	−16.5	7.6	−27.5	7.6	−35.6	7.6	−44.4	7.6	−63.8	13.3	−68.2	7.6	−83.6
		(2.94)	(−26.2)	(3.18)	(−24.3)	(2.59)	(−35.7)	(3.89)	(−42.0)	(2.59)	(−52.0)	3.1	−71.8	7.0	−74.2	1.6	−86.1
		0.5	−32.5	1.5	−31.3	1.6	−42.0	1.6	−50.1	1.6	−58.1	1.6	−76.3	2.9	−81.0		
		0.25	−38.7	0.8	−37.1	0.8	−47.9	0.8	−55.7	0.8	−63.1	0.8	−81.5				
		0.10	−45.9	0.3	−44.9	0.3	−54.6	0.3	−62.6	0.3	−72.1						
In 1,2-Dichloroethane																	
(87.52)	(34.4)	73.2	20.4	74.2	19.5	75.0	10.1	75.0	1.5								
(63.72)	(25.5)	47.7	10.3	48.9	10.5	(50.60)	(0.7)	(50.67)	(−7.4)								
(27.56)	(13.4)	23.3	1.7	(41.95)	8.7	27.0	−8.1	27.0	−15.7								
(6.27)	(2.6)	(18.86)	(0.2)	24.2	2.9	(18.24)	(−10.8)	(18.44)	(−18.4)								
(2.28)	(−4.8)	14.4	−3.0	(13.31)	(−1.9)	13.6	−12.5	13.6	−20.1								
(0.30)	(−17.1)	6.6	−7.8	6.9	−5.9	(5.71)	(−19.2)	(6.01)	(−26.1)								
		(4.92)	(−9.9)	2.9	−11.5	2.9	−23.7	2.9	−30.8								
		2.7	−14.5														

[a] Values in parentheses experimentally determined; others determined by isopleth reference method.

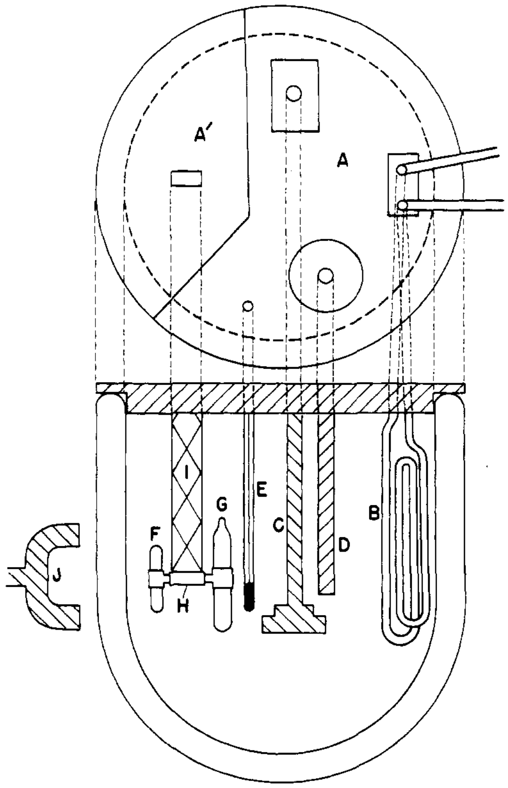

Figure 1. Low temperature solubility apparatus bath section

10-liter unsilvered Dewar flask ca. 10 inches inside diameter by 11 inches deep

A. = Permanently attached lid section
B. = Bath cooling coil
C. = Centrifugal stirring mechanism (capacity 5 to 6 gallons per minute)
D. = Bimetallic thermoregulator
E. = Thermometer (precision total immersion thallium-mercury +5° to −60° C graduated to 0.2° C)
F. = 2-Inch Teflon-covered magnetic stirring bar
G. = Clip for mounting sample tube
H. = Stainless steel shaft
I. = Teflon sleeve bearing
J. = Rotating No. 7 horseshoe magnet driven by 25-rpm geared output electric motor (Bodine KYC-25)

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29.76; methyl petroselaidate, 19.04; methyl elaidate, 10.27; methyl petroselinate, −0.42; methyl oleate, −19.66; methyl palmitoleate, −33.41; and methyl linoleate, −36.60 and −41.85° C. The freezing points of methyl heptadecanoate by the sealed tube method (*4*) were 28.1° and 29.8° C.

The acetone, *n*-hexane, toluene, and 1,2-dichloroethane used in the investigation were all reagent grade solvents. The acetone and toluene were freshly distilled before use.

Experimental solubilities were determined by the thermostatic sealed tube method. Weighed amounts of the sample and the solvent are placed in sealed glass tubes, along with two glass beads to ensure good agitation. The tube is then rotated end over end in a constant temperature bath. Two temperatures are determined at which the last crystal either disappears or remains undissolved after prolonged agitation. The mean of these two temperatures is thus the true equilibrium temperature between the crystals and the liquid. The freezing point thus determined corrected for thermometer calibration and emergent stem is considered accurate to within ±0.2° C.

The apparatus (Figure 1) consists of a 10-liter Dewar flask, essential for attaining the necessary low temperatures, a heat exchange system and cooling coil connected through a bimetallic relay for maintaining constant temperatures, and a sample tube holder capable of being rotated externally by using a rotating magnet.

The calculated data were obtained by the isopleth reference method (*1*). The procedure involves obtaining complete data for a solubility curve for a reference compound (R) and the freezing point and one or two solubility determinations for a homologous or analogous compound (A), both in a common solvent. A plot of the reciprocal of the solubility temperatures ($1/T_R$ *vs.* $1/T_A$) for equivalent molar compositions yields a straight or sometimes slightly curved line, from which the complete solubility data for the analogous or homologous compound can be obtained by graphical interpolation. The data so obtained are estimated to be accurate to within 0.2° to 0.3° C over the entire length of the reference solubility curve.

RESULTS AND DISCUSSION

Complete solubility data for a number of saturated and unsaturated fatty acid methyl esters in acetone, *n*-hexane, toluene, and 1,2-dichloroethane are presented in Table I. In many respects, the solubilities of the methyl esters are similar to those of the corresponding acids, being somewhat greater on a weight basis, as would be expected because of their lower melting points. The solubilities of the methyl esters are greatest in the least polar solvent, toluene, and least in the highly polar acetone. In general, the solubilities of the methyl esters in both polar and nonpolar solvents increase with the degree of unsaturation. The lower melting cis acids have higher solubilities than the corresponding trans acids. The location of the site of unsaturation also influences solubility. The 9-10 unsaturated esters, methyl oleate and methyl elaidate, have higher solubilities than the corresponding 6-7 unsaturated esters, methyl petroselinate and methyl petroselaidate. Methyl linoleate exhibited two polymorphic forms. The low melting form was obtained by shock-chilling with liquid nitrogen. On melting, the sample converts to the higher melting form when the temperature is maintained just above the melting point of the lower melting form. With the exception of the 59% solution in *n*-hexane, only the higher melting form was obtained when methyl linoleate crystallized from the polar and nonpolar solvents used in this investigation. Methyl palmitoleate was the only ester of those investigated to exhibit a transition point (−49.04° C).

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