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Binary Freezing Point Behavior of Some Normal Octadecenoic Acids

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Complete binary freezing point data have been obtained for the following fatty acid systems: oleic-elaidic, oleic-petroselinic, oleic-petroselaidic, elaidic-petroselinic, elaidic-petroselaidic, and petroselinic-petroselaidic. All these systems, representing the various binary combinations of two pairs of geometrical and positional isomers, were of the simple eutectic type. Calculated heats of fusion were obtained for each of the acids. Mixtures rich in elaidic acid acid gave two freezing points, proving the existence of two polymorphic forms. The common form, f.p. 43.7° C., is metastable and the new form, f.p. 44.8° C., is stable.

SINCE the classical work of de Visser (*2*) in 1898, solid-liquid phase diagrams have been published for binary systems involving various long-chain fatty acid combinations (*6*). Those systems involving two homologous saturated acids exhibit molecular compound formation. Combinations of a saturated and an unsaturated fatty acid or of fatty acids of two different degrees of unsaturation give simple eutectic freezing point diagrams. Griffiths and Hilditch (*1, 3*) published simple eutectic diagrams for the oleic–elaidic acid and the petroselinic-petroselaidic acid systems but observed only one polymorphic form of oleic and elaidic acids. The present report deals with the complete freezing point data for all six binary systems involving oleic, elaidic, petroselinic, and petroselaidic acids including polymorphic solid phases. These systems represent the various binary combinations of two pairs of geometrical and positional isomers.

EXPERIMENTAL

The pure oleic acid (f.p. stable form 16.3° C., f.p. unstable form 13.5° C.) and petroselinic acid (f.p. 29.8° C.) were prepared from olive oil and parsley seed oil, respectively, by methanolysis, fractionation on a Podbielniak column, conversion to the acids, and recrystallization from acetone until no further increase in freezing point was observed. The elaidic acid (f.p. 43.7° C.) and petroselaidic acid (f.p. 52.7° C.) were prepared by elaidinization of the pure cis acids followed by repeated recrystallization from acetone as above.

The freezing point determinations were made by the thermostatic sealed tube method (*5*), which involves finding two temperatures about 0.2° C. apart, one at which the last crystals disappear and the other at which a few crystals persist after prolonged agitation at constant temperature. The freezing point was taken as a mean of these two temperatures corrected for thermometer calibration and emergent stem.

RESULTS AND DISCUSSION

The results are given in Table I and are represented graphically in Figure 1. All six binary systems are of the simple eutectic type.

Compositions of both the elaidic and oleic acid branches of the diagrams had two freezing points, indicating that elaidic acid as well as oleic acid crystallizes in two polymorphic forms. The broken lines represent the binary freezing point curves for the low-melting modifications.

When mixtures rich in oleic acid were cooled to about

Table I. Binary Freezing Point Data^a

Mole % of I	Freezing Point, ° C. Stable Form	Freezing Point, ° C. Metastable Form	Mole % of I	Freezing Point, ° C. Stable Form	Freezing Point, ° C. Metastable Form
I. Oleic Acid			I. Petroselaidic Acid		
II. Elaidic Acid			II. Petroselinic Acid		
	Solid Phase II			Solid Phase II	
0.00	44.8	43.7	0.00	29.8	
9.22	43.3	42.3	4.42	29.1	
22.18	41.2	40.3	11.30	28.0	
26.80	40.2	39.4	14.60	27.4	
35.31	38.6	37.8	(16.1)	(17.2)	
44.28		35.7		Solid Phase I	
60.33	31.9	31.2	20.58	30.6	
70.65	27.7	27.2	30.53	35.8	
79.58		22.8	40.20	39.6	
87.22	17.6	16.8	50.55	42.7	
(89.1)^b		(14.6)^b	60.99	45.4	
(90.0)^b	(14.8)^b		65.89	46.6	
(90.8)^c		(11.8)^c	68.43	47.1	
(91.6)^c	(12.1)^c		70.72	47.5	
	Solid Phase I		80.52	49.5	
92.87	15.2	12.2	90.30	51.1	
95.81	15.6	12.7	100.00	52.7	
100.00	16.3	13.5			
I. Petroselaidic Acid			I. Petroselinic Acid		
II. Elaidic Acid			II. Oleic Acid		
	Solid Phase II			Solid Phase II	
0.00	44.8	43.7	0.00	16.3	13.5
10.34	43.1	42.3	11.14	14.8	11.6
20.19	41.4		20.66	13.3	9.7
30.33	39.9	39.1	(23.4)		(9.2)
(35.2)		(37.8)	(28.4)	(11.8)	
(36.5)	(38.3)			Solid Phase I	
	Solid Phase I		30.82	12.9	
38.91	39.3		39.37	16.2	
50.08	42.8		49.86	19.5	
60.02	45.2		59.56	22.1	
70.09	47.3		68.94	24.2	
80.29	49.5		79.06	26.3	
89.74	51.2		88.03	28.0	
100.00	52.7		100.00	29.8	
I. Petroselinic Acid			I. Petroselaidic Acid		
II. Elaidic Acid			II. Oleic Acid		
	Solid Phase II			Solid Phase II	
0.00	44.8	43.7	0.00	16.3	13.5
11.10	43.2	42.2	3.79	15.7	12.8
21.05	41.3	40.5	(5.5)		(12.6)
30.30	39.6	38.8	(6.4)	(15.3)	
38.73	37.6	37.0		Solid Phase I	
39.74		36.8	7.46	17.3	
49.94	35.2	34.3	10.61	21.7	
60.25	31.9	31.3	20.69	30.3	
69.71	28.6	27.9	30.59	35.8	
(74.9)		(25.5)	40.18	39.6	
(76.2)	(25.8)		50.63	42.9	
	Solid Phase I		61.02	45.4	
79.10	26.3		69.72	47.4	
89.14	28.2		79.84	49.2	
100.00	29.8		90.03	51.1	
			100.00	52.7	

[a] Values in parentheses are eutectics, obtained by graphical extrapolation. [b] Eutectic with stable form of I. [c] Eutectic with metastable form of I.

8° to 10° C. the samples suddenly became essentially solid, and on heating in the constant temperature bath gave the freezing point corresponding to the temperatures indicated by the lower (broken) line. Before equilibrium at this temperature was established, the sample sometimes became essentially solid again because of the formation of the higher-melting crystalline modification of oleic acid. The observed equilibrium temperature was then that indicated by the upper (solid) curve.

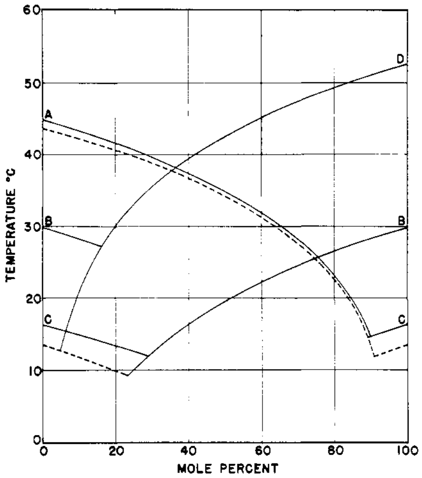

Figure 1. Binary freezing point diagrams for the systems
Elaidic acid (*A*)–petroselaidic acid (*D*)
Elaidic acid (*A*)–petroselinic acid (*B*)
Elaidic acid (*A*)–oleic acid (*C*)
Petroselinic acid (*B*)–petroselaidic acid (*D*)
Oleic acid (*C*)–petroselaidic acid (*D*)
Oleic acid (*C*)–petroselinic acid (*B*)

The freezing point of pure elaidic acid or of mixtures on the elaidic acid side of the binary systems depends upon the history of the sample. If it has been melted previously, or if it has been melted and cooled rapidly, the freezing point usually falls on the lower (broken) curve. If, on the other hand, it has been melted and allowed to cool very slowly, a small proportion of the crystals that form will usually be of the high-melting modification, and these do not dissolve until the temperature indicated on the upper (solid) curve is reached.

For each acid the three binary temperature-composition curves coincide from the freezing point of the acid down to the eutectic point. Superimposable straight lines are obtained when the logarithm of the mole fraction of a given acid is plotted against the reciprocal of the absolute freezing temperature for that portion of each binary freezing point diagram where that acid is the solid phase. The heats of fusion calculated from the slopes of these lines, assuming ideality, are given in Table II. They conform to the same general pattern as that for the melting dilations reported for some of these crystalline forms by Singleton and Ward (*7*), a property that would be expected to vary directly with the heat of fusion. For example, the heats of fusion of the acids increased in the order oleic (13.5° C.), oleic (16.3° C.), petroselinic, elaidic (44.8° C.), petroselaidic, elaidic (43.7° C.). The trans acids had higher heats of fusion than their cis isomers. Of the two modifications of oleic acid, the higher melting form had the higher heat of fusion as would be expected. The reverse was true of the two forms of elaidic acid. Of the two cis acids, the one with the double bond closer to the carboxyl end of the carbon chain had the higher calculated heat of fusion. The corre-

Table II. Calculated Heats of Fusion

Acid	Heat of Fusion, Kcal./Mole.	Melting Dilation^a, Ml./G.
Oleic (f.p. 13.5° C.)	11.1	. . .
Oleic (f.p. 16.3° C.)	11.9	0.1183
Petroselinic	12.2	0.1314
Petroselaidic	13.9	0.1403
Elaidic (f.p. 43.7° C.)	14.4	0.1615
Elaidic (f.p. 44.8° C.)	13.6	. . .

[a] Singleton and Ward (*7*).

sponding relationship for the two trans acids depends upon whether the comparison is made with the metastable or stable form of elaidic acid.

The standard deviations of the experimental data from the curves in Figure 1 and from the linear log N *vs.* $1000/T$ plots for each acid fall between 0.05° and 0.12° C. and between 0.04° and 0.12° C., respectively.

The isolation and characterization of the stable modification of elaidic acid will be reported in a forthcoming publication (*4*).

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Densities of Molten $BiCl_3$ and $AlCl_3$ Mixtures

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The "float" method was used to measure the liquid densities of $AlCl_3$–$BiCl_3$ mixtures containing 0.0, 20.0, 35.0, and 60.0 mole % of $AlCl_3$. All mixtures were studied over a range of temperatures and the data fitted to equations of the form $\rho = \alpha - \beta t$ by a least-squares analysis. Molar volumes showed negative deviations from additivity as large as 13%.

MOLTEN salt mixtures that are acidic in the Lewis sense are good solvents for stabilizing lower oxidation states (*3*). For example, $AlCl_3$-NaCl mixtures have been used as solvents for spectrophotometric studies of the lower oxidation states of bismuth (*1*). Density measurements on these mixtures were necessary for the calculation of optical extinction coefficients but were also of interest in themselves because of the very large deviations from linearity which were observed (*2*). The purpose of the present work was to determine densities on another acidic solvent system of spectroscopic interest—namely, $AlCl_3$-$BiCl_3$ mixtures. Again, the densities themselves should be of interest especially when compared with the results for $AlCl_3$-NaCl mixtures.

EXPERIMENTAL

Density Determination. The float method was used for measuring density. This consisted of measuring the temperature at which quartz floats of known density neither fell nor rose in the liquid under study. The apparatus has been described previously (*2*). Minor modifications were required to measure densities greater than that of quartz. The first was to seal a length of platinum wire into the quartz floats to produce a float density greater than that of quartz alone. The second modification was the use of a very low density float on top of the density floats to hold the latter just under the surface. This prevented the density floats from sticking at the surface because of surface tension. This top float was simply a flat-bottomed bubble of quartz, made a little heavier on the flat side so that this side would stay down, and of sufficient diameter to prevent the density floats from passing or becoming wedged next to it in the container tube. The top float density (1.8 grams per cc.) was considerably less than that of the liquids under study. Thus, it remained on the surface during all measurements.

Materials. The $AlCl_3$ was prepared from high purity aluminum metal and HCl by the method described by Bjerrum, Boston, and Smith (*1*). The $BiCl_3$ was prepared by the reaction of zone refined, 99.9999% bismuth metal with chlorine gas followed by several successive distillations.

RESULTS AND DISCUSSION

The density results are summarized in Table I. At each composition the temperature dependence of the density ρ is given by the usual expression, $\rho = \alpha - \beta t$, where

Table I. Density Equations for $AlCl_3$–$BiCl_3$ Mixtures

	$\rho = \alpha - \beta t$					
Composition, Mole % $AlCl_3$	α, grams/cc.	$\beta \times 10^3$, grams/cc./° C.	Std. Dev. $\times 10^3$, Grams/Cc.	Molar Volume at 220° C., Cc./Mole	Exptl. Temp. Range, ° C.	Reference
0.0	4.433	2.26	0.8	80.12	411–479	
0.0	4.417	2.20	1.0	80.19	239–331	(*5*)
20.0	3.837	1.90	0.8	81.59	201–84	
35.0	3.427	1.71	3.8	82.42	188–400	
60.0	2.751	1.43	2.6	84.61	167–281	
100.0	1.734	2.33	1.7	109.2	202–21	(*2*)