Binary Freezing Point Diagrams for a Number of Long Chain Fatty Acids in Dimethyl Sulfoxide

AUGUST V. BAILEY, JAMES A. HARRIS, and EVALD L. SKAU
Southern Regional Research Laboratory, New Orleans, La. 70119

Binary freezing point data have been obtained for dimethyl sulfoxide (DMSO) with capric, myristic, palmitic, stearic, oleic, and elaidic acids. Solubility data for lauric acid have been calculated. All of the acids form an incongruently melting, 1-to-1, acid–DMSO molecular compound, which in the capric, myristic, and palmitic acid systems appears in two crystalline modifications. More complex molecular compounds are indicated in the palmitic and stearic acid systems. Second polymorphic forms of myristic, capric, and oleic acids were also observed.

AN increasing interest has been shown in dimethyl sulfoxide (DMSO) as an organic solvent (1, 4, 6, 7). DMSO, the most polar of the aprotic solvents (1), dissolves both organic compounds and inorganic salts, and owing to its excellent solvating powers and its ionizing ability, it acts as a catalyst in many chemical reactions. Because of its high polarity, it is highly associated and tends to form complexes or molecular compounds with the solute. The lower members of homologous aliphatic series are soluble, but very few quantitative data have been reported. The present data were obtained to establish the conditions of temperature and concentration under which DMSO can be used suitably as a solvent for long chain fatty acids. Complete binary freezing point diagrams have been constructed for DMSO with capric, myristic, palmitic, stearic, oleic, and elaidic acids.

EXPERIMENTAL

The pure fatty acids were prepared by the procedures previously described (5). DMSO (Crown Zellerbach Corp.) was used without further purification. Its freezing point, 18.2° C. was in good agreement with the literature value, 18.42° C. (2).

The freezing point or solubility determinations were made by the thermostatic sealed-tube method (3), which gives the true equilibrium temperature between the crystals and the liquid of the given composition to within 0.1° to 0.2° C.

For compositions in the 1-to-1 compound region, the equilibrium temperatures were determined first for the metastable modification, formed by spontaneous crystallization from the melt as the bath temperature was lowered. Crystals of the stable modification then formed as the rotation of the sample tube was continued near the metastable solubility temperature. The same procedure was followed to obtain the metastable and stable crystals in the 2.03 and 7.24% palmitic acid compositions. The determinations for the metastable modification of the 1-to-1 compound in the capric acid system were less precise because of the difficulty of attaining equilibrium before the stable crystal modification started to form.

In the stearic acid system, the crystals in equilibrium on the lower curve for compositions containing 0.80 and 2.08% acid were formed by spontaneous crystallization. Those on the upper curve were obtained by chilling the melt in an ice bath.

RESULTS AND DISCUSSION

The experimental freezing point data are given in Table I. Included are the solubilities of lauric acid calculated

from the data for the other saturated acids by the isopleth method of graphical interpolation (8). All of the acids are completely miscible with DMSO at their melting points. The complexity of the binary freezing point diagrams for the saturated fatty acids increases progressively with the chain length of the acid (Figure 1).

Capric acid gave a typical diagram indicating the formation of a 1-to-1 molecular compound, $C_{10}H_{21}COOH$–DMSO, melting incongruently (48.5% acid, −6.5° C.) and forming a eutectic with DMSO (38.0%, −9.4° C.). Two freezing points were obtained for all the compositions in the compound region, corresponding to two polymorphic forms of the molecular compound. Two freezing points were also obtained for the 49.7% composition. At the upper temperature, −3.0° C., the liquid is in stable equilibrium with
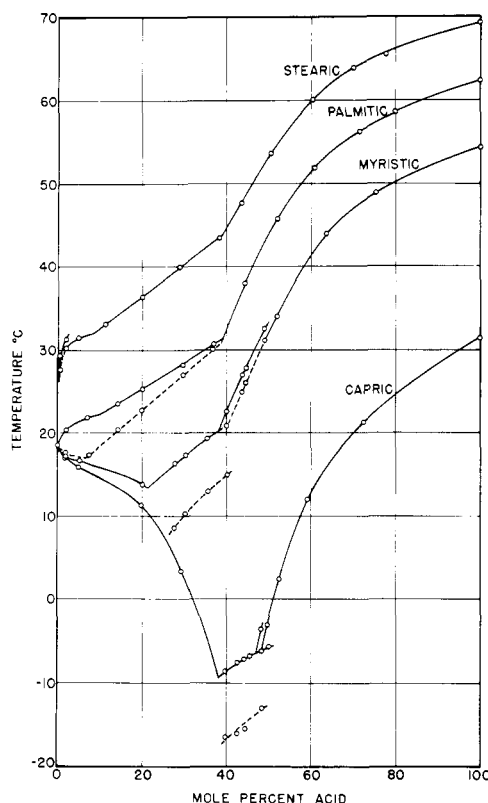

Figure 1. Binary freezing point diagrams for DMSO with stearic, palmitic, myristic, and capric acids

——— Stable equilibria

- - - - Metastable equilibria

Table I. Freezing Points of Binary Mixtures of DMSO with Long Chain Fatty Acids (Composition in Mole % Acid)

%	°C.	°C.	%	°C.	°C.	°C.	%	°C.	°C.
STEARIC			MYRISTIC				ELADIC		
100.00	69.5		100.00		54.4		100.00	43.7	
77.72	65.7		75.42		48.9		67.08	37.7	
70.90	64.1		63.66		44.1		55.91	32.3	
60.56	60.2		51.68		34.1		55.05	31.9	
50.53	53.7		49.00	32.7	31.2		53.60	30.9	
43.48	47.7		44.60	27.8	26.1		45.45	23.7	
39.0[a]	43.8[a]		43.70	27.0	25.0		37.36	16.9	
38.41	43.5		40.3[a]		21.0[a]		34.66	14.6	
28.86	39.9		40.08	22.7	20.8	15.1	33.3[a]	13.2[c]	
20.10	36.3		38.3[a]	20.3[a]			32.13	12.9	
11.31	33.2		35.56		19.3	13.0	30.34	12.5	
8.0[a]	31.7[a]		30.30		17.4	10.3	26.01	11.3	
5.17	31.5		27.60		16.4	8.7	25.0[b]	11.0[c]	
2.08	31.2	30.2	21.2[b]		13.3[b]		22.86	12.3	
0.80	29.3	27.6	20.10		13.9		17.92	14.6	
PALMITIC			5.24		16.7		12.96	15.9	
100.00	62.5		2.12		17.1		9.37	16.8	
80.07	58.8		CAPRIC				7.33	16.9	
71.29	56.3		100.00		31.6		4.56	17.1	
60.80	51.9		72.38		22.7		2.71	17.2	
52.09	45.7		59.23		12.2		1.39	17.5	
44.18	38.0		52.28		2.5		0.53	17.7	
39.2[a]	31.3[a]		49.70	-3.0	-6.5		OLEIC		
38.8[a]		30.8[a]	48.5[a]		-6.2[a]		100.00	16.2	13.3
37.00	30.6	30.2	48.30	-3.6	-6.2	-13.0	85.27	14.1	10.7
29.81	28.2	27.0	46.9[c]	-6.5[a]			74.08	12.2	8.3
20.24	25.2	22.7	45.42		-6.9		62.12	7.9	3.6
14.37	23.6	20.4	44.14		-7.1	-15.5	59.72	6.8	2.0
10.3[a]	22.3		42.46		-7.6	-16.0	51.31	0.3	
7.24	21.9	17.3	39.66		-8.7	-16.5	50.96	-0.3	
6.8[b]		17.0	38.0[b]		-9.4[b]		47.8[a]	-5.7[a]	
2.03	20.3	17.5	29.29		3.4		47.39	-5.8	
LAURIC[c]			19.88		10.1		46.29	-5.9	
100.00	43.8		4.99		15.9		45.58	-6.0	
90.0	42.0		2.03		17.1		41.35	-6.8	
80.0	39.3						39.5[b]	-7.3[b]	
70.0	35.5						37.32	2.3	
60.0	29.7						31.28	5.4	
50.0	17.1						20.02	13.5	
							10.13	16.3	
							5.09	16.9	

[a] Incongruent melting point (by extrapolation). [b] Eutectic (by extrapolation). [c] Calculated by isopleth correlation method (7).

capric acid crystals, and at the lower temperature, -6.5°C., it is in metastable equilibrium with the stable modification of the 1-to-1 compound. A third freezing point was observed for the 48.3% composition, above those for the two modifications of the 1-to-1 compound. Judging from a similar occurrence in the myristic acid system, the solid phase at the highest of these temperatures, -3.6°C., is another polymorphic form of capric acid.

The binary diagram for myristic acid has the same general characteristics as that for capric acid. The liquid compositions in equilibrium with the 1-to-1 compound extend over a wider concentration range—from the eutectic (21.2%, 13.3°C.) to the incongruent melting point (40.3%, 21.0°C.). Crystals of a second polymorphic modification of myristic acid were observed at concentrations from 49.0 to 38.3% acid, the composition at the incongruent melting point, 20.3°C.

An additional molecular compound is formed in the palmitic acid system. Compositions containing 2.03 and 7.24% acid had two freezing points. The lower curve in this region represents metastable equilibria with DMSO crystals. The upper curve can be interpreted as representing stable equilibria with an incongruently melting compound $C_{16}H_{33}COOH$–yDMSO where y is at least 2. The metastable modification of the 1-to-1 compound is in equilibrium with a much wider range of liquid compositions than in the myristic acid system—from its incongruent melting point (38.8%, 30.8°C.) to its eutectic with DMSO (6.8%, 17.0°C.). The stable form of the 1-to-1 compound is the solid phase in equilibrium between its incongruent melting point (39.2%, 31.3°C.) and the incongruent melting point of the molecular compound, $C_{15}H_{31}COOH$–yDMSO (10.3%, 22.3°C.).

The diagram for the stearic acid system resembles that representing the stable equilibria in the palmitic acid diagram. Only one modification of the 1-to-1 compound was observed, melting incongruently (39.0%, 43.8°C.). Compositions containing 0.8 and 2.08% of the acid gave two freezing points. These correspond, presumably to molecular compounds (possibly polymorphs) of a complexity equal to or greater than that of the crystals that formed in the same concentration range in the palmitic acid system. The crystals separating along the lower curve in this range exhibit an incongruent melting point (8.0%, 31.7°C.).

The oleic and elaidic acid systems showed 1-to-1 compound formation, but no polymorphic modifications of the compound were observed (Figure 2). The compound region extended from the incongruent melting point of the compound to the eutectic with DMSO—i.e., from 47.8% acid (-5.7°C.) to 39.5% acid (-7.3°C.) in the oleic acid system and from 33.3% acid (13.2°C.) to 25.0% acid (11.0°C.)
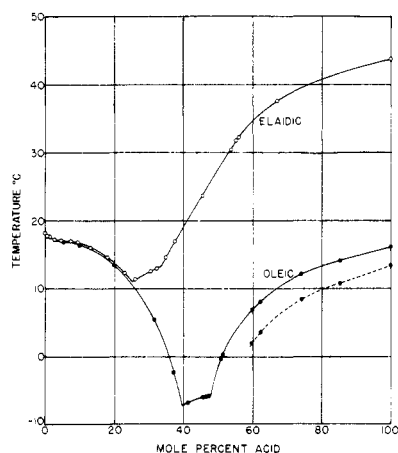
Figure 2. Binary freezing point
diagrams for DMSO with oleic
and elaidic acids

—— Stable equilibria

- - - - Metastable equilibria

in the elaidic acid system. Two freezing points were observed for compositions from 60 to 100% oleic acid, one for the unstable and the other for the stable modification of the acid.

ACKNOWLEDGMENT

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Solubilities and Activity Coefficients of Sodium Chloride and

Potassium Chloride in Organic-Water Mixtures

Methyl(2-ethylhexyl)sulfoxide and Several Quaternary
Ammonium Chlorides and Carboxylates Containing Water

C. F. COLEMAN
Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.   37830

Organic-phase activity coefficients $\gamma_{\pm}^{*}$ or ratios $\Gamma = \gamma_{\pm}^{*}/\gamma_{\pm}$, which measure the selectivity of an organic liquid for extracting water in preference to salt, were determined for inorganic salts in a series of quaternary ammonium salts and in methyl(2-ethylhexyl)sulfoxide (MEHSO). Results support the previous generalization (from esters and amides) that the selectivity is controlled mainly by the water content of the organic-rich phase, but the selectivities with the present compounds are relatively low. In the absence of inorganic salts, saturation mole ratios of water to quaternary salt at 25° C. ranged from 2 to 15 (up to 28 wt. % of water), increasing with decreasing molecular weight and with decreasing symmetry. Saturated MEHSO contained 57 wt. % of water at 25° C., with only 1.7 wt. % of MEHSO in the water-rich phase; mutual solubility increased to a lower consolute point at 8° C. and 86 wt. % of water.

$\mathbf{A}$S a part of a water research program directed toward a better understanding of selective hyperfiltration membrane behavior, the selectivity of a dialkylsulfoxide and of a series of quaternary ammonium salts for water over inorganic salts was examined by measuring the activity coefficients of sodium and potassium chlorides, via solubilities and liquid-liquid distributions. The principal objective was to test extension of the generalities previously observed for both esters (2) and amides (1) to still different types of organic compounds. The quaternary ammonium salts were varied in regard to both structure and equivalent concentration, in the hope of finding either unusually high selectivity for water over salt, or reversal to a useful selectivity for salt over water. The results do support the previous generalization that the selectivity for water over salt is controlled mainly by the water content of the organic-rich phase, and they show some consistent dependence of

water capacity on structure. However, the selectivities for water over salt were relatively low, and no instance of selectivity for salt over water was found.

The sulfoxide was examined because in the course of a study of metal-ion extractions by a series of dialkylsulfoxides (3), this one compound, the unsymmetrical methyl(2-ethylhexyl)sulfoxide (C_8H_{17}-SO-CH_3, MEHSO), was observed to dissolve a considerable amount of water although not itself very soluble in water.

EXPERIMENTAL

Solubility of water in the quaternary ammonium salts was measured in liquid-liquid equilibrations with inorganic salt absent, present at tracer concentration, or present at saturation. Solubility of the inorganic salt in the organic