Freezing Point Behavior of the Ternary Reciprocal Salt Pair System

. . . Involving Cyclohexylamine and 2,2′-Dipyridylamine Salts of Stearic and Palmitic Acids

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IN A PREVIOUS report (*3*) on the primary freezing point diagram for the ternary reciprocal salt pair system involving cyclohexylamine stearate (CS), cyclohexylamine palmitate (CP), 2,2′-dipyridylamine stearate (DS), and 2,2′-dipyridylamine palmitate (DP) apparent anomalies were observed in the freezing point behavior of certain mixtures rich in DS and DP. Further investigation has revealed that these anomalies were caused by metastable crystalline modifications which masked the existence of an incongruently-melting crystalline molecular compound, DS·DP, which forms in this region. Additional freezing point measurements have been made and a revised ternary diagram has been constructed which now accounts satisfactorily for the freezing point behavior of all mixtures of these four salts.

EXPERIMENTAL

Procedure. The preparation of the pure salts and the procedure for determining the freezing points have been described (*2, 3*). Mixtures *c, e, f, h, i, j, k,* and *l* were made by fusing the proper proportions, grinding, re-fusing, and regrinding to ensure homogeneity. Their compositions in mole per cent are given in the footnotes to Table I and are represented by the indicated points in Figure 3. In general the metastable crystalline modifications could be formed by seeding the supercooled melt by local chilling with a piece of ice held against the upper end of the partially immersed sample tube.

RESULTS AND DISCUSSION

The experimental data for the additional "binary" systems are given in Table I and represented graphically in Figures 1 and 2. The dashed lines in these diagrams represent metastable equilibria.

The diagram for the binary system DS-DP (Figure 1) reveals the existence of a 1:1 molecular compound DS·DP, the crystals of which melt incongruently at 54.8° C. and are in stable equilibrium with the melt between the peritectic (59.0% DP, 54.8° C.) and the eutectic (67.6% DP, 54.3° C.). They can also exist in metastable equilibrium from 59.0% to at least 50.0% DP and also from 67.6% to at least 70.2% DP. Their (metastable) congruent freezing point was found to be 55.2° C. That crystals of the molecular compound DS·DP can also exist in stable and unstable equilibrium in ternary mixtures of DS and DP with CS or CP is shown by the contours of the systems *i-j, k-l, c-h,* and *c*-CP in Figures 1 and 2.

The molecular compound DS·DP exists as a well-defined crystalline material even when it is the metastable phase but for both DS and DP, the stable solid phases for these compositions, the melt at equilibrium has the appearance of a turbid or opaque liquid. Microscopic examination of these opaque liquids in polarized and unpolarized light gave no indication of liquid crystals.

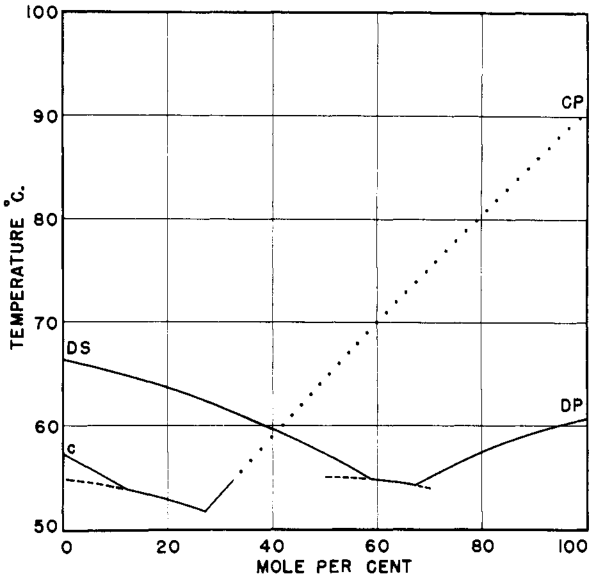

Figure 1. "Binary" freezing point diagrams
--- Metastable equilibria
. . . Obtained by interpolation from isothermal projection of ternary diagram

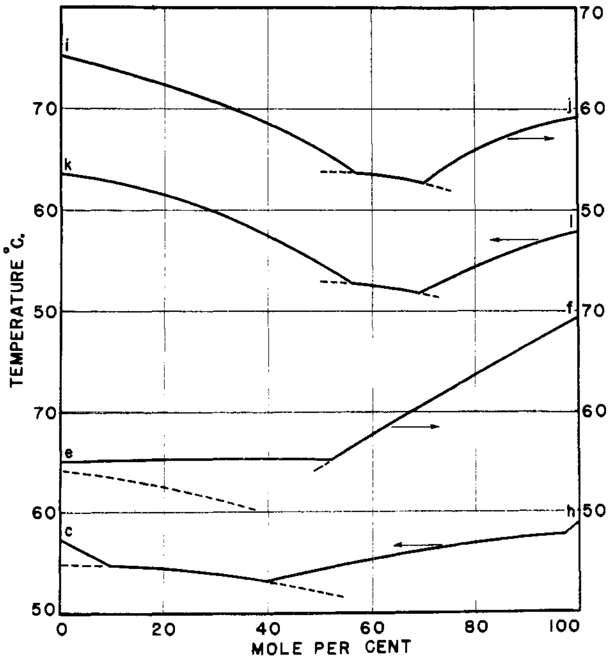

Figure 2. "Binary" freezing point diagrams
--- Metastable equilibria

Table I. Freezing Point Data for Binary and Quasi-Binary Systems

Mole % of A[a]	Freezing Point[b], ° C	Mole % of A[a]	Freezing Point[b], ° C.
Mixture *h* – Mixture *c*[c] System		Mixture *j* – Mixture *i*[c] System	
0.00	57.3 (55.2)[d]	0.00	65.2[e]
5.80	55.8 (54.7)	10.74	63.7
9.4	54.8[f]	14.0	63.4[e]
11.97	54.6	20.49	62.3
15.90	54.5	30.65	60.6
23.29	54.1	39.60	58.6
30.09	53.8	50.06	55.9 (53.7)
34.71	53.6	58.6	53.6[f]
39.0	53.3[f]	60.36	53.6
39.50	53.1	64.96	53.3
42.37	53.1	69.72	52.8
52.7	51.8[e]	70.2	52.8[f]
54.50	54.8 (51.5)	73.87	54.2 (52.1)
63.35	55.7	75.7	(52.0)[e]
64.2	55.8[e]	76.8	55.3[e]
65.0	55.9[e]	76.9	55.3[e] (51.6)[e]
74.16	56.4	79.22	55.9
84.19	57.3	86.1	57.2[e]
89.0	57.5[e]	88.5	57.5[e]
95.55	57.8	89.67	57.9
97.22	59.1	100.00	59.2
100.00			
Mixture *l* – Mixture *k*[c] System		Mixture *f* – Mixture *e*[c] System	
0.0	63.6[e]	0.00	55.1 (54.2)
11.34	62.7	16.84	55.0 (52.8)
21.15	61.6	27.9	55.3[e]
26.0	60.6[e]	27.99	55.3 (51.4)
31.00	59.8	28.0	55.2[e]
40.25	57.4	28.7	55.2[e] (51.6)[e]
49.67	54.9 (53.0)	36.00	55.4 (50.5)
56.2	52.8[f]	37.0	55.4[e]
59.74	52.6	37.4	(50.3)[f]
61.1	52.6	39.0	55.4[e]
61.9	52.3	48.0	55.6[e]
64.9	52.2	48.68	55.6 (54.0)
69.1	51.9[f]	52.4	55.4[f]
69.2	52.0[e] (51.8)[e]	59.25	57.6
69.51	51.7	79.58	63.4
76.0	53.9[e] (52.4)[e]	100.00	69.4
79.42	54.3		
83.4	55.4[e] (53.9)[e]		
95.5	57.6[e]		
100.00	58.0		
CP-Mixture *c*[c] System		DP-DS[c] System	
0.00	57.3 (55.2)[d]	0.00	66.3
5.05	56.0	15.37	64.1
10.60	54.3	25.03	63.0
12.4	53.8[f]	39.94	59.6
23.55	52.4	49.86	57.2 (55.2)
26.53	51.9	50.00	57.3 (55.2)[d]
27.1	51.7[f]	54.60	56.0 (55.2)
27.47	51.9	59.0	54.8[f]
29.65	53.0	59.80	54.8
100.00	90.6	64.54	54.4
		67.6	54.3[f]
		70.25	55.2 (54.0)
		73.76	55.8
		79.24	57.4
		89.49	59.2
		100.00	60.8

[a] A is first mentioned substance. [b] Parenthetical values are metastable equilibria. [c] CP = cyclohexylamine palmitate, CS = cyclohexylamine stearate, DP = dipyridylamine palmitate, DS = dipyridylamine stearate, Mixture *c* = 50% DP-50% DS: Mixture *e* = 68% DP-32% DS; Mixture *f* = 50% CP-50% DP; Mixture *h* = 27% CP-73% DP; Mixture *i* = 14% CS-86% DS; Mixture *j* = 14% CP-86% DP; Mixture *k* = 24% CS-76% DS; Mixture *l* = 24% CP-76% DP. [d] 1:1 compound. [e] By interpolation from an intersecting system. [f] Apparent eutectic or peritectic by graphical interpolation.

The supplemental data make it possible to construct the revised polythermal and isothermal projections (Figures 3 and 4) of the solid model for the complete system, formed (*1*) by plotting primary freezing points vertically above a square base representing the various compositions in mole per cent. The thin dashed lines in Figure 3 are projections of the various "binary" systems involved, including those for which complete data have already been reported (*3*).

In addition to the four bivariant crystallization areas within which the crystals of CS, CP, DS, and DP, respectively, are in equilibrium with the liquid at the

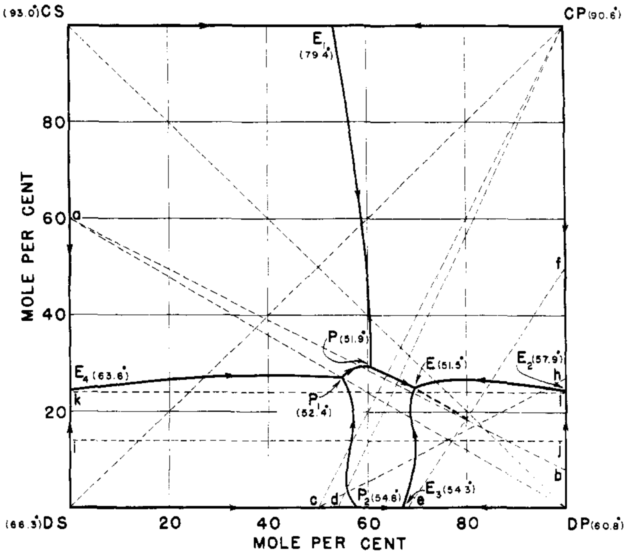

Figure 3. Polythermal projection of the crystallization surfaces for the ternary reciprocal salt pair system involving CS, CP, DS, and DP

--- Projections of all the "binary" systems investigated. The heavy dashed extension of PE represents the metastable eutectic trough between the CP and DP · DS crystallization surfaces

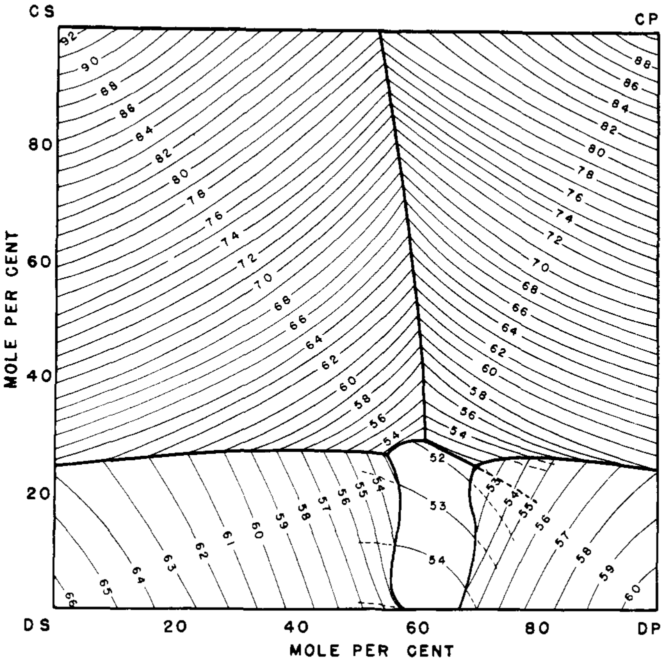

Figure 4. Freezing point diagram for the reciprocal salt pair system involving CS, CP, DS, and DP showing isothermal contour projections

--- Metastable equilibria

Table II. Eutectic and Peritectic Compositions and Temperatures

Invariant Point	Comp., Mole %				Temp., ° C.	Solid Phases
	CS	CP	DS	DP		
E_1	46.6	53.4			79.4	CS, CP
E_2		24.4		75.6	57.9	CP, DP
E_3			32.4	67.6	54.3	DP, DS·DP
E_4	24.3		75.7		63.6	CS, DS
P_2			41.0	59.0	54.8	DS, DS·DP
E		25.1	30.7	44.2	51.5	CP, DP, DS·DP
P_1		27.0	45.1	27.9	52.4	CS, DS, DS·DP
P		29.4	39.2	31.4	51.9	CS, CP, DS·DP

primary freezing point, there is a fifth crystallization area, $P_2P_1PEE_3$, within which the molecular compound DS·DP is the solid phase. The lines E_1P, E_2E, E_3E, P_2P_1, E_4P_1, P_1P, and PE represent all the univariant ternary systems. They correspond to the grooves formed by the intersections of the five crystallization surfaces of the solid model. Their positions are defined by the compositions and temperatures of the apparent eutectics and peritectics in the various "binary" systems and are further established on the basis of the isotherms (Figure 4) drawn through compositions having identical primary freezing points on each crystallization surface. (These isotherms were also used to establish the data for the dotted lines in Figure 1.)

In addition to the single components there are eight invariant points in the system. These include four binary eutectics (E_1, E_2, E_3, and E_4), one binary peritectic (P_2), one ternary eutectic (E), and two ternary peritectics (P_1 and P), as shown in Table II.

The freezing point diagrams in Figures 1 and 2 prove that the DP·DS crystallization surface $P_2P_1PEE_3$ extends into a metastable region below the DS crystallization surface and that both the DP·DS and CP surfaces extend metastably below the DP surface. The isotherms for these metastable equilibria are shown as broken lines in Figure 4. The heavy broken-line extension of PE in Figures 3 and 4, previously deduced on the basis of heating curves (*3*), is thus confirmed. It represents the metastable eutectic trough formed by the intersection of the metastable DS·DP and CP crystallization surfaces and explains the subnormal ternary eutectic halts, at about 48° C., observed in heating curves for compositions in this general region (*3*). The revised diagram also explains why, for specific compositions, halts in the heating curves were observed at about 51.5, 51.9, or 52.4° C.

From the ternary diagram it is possible to predict the freezing point behavior of any mixture of these salts, including the temperature at which crystals of each component will appear on cooling, the yields of the crystals and the composition of the liquid phase at various temperatures, and the temperature at which maximum yields of the crystals of the specific salts can be obtained under equilibrium conditions.

ACKNOWLEDGMENT

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