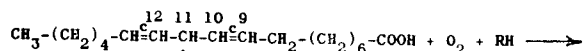


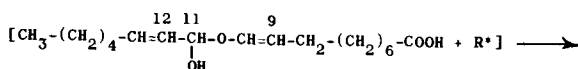
model experiment no 2-*trans*-octenal was detectable. To explain the occurrence of 1-octen-3-ol, we postulate the formation of the hemiacetal (VIII) from the unstable free radical of linoleic acid (VII) via an unstable intermediate. This hemiacetal (VIII) could possibly undergo an intermolecular cyclic rearrangement (IX) and could be cleaved to a secondary unsaturated alcohol (by allylic rearrangement) e.g., 1-octen-3-ol (X) and an unsaturated aldehydic acid (XI), as postulated recently also by Frankel et al. (20).

The presence of acetal functions in oxidized oils and fats was postulated as early as 1923 [cf. Powick (21)].

Proposed reaction scheme:

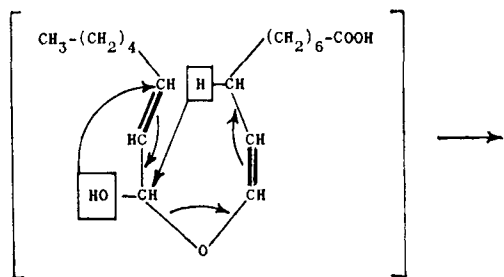


VII

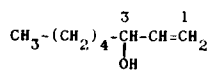


VIII

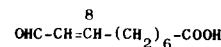
(in which RH = linoleic acid and R\* its free radical)



IX



X



XI

Some stabilizing interaction on the unstable free radical of linoleic acid (VII) by an unknown oil constituent may account for the presence of 2-*trans*-octenal in oils. In the absence of such a stabilizing constituent, 1-octen-3-ol will be formed, which can again secondarily be oxidized to 2-*trans*-octenal or other products.

### Acknowledgment

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## Freezing Point Behavior of the Ternary Reciprocal Salt Pair System Involving the Morpholine and 2,2'-Dipyridylamine Salts of Stearic and Palmitic Acids<sup>1</sup>

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### Abstract

Binary and quasi-binary freezing point data have been obtained to establish the freezing point diagram for the ternary reciprocal salt pair system, involving the morpholine and 2,2'-dipyridylamine salts of stearic and palmitic acids. The diagram shows that there are six crystallization surfaces representing equilibrium with crystals of MS, MP, DS, DP, DS·DP, and MS·DP. The compositions and primary freezing points of the six peritectic and five eutectic mixtures have

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

### Introduction

IN THE COURSE of an investigation of the use of mixed amines in the separation and purification of long chain fatty acids (2), fundamental information

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<sup>2</sup> One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.

was obtained on the freezing point behavior of various types of reciprocal salt pair systems. Reports have already been made on two such systems for palmitic and stearic acid salts. One, involving the cyclohexylamine and morpholine salts, gave a simple ternary freezing point diagram with no compound formation but with a ternary peritectic point (5). The other, for the cyclohexylamine and 2,2'-dipyridylamine salts, was more complicated because of the formation of a binary compound (6) and the existence of a binary and two ternary peritectics. The present paper deals with the reciprocal salt pair system involving morpholine stearate (MS), morpholine palmitate (MP), 2,2'-dipyridylamine stearate (DS) and 2,2'-dipyridylamine palmitate (DP). The freezing point diagram for this system shows one binary, one true quasi-binary, and four ternary peritectics. Both a binary and a ternary compound are formed. This diagram can be used to predict the freezing point behavior and the heating and cooling curve behavior of any mixture of these four salts.

The pure salts were prepared by mixing equimolar amounts of the acid and amine, all Eastman White Label products, and recrystallizing repeatedly from a solvent until there was no change in freezing point. The products were dried in a vacuum desiccator over solid potassium hydroxide and had the following freezing points and nitrogen analyses: MP, fp, 66.70C, N, 4.06%, theory 4.08%; MS, fp, 72.18C, N, 3.85%, theory 3.77%; DP, fp, 60.84C, N, 9.87%, theory 9.83%; and DS, fp, 66.31C, N, 9.19%, theory 9.22%.

Mixtures *a*, *b*, *c*, *d*, and *e* were prepared by mixing the amine salts in the correct proportions and then twice melting, solidifying, and grinding to ensure homogeneity. The compositions in mole % were as follows: Mixture *a*, 46.0% MS and 54.0% DS; Mixture *b*, 46.0% MP and 54.0% DP; Mixture *c*, 72.0% DS and 28.0% DP; Mixture *d*, 80.0% DP and 20.0% DS; Mixture *e*, 80.6% DP and 19.4% MP.

The freezing point determinations were made by the thermostatic, sealed tube method (3), which involves finding two temperatures a few tenths of a degree apart, at one of which liquefaction is complete and at the other a few crystals persist after a long period of agitation at constant temperature. To avoid decomposition of the morpholine salt care was taken not to heat the freezing point samples more than about 10 degrees above the melting point. That no decomposition took place was shown by the reproducibility of successive freezing point determinations on the same samples.

### Results and Discussion

Primary freezing point data were obtained for the following systems: MS-MP, MS-DS, MP-DP, DS-DP, MP-DS, MS-DP, *c*-MP, MS-*e*, MS-*d*, and *a*-*b*. The results are given in Table I and shown graphically in Figures 1 and 2. All compositions are given in mole %. The broken lines in these diagrams represent metastable equilibria. The establishment of stable or metastable equilibrium depended upon the original melt temperature (presence of crystal nuclei), the rate of cooling, the degree of agitation, the degree of supercooling, and whether crystallization was spontaneous or caused by seeding. Metastable crystals were usually obtained by seeding the supercooled melt with a piece of ice held against the upper wall of the partially immersed sample tube.

The binary systems MS-MP, MS-DS, and MP-DP are of the simple eutectic type. The binary system

DS-DP involves the molecular compound DS·DP which has an incongruent melting point of 54.8C and a (metastable) congruent melting point of 55.2C. It was found possible also to attain metastable equilibrium with this compound at a composition to the right of the eutectic (Figure 1), where DP is the stable solid phase.

TABLE I  
Freezing Point Data for Binary and Quasi-Binary Systems

Mole % of A <sup>a</sup>	Freezing point <sup>c</sup> C	Mole % of A <sup>a</sup>	Freezing point <sup>c</sup> C
MP-MS System <sup>b</sup>		Mixture <i>b</i> -Mixture <i>a</i> System <sup>b</sup>	
0.00	72.2	0.00	60.5
11.69	70.4	20.60	57.3
19.91	69.4	40.08	53.5
30.04	68.1	45.0 <sup>d</sup>	52.8 <sup>d</sup>
39.87	66.1	49.53	52.5
50.35	64.0	60.06	52.4 (48.0)
60.01	61.7	70.24	51.4
63.4 <sup>d</sup>	60.6 <sup>d</sup>	75.25	49.8
69.81	61.9	77.5 <sup>d</sup>	48.7 <sup>d</sup>
79.83	63.5	80.09	49.4
89.66	65.2	89.32	51.4
100.00	66.7	100.00	53.9
DP-MS System <sup>b</sup>		DP-DS System <sup>b</sup>	
0.00	72.2	0.00	66.3
20.39	66.3	15.37	64.1
30.38	62.9	25.03	63.0
39.58	58.9	39.94	59.6
45.33	56.0	49.86	57.2 (55.2)
50.12	53.8	50.00	55.2 (55.2) <sup>f</sup>
50.6 <sup>d</sup>	53.2 <sup>d</sup>	54.60	56.0 (55.2)
54.77	53.0	58.9 <sup>d</sup>	54.8 <sup>d</sup>
59.95	52.3	59.80	54.8
69.5 <sup>d</sup>	50.1 <sup>d</sup>	64.54	54.4
69.64	50.1	67.5 <sup>d</sup>	54.3 <sup>d</sup>
78.01	53.9	70.25	55.2 (54.0)
88.48	57.7	73.76	55.8
100.00	60.8	79.24	57.4
		89.49	59.2
		100.00	60.8
DS-MP System <sup>b</sup>		Mixture <i>d</i> -MS System <sup>b</sup>	
0.00	66.7	0.00	72.2
10.28	63.9	30.16	63.7
20.46	60.3	40.08	60.0
29.96	56.6	53.35	54.0
36.2 <sup>d</sup>	53.6 <sup>d</sup>	55.0 <sup>d</sup>	53.0 <sup>d</sup>
40.46	53.8	60.54	52.7
44.15	54.0	63.53	52.6
49.65	53.5	71.2 <sup>d</sup>	51.1 <sup>d</sup>
50.6 <sup>d</sup>	53.3 <sup>d</sup>	73.62	51.6
55.56	53.4	80.83	52.2
58.4 <sup>d</sup>	52.7 <sup>d</sup>	83.68	52.5
59.58	53.4	88.18	52.7
79.15	60.7	88.2 <sup>d</sup>	52.7 <sup>d</sup>
89.27	63.8	93.95	55.3
100.00	66.3	100.00	57.4
MP-Mixture <i>c</i> System <sup>b</sup>		Mixture <i>e</i> -MS System <sup>b</sup>	
0.00	62.2	0.00	72.2
19.52	57.2	20.61	66.8
31.56	53.1	37.18	61.3
34.8 <sup>d</sup>	51.8 <sup>d</sup>	46.17	57.9
36.60	52.4	54.76	53.9
41.67	52.7 (48.5)	56.8 <sup>d</sup>	53.0 <sup>d</sup>
45.82	53.1	63.27	52.5 (49.0) <sup>e</sup>
51.60	52.6	67.8 <sup>d</sup>	52.5 (46.0) <sup>d</sup>
55.9 <sup>d</sup>	51.7 <sup>d</sup>	70.22	51.2 (47.0)
59.44	53.4	76.4 <sup>d</sup>	49.4 <sup>d</sup>
79.58	61.4	78.46	50.2
100.00	66.7	100.00	58.3
DP-MP System <sup>b</sup>		DS-MS System <sup>b</sup>	
0.00	66.7	0.00	72.2
20.57	63.4	20.99	68.7
40.09	58.5	31.25	66.5
45.07	57.2	39.84	64.7
49.43	55.8	50.18	61.8
55.8 <sup>d</sup>	53.2 <sup>d</sup>	56.0 <sup>d</sup>	59.9 <sup>d</sup>
59.30	54.1	64.25	61.5
69.86	56.4	69.24	62.3
79.19	58.0	78.43	63.8
90.19	59.7	100.00	66.3
100.00	60.8		

<sup>a</sup> A is first-mentioned substance.

<sup>b</sup> MP = morpholine palmitate; MS = morpholine stearate; DP = 2,2'-dipyridylamine palmitate; DS = 2,2'-dipyridylamine stearate;

Mixture *a* = 46.0% MS - 54.0% DS; Mixture *b* = 46.0% MP - 54.0% DP;

Mixture *c* = 72.0% DS - 28.0% DP; Mixture *d* = 80.0% DP - 20.0% DS;

Mixture *e* = 80.62% DP - 19.38% MS.

<sup>c</sup> Temperatures in parentheses are for metastable equilibria.

<sup>d</sup> Apparent eutectic or peritectic by graphical interpolation.

<sup>e</sup> 1:1 compound.

<sup>f</sup> Also another metastable equilibrium at about 44C.

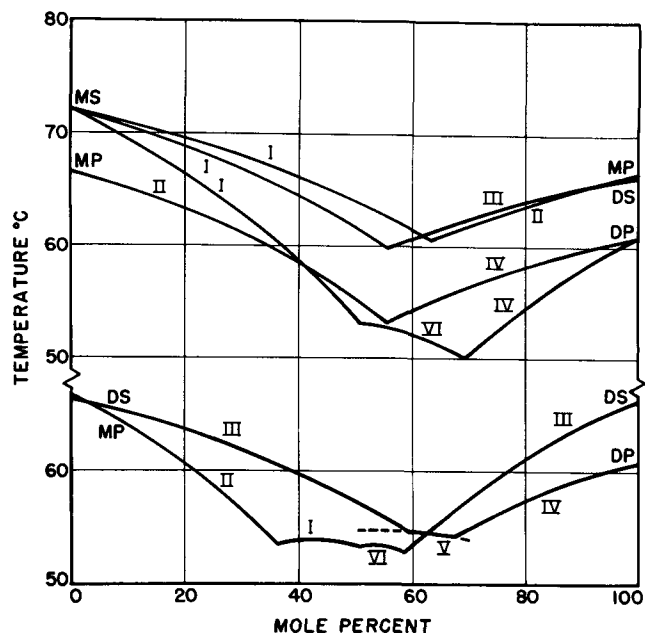


FIG. 1. Binary and quasi-binary freezing point diagrams. Roman numerals show crystal phase in equilibrium: I, MS; II, MP; III, DS; IV, DP; V, DS·DP; VI, MS·DP.

In interpreting the remaining freezing point diagrams, it must be kept in mind that the individual amine salts, when melted, dissociate into acid and amine molecules or the corresponding ions. They can therefore undergo double decomposition so that the following equilibrium exists in the liquid state:  $MS + DP \rightleftharpoons DS + MP$ . Any system involving these four substances is a ternary system of the reciprocal or metathetical type.

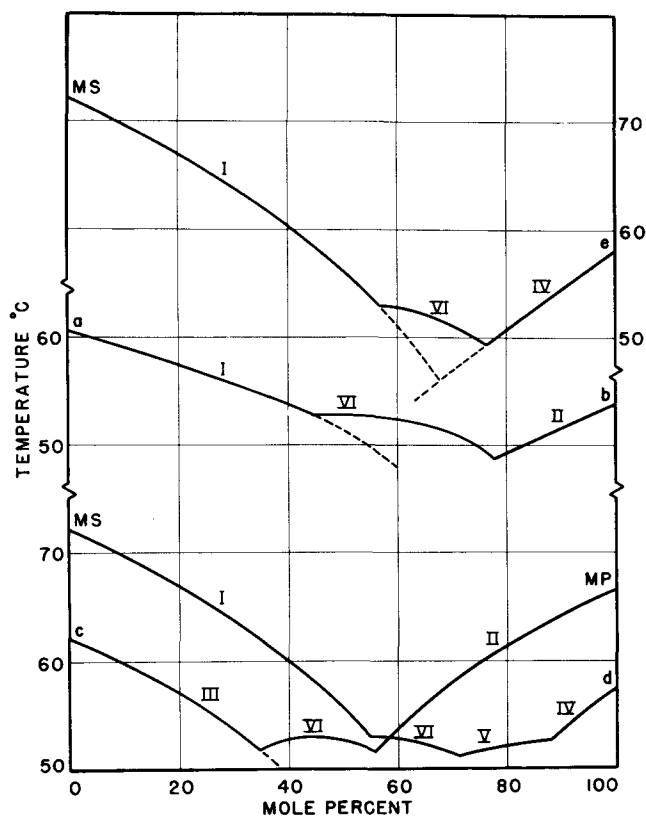


FIG. 2. Binary and quasi-binary freezing point diagrams. Roman numerals show crystal phase in equilibrium: I, MS; II, MP; III, DS; IV, DP; V, DS·DP; VI, MS·DP.

The graphical representation of the phase behavior of such systems has been developed by Jänecke (1). Figure 3 is a polythermal projection of the crystallization surface of the solid model formed by plotting primary freezing points vertically above a square base representing the various compositions in mole percentage. Each corner represents a pure substance, the sides represent binary compositions of substances having a common ion, and the interior includes all ternary compositions.

The lines  $E_1P_5$ ,  $E_2E$ ,  $E_3P_4$ ,  $E_4P_2$ ,  $P_3P_1$ ,  $P_1P_4$ ,  $P_4P_5$ ,  $P_5E$ ,  $EP_2$ , and  $P_2P_1$  represent all of the univariant systems, i.e., systems having two solids in equilibrium with the liquid. They correspond to the eutectic grooves formed by the intersections between the six bivariant crystallization surfaces of the solid model. Their positions were defined by finding the temperatures and compositions of the apparent eutectic and peritectic points in the various binary and quasi-binary systems (Table I, Figures 1 and 2), projections of which are shown in Figure 3 as broken lines. The position of the eutectic grooves and the compositions and temperatures at the invariant ternary eutectic and peritectic points,  $E$ ,  $P_1$ ,  $P_2$ ,  $P_4$ , and  $P_5$ , were further established on the basis of isotherms drawn through compositions having identical primary freezing points on each surface (Figure 4), as determined by interpolation in the various freezing-point diagrams in Figures 1 and 2. By extrapolation, the ternary eutectic composition  $E$  in mole % was found to be 44.1% MP, 34.6% DP, and 21.3% DS, and its freezing point was 48.0°C. The following are the corresponding compositions and primary freezing points for the various ternary peritectic points: for  $P_1$  29.4% MS, 56.3% DP, 14.3% DS, fp, 51.1°C; for  $P_2$ , 30.4% MS, 69.6% DP, fp 50.1°C; for  $P_4$ , 40.9% MP, 0.5% MS, 58.6% DS, fp, 52.7°C; and for  $P_5$ , 57.9% MP, 5.4% DP, 36.7% DS, fp, 52.5°C.

The various compositions in this diagram can also be expressed in terms of the mole percentage,  $m$ , of morpholine in the amine mixture (i.e. the ordinate in Figure 3), and the mole percentage,  $p$ , of palmitic acid in the acid mixture (i.e. the abscissa). The compositions of all the invariant points have been defined on this basis in Table II.

Figure 3 shows in projection the contours of the six crystallization surfaces representing stable equilibria. The crystals in equilibrium at the primary freezing point for compositions in the different areas are as follows: MS in area I, MP in area II, DS in area III, DP in area IV, the incongruently melting binary compound DS·DP in area V, and the incongruently-melting tetragene salt (4) MS·DP in area VI. The composition of the latter compound is represented by the intersection of the two diagonals,

TABLE II  
Eutectic and Peritectic Compositions and Temperatures

Invariant point	Composition <sup>a</sup>		Temperature °C	Solid phases
	$m$ (%)	$p$ (%)		
$E$	44.1	78.6	48.0	MP, DP, MS·DP
$E_1$	100.0	63.4	60.7	MS, MP
$E_2$	44.2	100.0	53.2	MP, DP
$E_3$	44.0	0.0	59.9	MS, DS
$E_4$	0.0	67.5	54.3	DS·DP, DP
$P_1$	29.4	56.3	51.2	DS, DS·DP, MS·DP
$P_2$	30.4	69.6	50.1	DP, DS·DP, MS·DP
$P_3$	0.0	58.9	54.8	DS, DS·DP
$P_4$	41.4	40.9	52.7	MS, DS, MS·DP
$P_5$	57.8	63.2	52.5	MS, MP, MS·DP
$f'$	49.4	50.6	53.2	MS, MS·DP

<sup>a</sup>  $m$  = mole % morpholine in amine mixture.  
 $p$  = mole % palmitic acid in acid mixture.

point *f*, which lies in area I. Its incongruent melting point is 53.2C, corresponding to the true quasi-binary peritectic point *f*. Figure 4 includes the isotherms representing both the stable solid-liquid equilibria and (as broken lines) the metastable equilibria.

By referring to Figures 3 and 4, one can more readily identify the crystalline phase in equilibrium with the liquid along each of the branches of the various binary and quasi-binary freezing point diagrams. These crystal phases have been indicated in Figures 1 and 2 by Roman numerals corresponding to the stable crystallization areas in Figure 3. Thus,

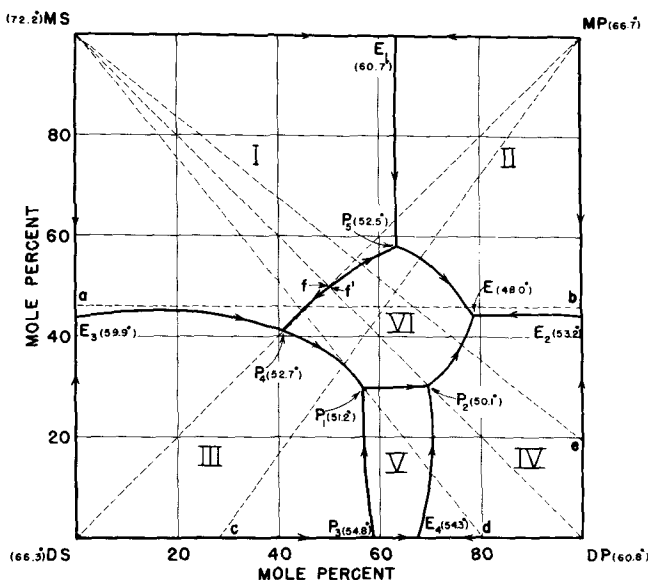


FIG. 3. Polythermal projection of the crystallization surfaces for the ternary reciprocal salt pair involving MS, MP, DS, and DP. The broken lines are projections of the quasi-binary systems investigated. Roman numerals refer to crystal phase in stable equilibrium: I, MS; II, MP; III, DS; IV, DP; V, DS·DP; VI, MS·DP.

since the section MP-DS crosses areas II, I, VI, and finally III, it is obvious the crystals in stable equilibrium with the liquid on the four branches of MP-DS curve in Figure 1 are, from left to right, MP, MS, MS·DP, and DS.

The DS crystallization surface, III, (Figures 3 and 4) extends into the metastable region below the MS·DP surface, VI. That is, in the *c*-MP diagram (Figure 2), DS is the solid phase along the left branch of the diagram and is the metastable solid phase along the extension of this branch. MS·DP is the crystalline phase along the middle branch.

Similarly the MS and DP surfaces extend under area VI as metastable equilibria and actually intersect at a eutectic groove (at about 46C in the system MS-*e*). In fact, the DP surface extends beyond this intersection, underneath the metastable MS surface. This was shown by a second (lower) metastable freezing point, at about 44C for the composition designated by a black circle in area VI of Figure 4. This corresponds to the MS-*e* composition containing 63.27% of Mixture *e* for which three primary freezing points 52.5C, 49.0C, and about 44.0C were obtained (see Figure 2). The lowest of these freezing points could not be determined accurately. Before equilibrium could be completely established crystals of MS started to separate slowly and these did not disappear until the metastable 49.0C equilibrium was reached.

Figures 3 and 4 give a complete picture of the freezing and melting behavior and the heating and cooling curve behavior of all possible mixtures of palmitic acid, stearic acid, morpholine, and 2,2'-dipyridylamine in which the total number of moles of acid and amine are equal. If only the stable solid phases

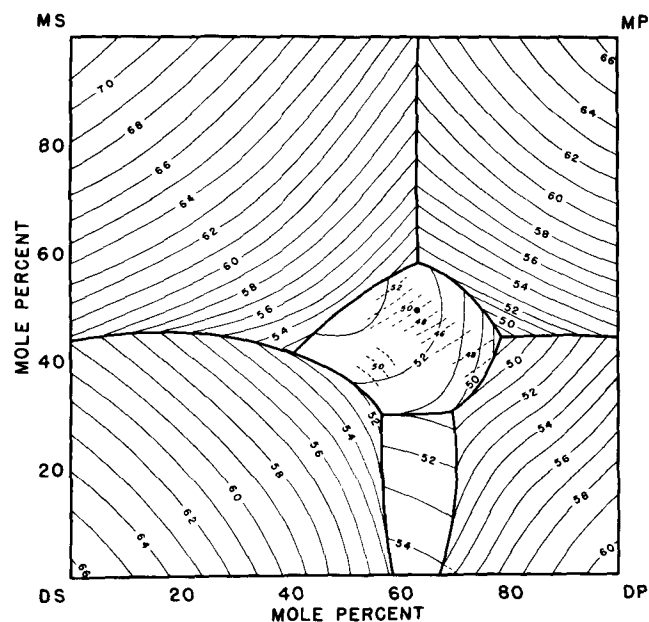


FIG. 4. Freezing point diagram for the reciprocal salt pair system involving CS, CP, DS, and DP showing isothermal contour projections. Broken lines represent metastable equilibria. Black circle represents lower metastable freezing point, 44C.

and perfect equilibrium conditions are considered, the crystallization end-point reached for molten compositions represented by any point within the triangle MS-*f*-MP would be  $P_5$ . For compositions within the triangle MP-*f*-DP, it would be *E*, and for those within triangle MS-*f*-DS, it would be  $P_4$ . Compositions within the triangle DS-*f*-DP would have  $P_1$  as the crystallization end point if *p* is less than 50% and  $P_2$  if *p* is greater than 50%.

Since  $P_2$  lies on the MS-DP diagonal the MS-DP system can be expected to behave like a true binary system. That is, considering stable equilibria only, compositions on this diagonal containing more than 50% of DP would have  $P_2$  (50.1C) as their crystallization end points. For those containing 50% or less of DP the crystallization would terminate at *f*' (53.2C), the incongruent melting point of this binary system (Figure 1).

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