[CONTRIBUTION FROM AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The System Trimethyl Phosphate-Acetic Acid

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The two solid phases of trimethyl phosphate have been described in an earlier paper.¹ The freezing points of the system trimethyl phosphatewater, involving the "alpha" form of the solid ester, were presented later.² The present paper pertains to the freezing points of the system trimethyl phosphate-acetic acid, including both of the solid forms of the ester.

Experimental.—Acetic acid was purified by fractionally crystallizing reagent acetic acid four times. The purified product froze at $16.58 \pm 0.05^{\circ}$, which is in satisfactory agreement with the value $10.60 \pm 0.005^{\circ}$ given by Bousfield and Lowry.³ The method of purifying the ester and also the apparatus and technique used in the freezing point determinations were the same as those described in the previous work.^{1,2}



Discussion.—Mixtures between the limits of about 47 to 71% of the ester became increasingly viscous at their freezing points as the eutectic composition was approached. In general the accuracy of the freezing points given in this region varies quite regularly from $\pm 1^{\circ}$ at the eutectic to $\pm 0.3^{\circ}$; elsewhere the accuracy is close to $\pm 0.1^{\circ}$. No reliable data could be obtained with mixtures containing less than 75 mole per cent. of the ester, when seeded with *beta* form of solid ester. In these cases, a very slow and more or less continuous temperature rise was usually observed after seeding, indicating that the meta-

- (1) Pagel and Schroeder, THIS JOURNAL, 62, 1837 (1940).
- (2) Pagel and Maxey, *ibid.*, **63**, 2499 (1941).
- (3) Bousfield and Lowry, J. Chem. Soc., 99, 1436 (1911).

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EXPERIMENTAL VALUES OF THE FREEZING POINTS OF THE SYSTEM TRIMETHYL PHOSPHATE-ACETIC ACID

MeiPO	F. p., °C.	Mole % MerPOr	F. p., °C.
0.0	16.6	Alpha Fe	orm (Stable)
0.7	16.2	55.2	-87.5
1.1	15.8	58.4	-82.8
4.0	13.9	62.9	-72.9
6.6	11.9	71.2	-60.6
8.6	10.4	80.9	-55.4
10.3	8.7	88.7	-50.4
13.3	5.8	100	-46.1
19.2	0.7	Bata Barry	(Matastahla)
25.0	- 8.3	Deta Porm	(Metastable)
29.1	-15.2	75.1	-75.6
33.6	-22.9	80.9	-72.1
37.0	-30.0	84.1	-70.4
41.2	-41.3	85.7	-68.9
46.9	-61.8	88.7	-67.3
48.6	-70.2	100	-62.4
51.3	-83.8		
52.9	-89.9		
	(Eutentic)		

stable (*beta*) form might be spontaneously changing slowly into the stable *alpha* form. The entire area (Fig. 1) bounded by Curve A and the horizontal eutectic solidus line represents a definite phase equilibrium field; whereas the incomplete curve B indicates the partial upper boundary of the undetermined metastable field.

Summary

1. Freezing points of the system trimethyl phosphate-acetic acid, involving both forms of the solid ester, have been studied.

2. The eutectic composition with the so-called *alpha* form of solid ester was found at 52.9 mole per cent. of the ester with a freezing point of $-89.9 \pm 1^{\circ}$.

3. Attempts to determine the freezing points of the *beta* form proved unsuccessful with mixtures containing less than 75 mole per cent. of the ester.

4. Tabulated data, graphical representation and references to experimental methods, and some discussion have been included.

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