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EXPERIMENTAL STATION

SUFFIELD, ALBERTA

TECHNICAL MINUTE NO. 109

PREPARATION AND PROPERTIES OF DIMETHYLAMINO CYANOPHOSPHORIC ACID ETHYL ESTER.

SUMMARY

A quantity of dimethylamino cyanophosphoric acid ethyl ester was prepared and purified by successive fractionations. The density, refractive index, viscosity, and surface tension were measured over a wide temperature range. These data, along with specific refractivities and parachor are recorded.

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JWY:JS

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INTRODUCTION

1. Several papers have appeared on the subject of dimethylamino cyanophosphoric acid ethyl ester (MCE) (1,2,3). However only fragmentary data on physical properties have been reported.

2. In an effort to fill gaps in the knowledge, which existed at the time when this work was started, a supply of MCE has been prepared and purified for the measurement of certain physical constants.

PREPARATION AND PROPERTIES

3. The method of preparations described in U.S. Army Intelligence Division Report No. 3709. (1) was followed. Details of the preparation and purification, including properties of the various fractions, are given.

4. Two products (A-2 and C-2 in Appendix I), of different degrees of purity, were used for the physical tests.

The purest material obtained (fraction C-2) had a melting point of $-48.9 \pm 0.3^{\circ}C$. The refractive index n 25/D was 1.4221, which compares with 1.4225 reported previously (1,3).

5. Tables I and 2 summarize the values for density, refractive index, surface tension, viscosity and derived functions for the two selected fractions. Methods are discussed in Appendix 2.

TABLE I

PROPERTIES OF MCE

Fraction A-2
(Appendix I)

T	D t/4	Refractive Index n D	Surface Tension γ dynes/cm	Viscosity		Parachor	Specific Refractivity	
				Centi-stokes	Centi-poises		$\frac{n^2-1}{n^2+2}\frac{1}{d}$	$\frac{n-1}{d}$
-50	1.1617							
-40	1.1517							
-30	1.1419							
-20	1.1320							
-10	1.1220							
0	1.1108							
5	1.1069							
10	1.1019	1.4301	34.8	3.29	3.63	358	0.2349	0.3903
15	1.0970	1.4284	34.3	2.91	3.19	358	0.2347	0.3905
20	1.0911	1.4267	33.8	2.60	2.84	358	0.2352	0.3911
25	1.0872	1.4249	33.4	2.34	2.54	359	0.2351	0.3908
30	1.0813	1.4231	32.9	2.11	2.28	359	0.2356	0.3913
35	1.0773	1.4214	32.5	1.91	2.06	360	0.2356	0.3912
40	1.0714	1.4197	32.0	1.74	1.87	360	0.2360	0.3917
45	1.0676							
50	1.0618							

TABLE 2

PROPERTIES OF MCE

Fraction C-2

T	Dt/4	Refractive Index n D	Surface Tension γ dynes/cm	Viscosity Centi-stokes	Viscosity Centi-poises	Parachor	Specific Refractivity $\frac{n^2-1}{n^2+2}\times\frac{1}{d}$	Specific Refractivity $\frac{n-1}{d}$
-50	1.1485							
-40	1.1388							
-30	1.1290							
-20	1.1194							
-10	1.1097							
0	1.1000							
5	1.0951		34.5	3.83	4.20	359		
10	1.0903	1.4278	34.0	3.28	3.58	359	.2359	.3924
15	1.0854	1.4258	33.5	2.89	3.14	359	.2360	.3926
20	1.0804	1.4239	33.0	2.56	2.77	360	.2361	.3924
25	1.0756	1.4221	32.5	2.30	2.47	360	.2363	.3924
30	1.0708	1.4202	32.0	2.08	2.23	360	.2364	.3924
35	1.0660	1.4182	31.5	1.89	2.02	361	.2365	.3923
40	1.0612	1.4163	31.0	1.73	1.84	361	.2366	.3923
45	1.0563							
50	1.0515							

6. An approximate determination of the specific heat of Fraction C-2 gave a value of 0.45 cal/gm (25° to 50°C). The accuracy of the determination, which was made by an improvised calorimeter is estimated at ± 5 per cent.

7. The solubility in water was measured by shaking 2.5 g. of fraction C-2 with 20 cc. of distilled water, pH 5.2, at 0°C, separating from excess MCE, and titrating for cyanide after alkaline hydrolysis. The value found was 8.2 g./100 ml. of solution. This was checked by adding small increments of MCE to water in a graduated flask at 0°C until a turbid solution remained after shaking. This method also gave 8.2 grams/100 ml. Subsequent work has shown that hydrolysis would be inappreciable under the conditions used. (4). This solubility of 8.2 g./100 ml. compares with a previously reported value of 2-3 per cent at room temperature (2).

DISCUSSION

8. It will be noted that the viscosity is relatively low, and that the surface tension follows a linear relationship.

9. The molecular parachor as calculated shows little change with temperature over the range of 0 to 40°C. Due to lack of data for the atomic parachor of phosphorus, theoretical values have not been calculated.

10. The specific refractivities by the Lorenz-Lorentz and the Gladstone-Dale formulae are computed.

This paper was written by Major J.W. Young, Mr. F.A. Hochstein and Pte. L.W. Emmerson.

Literature Cited.

1. American Army Intelligence Division Report No. 3709 U.S. - CWS. 28 April 1945.

2. Ptn. 4240 (V.3956).

3. Army Service Forces Office of the Chief Chemical Warfare Service Memorandum of 21 May 1945.

4. The Hydrolysis of MCE T.D.M.R. 1121.

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TWY.TS

APPENDIX I

Preparation of Dimethylamino cyano phosphoric acid ethyl ester.

Dimethylamino phosphoric acid chloride was prepared by refluxing 81 gms. (1 mole) of dry dimethylamine hydrochloride (M.P. 163-170) with 600 gms (3.9 moles) of phosphorus oxychloride for five hours. Excess phosphorus oxychloride was removed under vacuum and the product distilled through a short Vigreux column at 55-60°/4.5 mm. The yield of product was 100 g. (0.62 mole) 62% of theory.

The final product, dimethylamino cyano-phosphoric acid ethyl ester, was prepared by adding dropwise 103 gms (0.63 mole) of dimethylamino phosphoric acid chloride to a vigorously stirred suspension of 89 gms (1.81 moles) of dry sodium cyanide crystals in 32 gms (0.68 mole) of absolute ethanol and 115 ml of benzene, at 40°C. The reaction was slightly exothermic but temperature was controlled manually with an ice bath to within 1°C without difficulty. Stirring was continued for one hour after addition of all the dimethylamino phosphoric acid chloride ceased. The reaction mixture was filtered, the solvent stripped off under vacuum; and the residue distilled at 1 mm pressure. The yield was 75 gms (0.47 mole) of dimethylamino cyano-phosphoric acid ethyl ester, boiling at 65-70°. This yield is 75% of theoretical, based on dimethylamino phosphoric acid chloride.

An attempt to purify this fraction by fractional freezing gave poor results, and was abandoned. Further purification was effected by two distillations at reduced pressure. All distillations are shown in the diagram below.

Crude Product

Distilled at 1 mm.

A_1	A_2	A_3
10.5 g	75 g. 70-72°C	10 g.
$n_D^{25} = 1.4301$	$n_D^{25} = 1.4249$	$n_D^{25} = 1.4245$

Dist. at 0.35 mm.

B_1	B_2	B_3
18 g.	28 g. 56°C.	20g. 56°C
$n_D^{25} = 1.4260$	$n_D^{25} = 1.4220$	$n_D^{25} = 1.4214$

Dist. at 0.2 mm

C_1	C_2	C_3
7 g. 51-52°C	36 g. 52°C	3 g. 52°C
$n_D^{25} = 1.4232$	$n_D^{25} = 1.4221$	$n_D^{25} = 1.4215$

Fractions A_2 and C_2 were tested for purity by a titration for cyanide (Liebig) after hydrolysis in alcoholic NaOH. Fractions A_2 and C_2 showed 94.1% and 98.5% purity respectively. These are felt to be minimum figures only and not a true indication of purity.

APPENDIX 2

Determination of Physical Constants of dimethylamine cyano-phosphoric acid ethyl ester.

Density.

Three dilatometers, having capacities of 7.5, 9.6 and 1.1 ml., respectively, were used. Each instrument consisted of a bulb with graduated neck, readable to 0.005 per cent of the bulb volume. All were of Pyrex glass, and each was calibrated at various positions of the scale, using water. After filling and closing by glass stoppers they were placed in a transparent Dewar flask which contained acetone at -60°C. Volumes were read during the period of warming to room temperature, temperatures being taken by calibrated thermometers. Warm water (50°C) was then placed in the flask, and volumes read during cooling. Densities were computed, correcting all weights to vacuum, and applying appropriate expansion corrections. Densities so determined were plotted against temperatures, and a curve drawn through the points. Mean deviation of individual points from the curve was 0.0001, the maximum deviation being 0.0005.

Refractive Index.

Two Abbé refractometers were used, one being a compensated Hilger instrument, the other a Spencer type using a sodium lamp. Both were calibrated with water and the wedges supplied by the manufacturer, the corrected values on the two instruments agreeing to within 0.0002. Results are considered to be accurate within 0.0002.

Viscosities.

Viscosities were measured on a modified form of Ubbelohde viscometer (1) which had been calibrated with aniline, water, chloroform, and benzyl alcohol. The results are considered to be accurate to within ± 0.5 per cent.

Surface Tension.

Three stalagmometers were used. Each consisted of a simple U-tube, one arm of which was of selected capillary tubing. They were mounted in a transparent Dewar flask, the open ends being fitted with charcoal guard tubes. They were calibrated with water, benzene and nitrobenzene. It is considered that the surface tensions determined have a precision of 0.2 dyne, the absolute accuracy being somewhat better than 1 dyne.

In all cases the results determined were plotted against temperature, and results read off for even temperatures as given in the body of the paper.