Vapor Pressure of Triacetin, Triethylene Glycol Dinitrate, and Metriol Trinitrate

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The vapor pressures of triacetin, triethylene glycol dinitrate, and metriol trinitrate for temperatures ranging from 11 to 75° C. and the constants of the integrated Clausius-Clapeyron equation are reported. Densities and refractive indices were also determined. The results obtained with metriol trinitrate are compared with those obtained by Piccardo.

IN ESTABLISHING the physical properties of some plasticizers for nitrocellulose the vapor pressures of triacetin, triethylene glycol dinitrate, and metriol trinitrate (2-hydroxymethyl-2-methyl-1,3-propanediol trinitrate) as a function of temperature were determined. The vapor pressure data of metriol trinitrate are not in agreement with those previously reported (*2*). An explanation of the causes for the discrepancy are given.

The infrared spectrum of triacetin, obtained from Eastman Kodak Co., agreed with that obtained by Pristera (*3*). However, the NMR spectrum contained one small extraneous peak; this peak disappeared when the triacetin was treated with acetic anhydride and vacuum distilled (b.p. 159.7° C./25.4 mm. Hg). The infrared spectrum and the vapor pressure were unchanged by this treatment. The physical properties of the compound are tabulated in Table I.

Metriol trinitrate and triethylene glycol dinitrate samples were obtained from our pilot plant facilities. The infrared spectra obtained with the compounds were the same as those reported by Pristera (*3*). Correlation of the infrared spectra with nitrate ester analysis done previously at our pilot plant facilities show that the compounds have a minimum purity of 99.5%. The physical properties of these substances are tabulated in Table I.

The vapor pressures were measured with the pistion manometer apparatus of Ernsberger and Pitman and are accurate to within 1% (*1*). Approximately 1 ml. of sample was used. In the cases of both triethylene glycol dinitrate and metriol trinitrate, a small amount of volatile impurity was removed before any vapor pressure measurements were made; however, once these impurities were removed, the vapor pressures were very reproducible. The sample of each compound was left in the manometer under vacuum approximately 1 week between runs to make sure that there were no more volatile impurities. The bath was controlled to ±0.008° C. and the temperature was read to the nearest 0.01° C. on a thermometer which had been calibrated with a National Bureau of Standards platinum resistance thermometer.

Table I. Plasticizer Physical Properties

Compound	Refractive Index		Density, d_4^{25}
	n_D^T	T, ° C.	
Triacetin	1.4294	24.5	1.1541
Metriol trinitrate	1.4748	25.0	1.4607
Triethylene glycol dinitrate	1.4527	24.5	1.3194

Table II. Vapor Pressure–Temperature Data

T, ° C.	p, μ Hg		Dev., %
	Obsd.	Calcd.	
Triethylene glycol dinitrate			
30.27	0.188	0.187	−0.5
37.30	0.407	0.412	+1.2
43.88	0.838	0.839	−0.1
50.55	1.675	1.673	+0.1
55.69	2.797	2.795	−0.1
60.44	4.450	4.427	−0.5
65.57	7.166	7.172	+0.1
70.29	11.06	11.04	−0.2
74.89	16.55	16.61	+0.4
Metriol trinitrate			
26.51	0.183	0.183	0.0
29.78	0.268	0.268	0.0
30.91	0.305	0.305	0.0
35.46	0.503	0.510	−1.4
40.25	0.863	0.862	+0.1
46.16	1.623	1.612	+0.7
50.78	2.616	2.588	+1.1
56.25	4.494	4.457	+0.8
64.04	9.370	9.373	0.0
67.08	12.35	12.41	−0.5
70.26	16.59	16.56	+0.2
72.15	19.46	19.61	−0.8
Triacetin			
11.09	0.384	0.389	+1.3
16.23	0.724	0.721	−0.4
21.08	1.264	1.264	0.0
25.12	2.000	1.991	−0.5
30.27	3.538	3.491	−1.3
35.26	5.927	5.908	−0.3
40.15	9.724	9.734	+0.1
45.05	15.61	15.81	+1.3

RESULTS AND DISCUSSION

The vapor pressure-temperature data for the three compounds are given in Table II. The data for triacetin and triethylene glycol dinitrate are the averages of three runs on two different samples, while the points for metriol trinitrate are the averages of two runs on the same sample. A least squares analysis of the log p *vs.* $1/T$ data was used to calculate the constants A and B in the Clausius-Clapeyron equation

$$\log p = A - B/T$$

in which p is the pressure in microns and T is the absolute temperature. Table III lists the contants, A and B, and

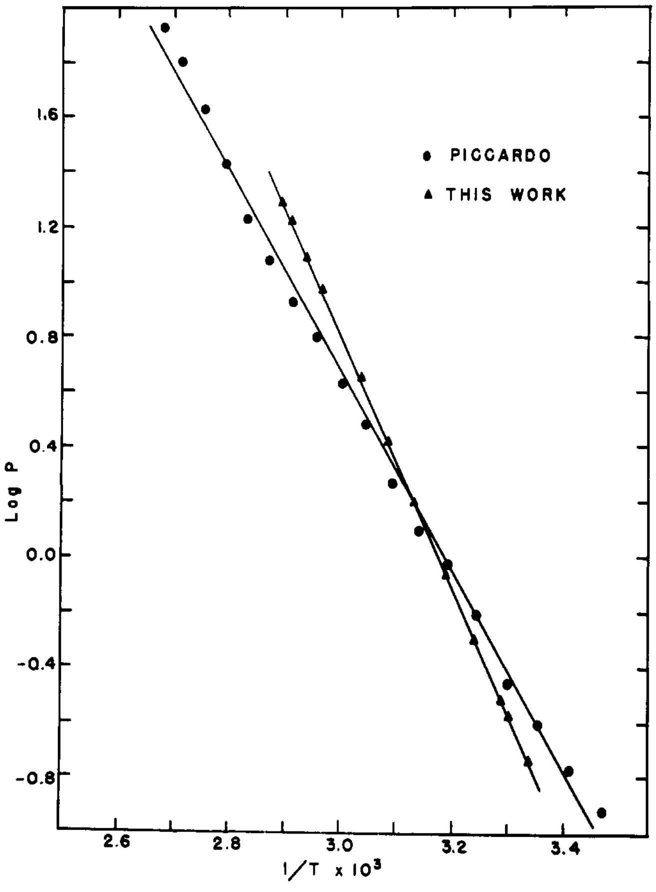

Figure 1. Vapor pressure of metriol trinitrate

Table III. Vapor Pressure Equations, Constants in the Equation $\log p\ (\mu) = A - B/T$

Compound	A	B	Ht. of Vap., Kcal./Mole
Triethylene glycol dinitrate	14.4792	4614.7	21.12 ± 0.03
Metriol trinitrate	14.6237	4603.4	21.07 ± 0.03
Triacetin	14.6673	4285.8	19.61 ± 0.05

the heats of vaporization which were calculated from the slopes of the log *p vs.* 1/*T* plots.

Piccardo determined the vapor pressure of metriol trinitrate over the temperature range 15° to 100° C. by the air saturation method (*2*). Figure 1 shows that the agreement between the two different determinations is not good. By drawing the best line through the data points of Piccardo, a heat of vaporization of 16.58 kcal. per mole is obtained, compared with 21.07 kcal. per mole obtained in this work. Since Piccardo's vapor pressure data for mercury agree within 2% with those obtained in this laboratory (*1*), the lack of agreement in the results for metriol trinitrate is possibly due to the presence of impurities in his sample. Some of these impurities could have been produced by the passage of air through the warm sample inducing some decomposition.

LITERATURE CITED

(1) Ernsberger, F.M., Pitman, H.W., *Rev. Sci. Instr.*, **26**, 584 (1955).
(2) Piccardo, G., *Ann. chim. (Rome)* 40, 604 (1950).
(3) Pristera, F., *Anal. Chem.* **25**, 844 (1953); **32**, 495 (1960).

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Acetal Esters of Polyols as Lubricants

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AMONG THE aliphatic esters which have been tested recently as synthetic lubricants, the esters of pentaerythritol (PE) and 2-(hydroxymethyl)-2-methyl-1,3-propanediol (trimethylolethane, TME) have shown promise because of their good viscosity indices and high temperature stability (*3*). Acetals have been ignored as compounds with possible application as synthetic lubricants, even though the acetal grouping might well possess the desired stability. For example, it has been shown that the bis-formal of PE is equal to diethyl ether in its stability to acid hydrolysis (*4*). We, therefore, synthesized some acetal diesters of PE and acetal monoesters of TME by reaction of the monoacetals with the appropriate acid chlorides (Table I). Some of the viscosity properties of these ester acetals were determined according to ASTM procedures (Table II).

SYNTHESES

The preparation of the acetals of PE and TME used in the synthesis of the esters has previously been reported (*2*). The following method for the preparation of the Hexanal dibutyrate of PE (Table I, J) is illustrative of how all the esters were prepared. To a mixture of 21.8 grams (0.1 mole) of the monoacetal of hexanal and PE,