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Vapor Pressure of Tri-*n*-butyl Phosphate

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The vapor pressures of tri-*n*-butyl phosphate (TBP) and dibutylphenyl phosphate (DBPP) have been determined from gas chromatographic retention times and from measurement of the equilibrium vapor concentrations. Also, the partial pressures of these compounds in the headspace of a hydraulic fluid were measured. The obtained values have been compared with published data.

Introduction

Phosphate esters comprise a large group of commercially important compounds as diverse as pesticides, nerve gases, plasticizers, solvents, and hydraulic fluids. Those used as hydraulic fluids are aromatic and aliphatic esters of orthophosphoric acid. Due to their superior physicochemical properties, they have almost entirely replaced mineral oils as hydraulic fluids in modern aircraft. Unfortunately, some of them are toxic. Inhalation of their vapors and/or aerosols, even at low levels, causes headaches, nausea, general discomfort, and sometimes mental imbalance in humans. Most toxic seems to be tri-*n*-butyl phosphate (TBP), which is also the most common component of commercial hydraulic fluids. It is thus advisable that the presence of TBP in the work place environment be monitored and limited to the lowest possible level.

It is not entirely clear whether TBP is present in air as an aerosol or as a vapor and, consequently, it is not clear what should be monitored: aerosol, vapor, or both. The threshold limit of time-weighted average of airborne concentration of TBP is 0.2 ppm (*1*). This corresponds to the equilibrium concentration at 25 °C of a compound having a vapor pressure of 2.02×10^{-2} Pa. Laham (*2*, *3*) reports that TBP vapor pressure is 969 Pa at 150 °C and $>6.64 \times 10^4$ Pa at 200 °C. The values calculated from the equation derived from experimental data by Evans et al. (*4*) and later quoted by Burger (*5*) and Parker (*6*) are 0.89 Pa at 25 °C, 1340 Pa at 150 °C, and 8510 Pa at 200 °C. Our preliminary analysis of the headspace of a hydraulic fluid indicated that the concentration of TBP was at least an order of magnitude lower than suggested by those values.

Since reliable vapor pressure data were essential for the development of a technique for monitoring airborne tributyl phosphate, we undertook to determine the TBP vapor pressure at the temperature range common in a work place environment. To this end, we used two methods: direct gas chromatography (DGC) and solid sorbent trapping/thermal desorption gas chromatography (STTD). Although both methods involve capillary gas chromatography, they are based on different principles. Whereas in the DGC method the vapor pressure is calculated from the retention data of TBP and that of a standard, the STTD method relies on dynamic headspace sampling.

The DGC method was used earlier to determine vapor pressures of phenoxyacetic herbicides (*7*, *8*), polychlorinated biphenyls, chlorinated (*9*) and organophosphorous pesticides (*10*, *11*), and tris(2-ethylhexyl) phosphate (*11*).

In this paper, we describe the analytical procedures and report the vapor pressure of pure DBPP and TBP and the partial pressure of TBP in the headspace of a hydraulic fluid. We also compare our TBP vapor pressure values with those quoted in the literature.

Experimental Section

Materials. TBP (126-73-8) and dibutyl phthalate (DBP) (84-74-2) were 99+% Gold Label (Aldrich Chemical Co.); hydraulic fluid was Skydrol 500B-4 (Monsanto Co.). Nominally the fluid contains approximately 30% TBP and 60% DBPP. The materials were used without further purification.

DGC Method. A Varian 4600 gas chromatograph (GC) with a Vista 401 data station was used. The GC was fitted with a flame ionization detector (FID) and a 25 m × 0.32 mm, 0.25 μm-d_f (film thickness), DB-1 fused silica column. The carrier gas was helium at a linear velocity of 55 cm/s at 170 °C. The makeup gas was nitrogen at a flow rate of 34 cm^3/min. The FID hydrogen and air flow rates were 25 and 300 cm^3/min, respectively. The oven temperature was isothermal at 200, 185, and 170 °C. Injector and detector temperatures were 220 °C.

STTD Method. A Tracor 540 gas chromatograph fitted with a Tracor Model 702 nitrogen–phosphorus detector (NPD) and a 5 m × 0.52 mm, 1.5 μm-d_f (film thickness), DB-5 fused silica column was used. The flow rate of helium carrier gas was 3.5 cm^3/min (linear velocity of 27 cm/s at 185 °C). The NPD hydrogen and air flow rates were 3.2 and 125 cm^3/min, respectively. The oven temperature was isothermal at 185 °C. Injector and detector temperatures were 200 and 210 °C, respectively. The injection port of this GC was modified to accept an adsorber tube for thermal desorption. The adsorber was a 6.4 mm o.d. glass tube containing a 1 cm length of nickel mesh coated with Tenax GC. The desorbed sample was focused on a second adsorber before transfer to the GC column. The second adsorber was a miniature nickel tube filled with Tenax TA.

The system was calibrated by depositing of 1 μL of standard solution (10–40 ng/μL) in the first adsorber and analyzing it in the same way as the vapor sample. The detector response was compared to that of the same amount of the standard injected into the standard GC injector (bypassing the adsorbers). The trapping efficiency (breakthrough volume) was determined by sampling the increasing volumes of TBP vapor until the increase in sample volume did not produce the proportional increase in the determined amount of analyte. The volume was greater than 100 L.

The generation of a continuous stream of saturated vapor was described earlier (*12*). The TBP vapor was generated

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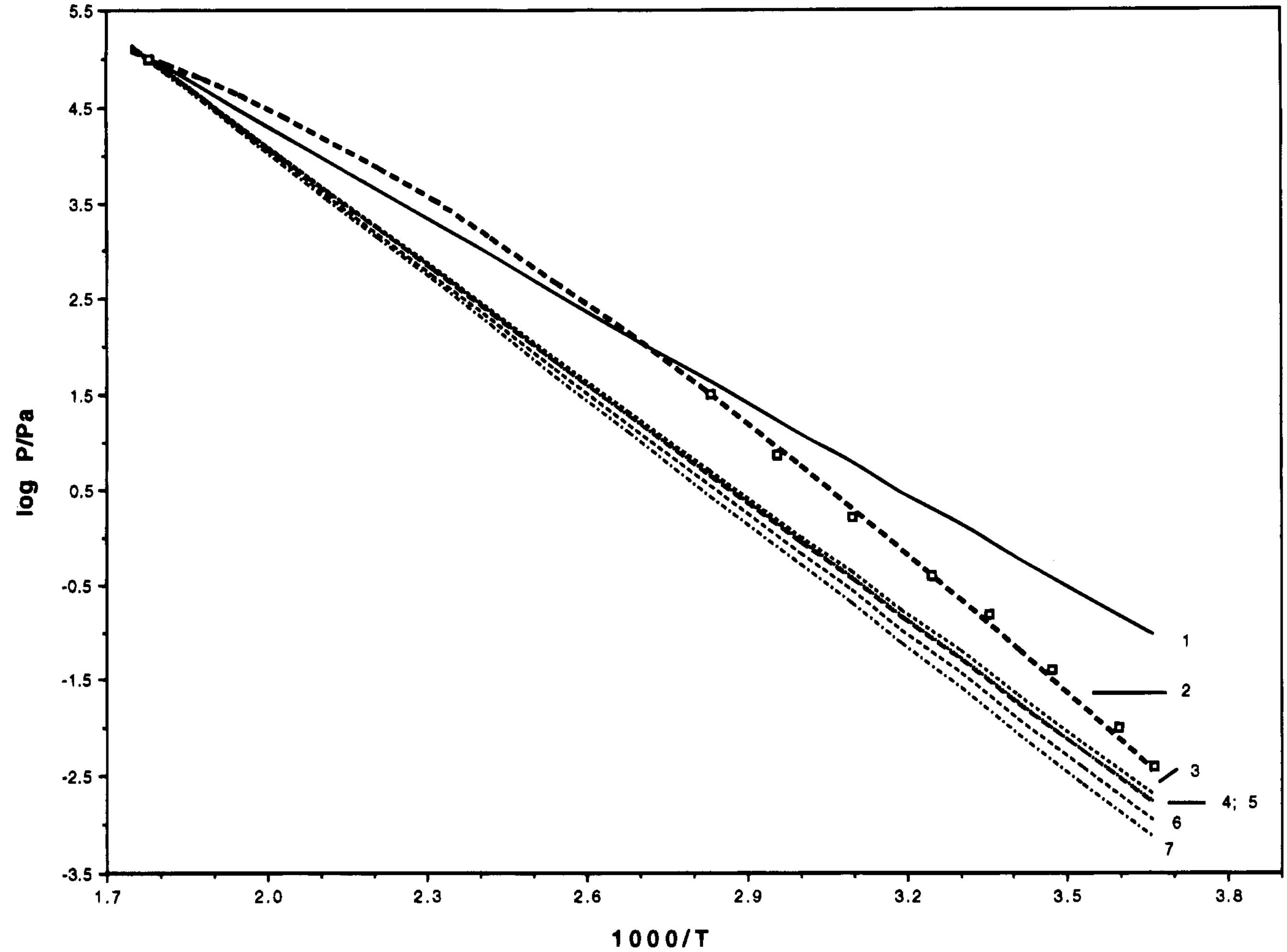

Figure 1. Logarithms of tributyl phosphate vapor pressure (including boiling point) as a function of the reciprocal of the absolute temperature: linear extrapolation of the experimental data obtained by the DGC method using DBP vapor pressure according to (3) Small et al., (4) Hammer and Lydersen, (5) Dean, (6) *Perry's Hankbook*, and (7) Perry and Weber. Also shown are (□) STTD experimental points and boiling point of TBP, (2) STTD interpolated values [log (*P*/Pa) = 8.85629 − 1690.26/[(*T*/K) − 123.431] and (1) linear extrapolation of Evans's data using his equation (8.5861 − $\log_{10} p$ = 3206.5/(*t* + 273), where *p* is in mmHg).

Table 1. Vapor Pressure of Dibutyl Phthalate

	P/Pa				
t/°C	Hammer and Lydersen (*14*)[b]	Perry and Weber (*15*)[c]	Small et al. (*16*)[d]	Dean (*17*)[e]	Perry's (*18*)[f]
170	(405)	360	(431)	(412)	386
185	856	664	879	(839)	746
200	1727	1178	1714	(1595)	1384

[a] Values shown in parentheses are in the authors' range of measurement. [b] log *P* = 12.547 − 4404.5/*T*. [c] log *P* = 12.705 − 4450/*T*. [d] log *P* = 12.090 − 4189.8/*T*. [e] log *P* = 12.073 − 4194/*T*. [f] log *P* = 11.341 − 3879.4/*T*.

by passing a stream of pure air through a 6 mm o.d. glass U-tube containing glass beads coated with liquid TBP. The column of glass beads was immobilized by plugs of silanized glass wool at each end of the U-tube. The U-tube was immersed in a constant temperature bath maintained at a set temperature ±0.1 °C. The plumbing downstream of the U-tube was heated to a temperature at least 30 °C higher than the temperature of the bath to prevent condensation of the TBP vapor. The low velocity of the vapor carrier gas and the absence of a free-flowing liquid in the U-tube prevented formation of aerosols. For bath temperatures of 25 °C and higher, the TBP vapor-carrying stream was combined with a diluting stream of air to lower the concentration to the analytical level.

Table 2. Average Measured Retention Times t_r and Adjusted Retention Times t_a[a]

	t_r/min				t_a/min		
t/°C	CH_4[b]	TBP	DBPP	DBP	TBP	DBPP	DBP
170	0.905	5.459	7.270	12.623	4.553	6.365	11.718
RSD%	0.28	1.78	1.58	1.01			
185	0.996	3.538	4.510	7.297	2.542	3.514	6.301
RSD%	1.33	2.25	2.29	2.41			
200	1.196	2.581	3.142	4.758	1.385	1.946	3.562
RSD%	0.25	7.79	6.99	4.89			

[a] Each value is an average of five measurements. [b] Methane was used as a nonretained gas to determine the column hold-up time.

Results and Discussion

DGC Method. The equation relating retention volume and vapor pressure was given by Herington (*13*)

$$\log V_{21} = \log(P_1/P_2) + \log(\gamma_1/\gamma_2) \qquad (1)$$

where V_{21} is the relative retention volume of components 1 and 2 and P_1, P_2, γ_1, and γ_2 are vapor pressures and activity coefficients of components 1 and 2, respectively. Since retention volume is directly related to retention time, the equation becomes

Table 3. Vapor Pressure *P* of Tributyl Phosphate and Dibutylphenyl Phosphate Determined by DGC Method

ref		*P*/Pa		
		170 °C	185 °C	200 °C
Hammer and Lydersen (*14*)	TBP	1042	2122	4442
	DBPP	746	1535	3161
Perry and Weber (*15*)	TBP	927	1646	3030
	DBPP	663	1191	2156
Small et al. (*16*)	TBP	1109	2179	4408
	DBPP	794	1577	3137
Dean (*17*)	TBP	1060	2080	4102
	DBPP	758	1504	2920
Perry's Handbook (*18*)	TBP	993	1849	3559
	DBPP	711	1338	2533

Table 4. *A* and *B* Constants of Linear Extrapolation Equations[a]

	A		*B*	
	TBP	DBPP	TBP	DBPP
Hammer and Lydersen (*14*)	12.335	12.303	4124.2	4175.8
Perry and Weber (*15*)	12.633	10.522	4306.7	3409.8
Small et al. (*16*)	12.253	11.876	4080.7	3974.6
Dean (*17*)	12.333	11.684	4127.8	3897.6
Perry's Handbook (*18*)	12.480	11.151	4215.3	3674.8

[a] $\log P/\mathrm{Pa} = A - B/(T/\mathrm{K})$.

Table 5. Vapor Pressure of Tributyl Phosphate by STTD Method

t /°C	TBP *P*/Pa	SD	TBP in Skydrol *P*/Pa	SD
0	0.004	8.0×10^{-4}	0.0005	4×10^{-5}
5	0.01	1.2×10^{-3}		
15	0.04	8.0×10^{-3}		
25	0.15	0.027	0.015	7×10^{-4}
35	0.39	0.016		
50	1.59	0.015	0.199	0.13
65	7.17	1.2	0.943	0.40
80	31.9	2.7		

$$\log(t'_2/t'_1) = \log(P_1/P_2) + \log(\gamma_1/\gamma_2) \qquad (2)$$

where t'_1 and t'_2 are adjusted retention times of components 1 and 2, respectively. If a nonpolar liquid phase is selected, the retention is affected solely by the vapor pressure. Thus, the last equation reduces to

$$\log(t'_2/t'_1) = \log(P_1/P_2) \qquad (3)$$

or

$$t'_2/t'_1 = P_1/P_2 \qquad (4)$$

which is a theoretical confirmation of an empirical observation that retention times on a nonpolar or "boiling point" column are inversely proportional to the vapor pressure or directly proportional to the boiling point of a chromatographed compound.

Dibutyl phthalate was selected as a standard for its similar chemical structure and similar volatility to those of TBP. Its vapor pressure has been determined by numerous researchers using different methods. The literature values of the vapor pressure of DBP are listed in Table 1.

The vapor pressure values determined according to this method are not affected by the impurities present in the sample. It is possible to determine vapor pressures of the individual components of a mixture. The vapor pressures of the two major components of Skydrol 500B-4 hydraulic fluid, TBP, and dibutylphenyl phosphate (DBPP) were calculated from eq 4 using the retention times of DBP, TBP, and DBPP presented in Table 2. Table 3 lists the vapor pressures of TBP and DBPP at the temperatures at which the retention times were measured.

Logarithms of the vapor pressure values, including the boiling point of TBP from Evans et al. (*4*), were plotted against the reciprocal of the absolute temperatures (Figure 1). The experimental points were extrapolated to the temperature range of STTD measurements using the linear regression. The *A* and *B* constants of the linear regression equation

$$\log P/\mathrm{Pa} = A - B/(T/\mathrm{K}) \qquad (5)$$

for each reference DBP vapor pressure for both TBP and DBPP are presented in Table 4. The scatter of the extrapolated values in the ambient temperature range results from the differences in reference vapor pressures of DBP, the experimental error, few experimental points (the temperature range is limited by gas chromatography), and the uncertainties of the extensive extrapolation. The linear extrapolation (Figure 1 and Table 6) was preferred over nonlinear extrapolation because it gave more consistent values, approximately 1 order of magnitude lower than the STTD experimental points. The nonlinearly extrapolated DGC data were spread over 3 orders of magnitude at 0 °C.

STTD Method. The validity of this method is based on the assumptions that the static equilibrium vapor pressure in the U-tube containing TBP liquid is nearly maintained and that the TBP vapor is quantitatively trapped and thermally desorbed from the adsorber tube. The concentration measured in the diluted stream (*c*) is related to the equilibrium vapor phase concentration (c_0)

$$c_0 = c(f + F)/f \qquad (6)$$

where *f* and *F* are flow rates of the sample carrier gas and diluting gas stream, respectively. The equilibrium conditions exist if the measured concentration (*c*) is a linear function of the sample carrier gas flow rate at a constant temperature and a constant diluting gas flow rate (*12*).

The vapor pressure *P* is calculated from a relation

Table 6. Vapor Pressure *P*/Pa of Tributyl Phosphate Measured and Extrapolated Using Antoine's Equation and Linear Regression Fit***

t/°C	*T*/K	Hammer and Lyndersen* (*14*)	Perry and Weber* (*15*)	Small et al.* (*16*)	Dean* (*17*)	*Perry's Handbook** (*18*)	STTD**	STTD measd	Evans* (*4*)
0	273	0.002	0.001	0.002	0.002	0.001	0.004	0.004	0.092
5	278	0.003	0.001	0.004	0.003	0.002	0.008	0.01	0.150
10	283	0.006	0.003	0.007	0.006	0.004	0.018		0.239
15	288	0.010	0.005	0.012	0.010	0.007	0.039	0.04	0.376
20	293	0.018	0.009	0.021	0.018	0.012	0.077		0.583
25	298	0.031	0.015	0.036	0.030	0.022	0.149	0.15	0.890
30	303	0.053	0.026	0.061	0.051	0.037	0.278		1.339
35	308	0.088	0.045	0.101	0.085	0.062	0.499	0.39	1.989
40	313	0.144	0.075	0.164	0.140	0.103	0.871		2.917

derived from the ideal gas equation:

$$P = c_0RT \qquad (7)$$

With this method it was possible to determine the vapor pressure of pure TBP as well as its partial pressure over the hydraulic fluid. The latter is relevant when the vapors emitted by those fluids are assessed.

The advantage of the STTD method was its ability to measure the vapor pressure at a temperature range that included the temperatures usually found in the work place, thus avoiding the uncertainties of extrapolation.

Table 5 lists the vapor pressures of pure TBP and that over Skydrol fluid. The values presented in the table are averages of at least five measurements. Again, logarithms of the vapor pressures were plotted against the reciprocal of the absolute temperatures. The experimental points were interpolated to the TBP boiling point (*4*) using the Antoine equation (Figure 1 and Table 6).

Comparison of the Experimental Results with Literature Data. The plots (Figure 1) clearly indicate that the linear extrapolation of Evans's data gives values higher than our experimental values obtained by either method, with the linearly extrapolated DGC values lowest of all three sets. The STTD values extrapolated to Evans's and the DGC experimental temperature range are highest of the three sets. The linearly extrapolated DGC values are lower than the experimental values of both Evans's and STTD method.

Table 6 lists measured (STTD) and linearly extrapolated vapor pressures of TBP in the temperature range that includes temperatures usually found in the work place.

Conclusions

The STTD method, although experimentally more complex, allows determination of the vapor pressure at ambient temperature and thus avoids the uncertainties of extrapolation.

The DGC method is technically simple and fast, but its accuracy depends on availability of a suitable standard and is limited by approximations in eq 4 and by extrapolation over a wide temperature range. This method allows the measurement of the vapor pressures of individual components of a mixture.

The partial pressure of TBP over Skydrol 500B-4, as measured by the STTD method, is approximately 1 order of magnitude lower than the vapor pressure of pure TBP.

The vapor pressure of a component of a mixture determined by the STTD method is the partial pressure of this component in the gaseous phase above the solution.

The literature values for TBP vapor pressure are approximately an order of magnitude higher that those measured by either the DGC or STTD method.

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