Density, Viscosity, and Vapor Pressure of Phenylphosphorus Dichloride and Phenylphosphonic Dichloride

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The density of phenylphosphonic dichloride ($C_6H_5POCl_2$) over a temperature range from 293.17 K to 342.85 K and viscosity over a temperature range from 293.21 K to 341.85 K were measured. The vapor pressure of phenylphosphorus dichloride ($C_6H_5PCl_2$) and phenylphosphonic dichloride in the ranges from 349.26 K to 426.06 K and from 377.15 K to 457.65 K, respectively, were measured by a static method. The density data were fitted to a second-order polynomial, and the viscosity data were fitted to the Andrade equation. The results of vapor pressure of phenylphosphorus dichloride and phenylphosphonic dichloride were fitted to the Antoine equation. The density data of phenylphosphonic dichloride and vapor pressure data of phenylphosphorus dichloride and phenylphosphonic dichloride were compared with literature values.

Introduction

Phenylphosphorus dichloride (DCPP, $C_6H_5PCl_2$) and phenylphosphonic dichloride (DCPPO, $C_6H_5POCl_2$) both have two reactive chlorine atoms, which enable them to readily react with alcohols, phenols, amines, and aldehydes. They are two important intermediates in organic synthesis and are widely used in the preparation of flame retardants,[1,2] herbicides,[3] etc.

Though commercially available, the density, viscosity, and vapor pressure of DCPP and DCPPO in a range of operating temperatures, which are very important and necessary for the design of industrial processes, are not available in the literature. Up to now, the density of DCPP over a temperature range from 30.90 °C to 66.00 °C and viscosity of DCPP over a temperature range from 23.00 °C to 55.00 °C have been measured in our laboratory and have been reported.[4] For DCPPO, different density values at 293.15 K were reported in the literature ($\rho = 1.399$ g·cm^{-3} [5] and $\rho = 1.1977$ g·cm^{-3} [6]). The viscosity of DCPPO has not been reported. So, in this work, we only measured the density and viscosity of DCPPO.

Buchner and Lockhart[7] measured six boiling temperatures of DCPP in the range from 1.33 kPa to 10.67 kPa by means of a fractionating column, and the relations between boiling temperatures and pressure were indicated by the plot of log P vs $1/T$. But the measured values were not reported. In addition, Kosolapoff reported the boiling temperatures of DCPP at 12 mm Hg (1.60 kPa)[8] and 57 mm Hg (7.60 kPa).[9] For DCPPO, Toy[10] reported its boiling temperatures at 2.0 kPa and 0.53 kPa.

In this paper, the density and viscosity of DCPPO are presented in the ranges of 293.17 K to 342.85 K and 293.21 K to 341.85 K, respectively, and the results were compared with the literature. The vapor pressure of DCPP and DCPPO in the ranges of 349.26 K to 426.06 K and 377.15 K to 457.65 K, respectively, were measured by a static method.

Table 1. Density of DCPPO

T/K	ρ/(g·cm^{-3})	$100\delta\rho/\rho^a$
293.17	1.4000	−0.179
299.19	1.3949	−0.122
303.25	1.3908	−0.129
309.05	1.3848	−0.152
313.75	1.3801	−0.159
319.25	1.3739	−0.211
323.31	1.3697	−0.226
329.4	1.3643	−0.176
334.75	1.3587	−0.199
338.85	1.3543	−0.222
342.85	1.3504	−0.215

[a] $100\delta\rho/\rho = 100(\rho - \rho_{calc})/\rho$, where the suffix "calc" stands for the values calculated from eq 2.

Experimental Section

Chemicals. DCPP and DCPPO were synthesized in our laboratory according to the literature.[10,11] They were fractionally distilled with the middle 60% collected under reduced pressure (1.333 kPa). The purity of DCPPO after distillation was 99.9% as analyzed by Nippon Chemical Industry, Co., with gas chromatography. The refractive index values were obtained at 20 °C and 25 °C on an Abbe Model refractometer with an uncertainty of ±0.0001 n_D. The measured values were $n_D^{20} = 1.5950$ for DCPP and $n_D^{25} = 1.5586$ for DCPPO, which agree within ±0.0002 with the values in the literature[5] (DCPP, $n_D^{20} = 1.5952$; DCPPO, $n_D^{25} = 1.5585$).

Density Measurements. A 50-cm^3 pyknometer calibrated with deionized and double-distilled water was used for all measurements. The mass was determined on an electronic balance with a precision of ±0.1 mg. The pyknometer was then immersed in a thermostated bath with temperature control precision of ±0.01 K. The density of DCPPO is listed in Table 1. The densities of pure water are obtained from the literature.[12] The estimated uncertainty in density was $\pm 5 \times 10^{-4}$ g·cm^{-3}.

Viscosity Measurements. An Ubbelohde capillary viscometer was used to measure the viscosity. The capillary was calibrated for kinetic energy correction with pure water

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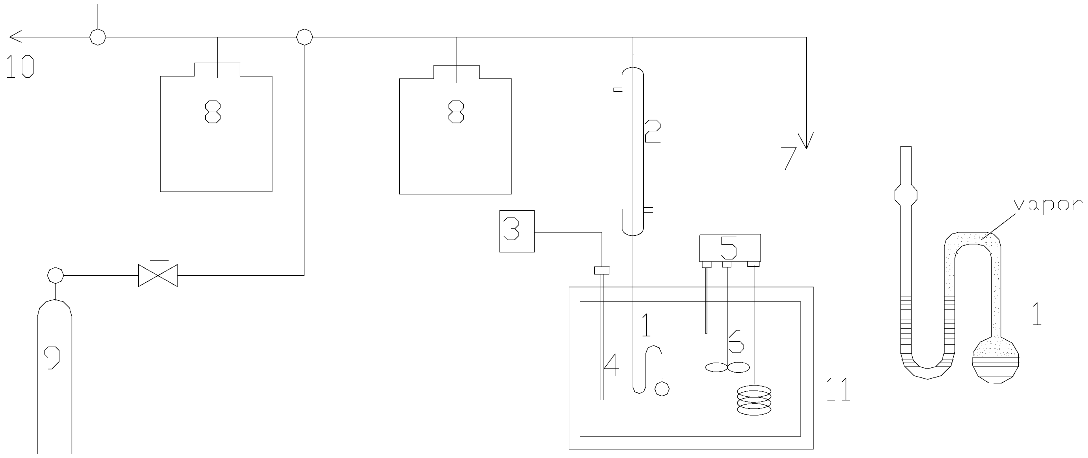

Figure 1. Apparatus for the measurement of vapor pressure: 1, the equilibrium tube; 2, the condenser; 3, the temperature indicator; 4, the platinum-resistance thermometer; 5, the thermoregulator; 6, the agitator blade; 7, to mercury pressure gauge; 8, the buffer bottle; 9, the nitrogen cylinder; 10, to vacuum pump; 11, the thermostat bath.

Table 2. Viscosity of DCPPO

T/K	η/(mPa·s)	$100\delta\eta/\eta$[a]
293.21	4.6867	−0.01
299.58	4.1435	2.56
303.77	3.6742	−0.06
307.97	3.3313	−0.71
312.95	2.9791	−1.37
318.95	2.6417	−1.15
322.75	2.4506	−1.14
327.85	2.2466	−0.01
332.35	2.0463	−0.95
338.25	1.8732	0.90
341.85	1.7703	1.58

[a] $100\delta\eta/\eta = 100(\eta - \eta_{\mathrm{calc}})/\eta$, where the suffix "calc" stands for the values calculated from eq 3.

and 1-propanol at the experimental temperature range

$$\nu = k_1 t - k_2/t \quad (1)$$

where t is flow time. The kinematic viscosity ν for calibration was obtained from literature values of the absolute viscosity and density.[13] The capillary was 0.05 mm in diameter and 40 mm in length; therefore, the end correction could be neglected. The same viscometer was used for all measurements.

The temperature control setup used was identical to that used for density measurements described earlier. The flow time t was recorded with a stopwatch of precision 0.01 s. Each measurement was repeated 10 times and averaged as the final result. The measurement uncertainty was within ±0.1 s. The density values used to convert kinematic viscosity to absolute values were calculated from the fitted equation. The viscosities of DCPPO over a range of temperature are listed in Table 2. The estimated uncertainty in viscosity was within ±0.5%.

Vapor Pressure Measurements. The vapor pressure was measured by a static method. The apparatus setup is schematically shown in Figure 1. It consists of a temperature control and measurement system, a vacuum pump, and a pressure-measurement system. An equilibrium tube, shown in Figure 1, containing a liquid sample was immersed in the thermostat oil bath. The temperature of the oil bath is controlled automatically by a YCC-16 intelligent controller to ±0.1 K and measured with a standard platinum resistance thermometer MKT100 and displayed on a digital indicator. In the pressure measurements, a U-type mercury pressure gauge was used and the height difference was measured by a cathetometer. The measured pressures were corrected by temperature, latitude, and altitude. The accuracy of the pressure measurements was better than 0.0067 kPa.

Table 3. Vapor Pressure Data of DCPP and DCPPO

DCPP		DCPPO	
T/K	p/kPa	T/K	p/kPa
349.26	0.614	377.15	0.529
352.16	0.719	382.65	0.646
355.14	0.842	387.96	0.813
357.45	0.949	393.09	1.031
360.35	1.099	397.40	1.277
363.46	1.282	402.60	1.535
366.40	1.476	410.21	2.011
369.51	1.708	413.57	2.266
374.35	2.126	415.95	2.693
377.89	2.483	419.63	3.136
380.29	2.751	424.32	3.788
383.46	3.141	428.54	4.226
388.15	3.891	431.35	5.000
392.55	4.466	435.95	5.666
395.55	5.321	439.85	6.506
398.35	5.853	442.85	7.533
402.05	6.279	446.35	7.826
404.85	6.866	448.84	8.893
408.49	7.653	456.05	10.532
412.55	9.346	457.65	11.532
414.04	9.813		
415.05	10.186		
418.03	11.386		
420.25	12.279		
424.25	12.972		
426.06	13.906		

The apparatus setup had been tested by measuring the vapor pressure of water from 293.15 K to 353.15 K and comparing the results with literature values.[12] The percent deviations between the experimental values and the literature values were within ±0.2%, which showed the apparatus to be reliable.

As shown in Figure 1, the equilibrium tube consists of a U-type pressure gauge and a sample bottle and it was made of thin-walled glass to aid the sample to reach rapid temperature equilibrium with the surrounding silicon oil bath. In the measurement, both the U-type pressure gauge and the sample bottle would contain the same liquid sample. Before setting the equilibrium tube in the thermostat bath, it was necessary to degas the system and the sample thoroughly. The liquid sample was degassed by repeated freeze−evacuate−thaw cycles. After degassing,

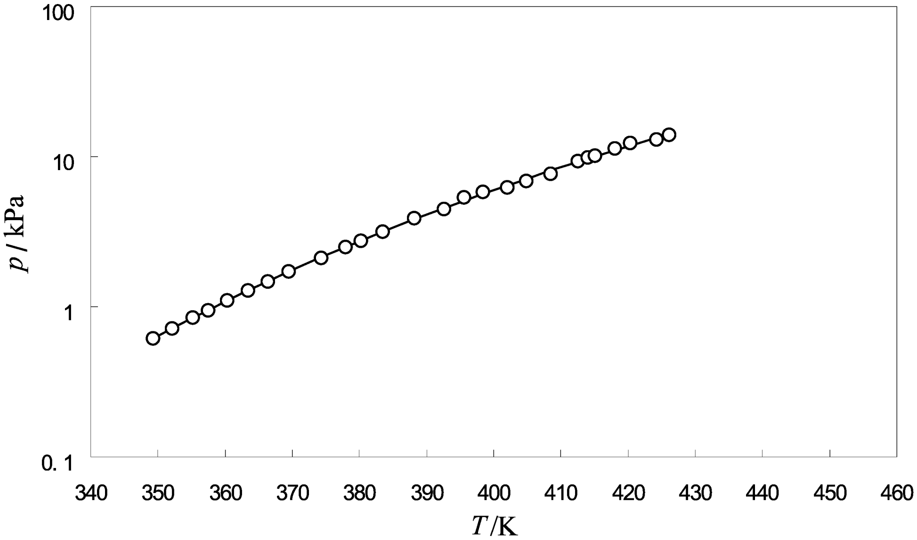

Figure 2. Experimental and calculated vapor pressure data for DCPP: ○, experimental data; solid line, calculated by eq 6.

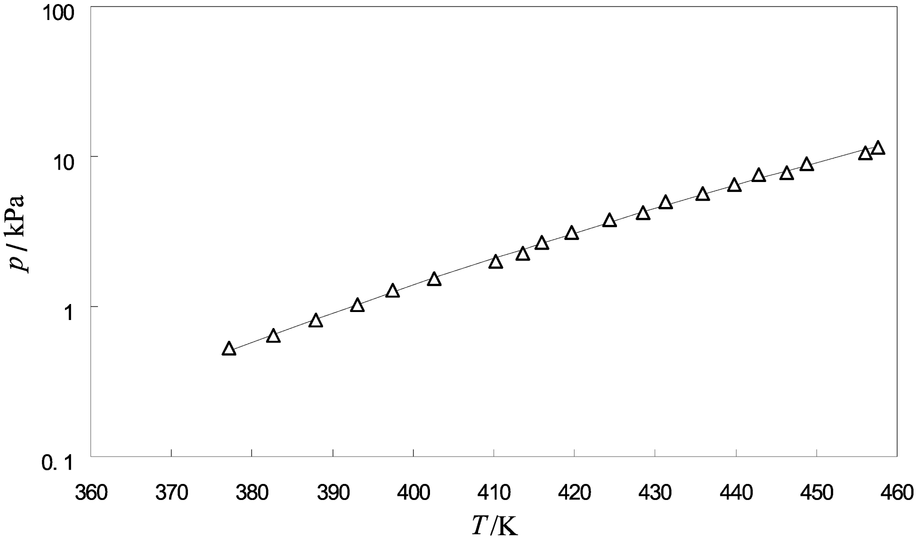

Figure 3. Experimental and calculated vapor pressure data for DCPPO: △, experimental data; solid line, calculated by eq 6.

the equilibrium tube was immersed in the thermostat bath. At this time, the space between the U-type gauge and the sample bottle is filled with pure vapor of the liquid sample. At the selected temperature, the nitrogen gas was filled into the system and the pressure was adjusted to equal the vapor pressure of the sample by observing the U-type pressure gauge in the equilibrium tube. The temperature and pressure were recorded and corrected correspondingly. The experiment was repeated (7−8) times at each temperature, and an averaged value was adopted. The maximum percent deviation between the measured value each time and the averaged value was within ±0.05%. The vapor pressure measurement vs temperature were performed in every (2−5) K intervals.

Results and Discussion

Results. The measured data of the density and viscosity of DCPPO were fitted to the following equations.

Density vs temperature was fitted to the second-order polynomial

$$\rho/\text{g}\cdot\text{cm}^{-3} = 1.6628 - 0.0008(T/\text{K}) - 3 \times 10^{-7}(T/\text{K})^2 \quad (2)$$

Viscosity vs temperature was fitted to the Andrade equation

$$\ln(\eta/\text{mPa}\cdot\text{s}) = -5.4012 + 2036.2/(T/\text{K}) \quad (3)$$

The absolute average deviation (AAD %) of measured data from the fitted data is defined as follows

$$\text{AAD\%}(\rho) = 1/N \sum |\rho_i - \rho_{i,\text{calc}}|/\rho_i \times 100 \quad (4)$$

$$\text{AAD\%}(\eta) = 1/N \sum |\eta_i - \eta_{i,\text{calc}}|/\eta_i \times 100 \quad (5)$$

where the suffix “calc” stands for the values calculated from eqs 2 and 3.

The absolute average deviations of density and viscosity for DCPPO are 0.2% and 1.0%, respectively.

The experimental vapor pressure data for DCPP in the range of 349.26 K to 426.06 K and for DCPPO in the range of 377.15 K to 457.65 K are shown in Table 3.

The results were fitted to the Antoine equation

$$\log(p/\text{kPa}) = A - \frac{B}{C + T/\text{K}} \quad (6)$$

where p is the vapor pressure, T is the temperature, and A, B, and C are the Antoine constants. The constants A, B, and C determined from least-squares fitting and the absolute average deviation are shown in Table 4. In Figures

Table 4. Antoine Constants for DCPP and DCPPO

	Antoine constants			temperature range/K	AAD
	A	*B*	*C*		%
phenylphosphorus dichloride	4.896	1077.325	−138.410	349.6−426.06	1.63
phenylphosphonic dichloride	8.011	3399.726	32.073	376.95−457.65	2.82

2 and 3, the experimental data and calculated vapor pressure have been presented graphically as a function of temperature.

Discussion

The measured density of DCPPO at 293.15 K was 1.400 g·cm^{-3}, which is in good agreement with the literature value of 1.399 g·cm^{-3} at 293.15 K[5] but differs considerably from another value of 1.1977 g·cm^{-3} at 293.15K.[6]

The variation of density over a temperature range from 293.17 K to 342.85 K is approximately linear, while the viscosity data over a temperature range from 293.21 K to 341.85 K were fitted to the Andrade equation.

The boiling temperatures of DCPP vs pressures reported in the literature[7] in the range of 1.33 kPa to 10.67 kPa were only provided in a plot. They seemed very close to the results obtained in this work. Kosolapoff reported two boiling temperatures, 94 °C/1.60 kPa[8] and (140 to 142) °C/7.60 kPa.[9] The boiling temperatures calculated from eq 6 are 94.87 °C/1.60 kPa and 133.57 °C/7.60 kPa, respectively.

Toy[10] reported two boiling temperatures of DCPPO, (137 to 138) °C/2.0 kPa and 104 °C/0.53 kPa. Compared with the data of this work, 410.21 K (137.06 °C)/2.011 kPa and 376.95 K (103.80 °C)/0.52 kPa, they are in fairly good agreement.

DCPP and DCPPO are both colorless transparent liquids at ambient temperature. When the temperature was raised to 426.06 K for DCPP and 457.65 K for DCPPO, the color of the samples began to change and became yellowish brown. This phenomenon indicated the samples had decomposed.

CA Registry No. Phenylphosphorus dichloride, 644-97-3; phenylphosphonic dichloride, 824-72-6.

Literature Cited

(1) Wang, L.-S.; Wang, X.-L.; Yan, G.-L. Synthesis, Characterization and Flame Retardance Behavior of Poly(ethylene terephthalate) Copolymer Containing Triaryl Phosphine Oxide. *Polym. Degrad. Stab.* **2000**, *69*, 127−130.

(2) Okamoto, T.; Kondo, Y.; Yamanaka, T. Fire-Resistant Polyesters and Their Uses. Jpn. Kokai Tokkyo Koho JP 05 51, 441 [93 51, 441].

(3) Zhou, J.; Qiu, Y.-G.; Feng, K,-S.; Chen, R.-Y. Synthesis and Herbicidal Activity of 1-Aryl-2-phenyl-3-methyl-3-isopropyl-1,4,2-diazaphospholidin-5-one-2-oxides. *Chem. J. Chin. Univ.* **1999**, *20*, 1058−1062.

(4) Wu, J.-S.; Sun, X.-Y.; Wang, L.-S. Density and Viscosity of Phenylphosphorus Dichloride and Dichlorophenyl Phosphine Sulfide. *J. Chem. Eng. Data* **2001**, *46*, 1123−1124.

(5) Zhang, S.-G. *Handbook of Practical Fine Chemicals*; Chemical Industry Press: Beijing, 1996.

(6) Vierte. *Beilsteins Handbook of Organic Chemistry*; Beilsteins Press: Berlin, 1986.

(7) Buchner, B.; Lockhart, L. B. An Improved Method of Synthesis of Aromatic Dichlorophosphines. *J. Am. Chem. Soc.* **1951**, *73*, 755−756.

(8) Kosolapoff, G. M. A New Synthesis of Phosphinic Acids. *J. Am. Chem. Soc.* **1950**, *72*, 4292−4293.

(9) Kosolapoff, G. M. *Organophosphorus Compounds*; John Wiley & Sons: New York, 1950.

(10) Toy A. D. F. Allyl Esters of Phosphonic Acids. I. Preparation and Polymerization of Allyl and Methallyl Esters of Some Arylphosphonic Acids. *J. Am. Chem. Soc.* **1948**, *70*, 186.

(11) Amonoo-Neizer, E. H.; Ray, S. K.; Shaw, R. A.; Smith, B. C. Sulphoxides. Part I. The Oxidation of Trivalent Phosphorus Compounds by Dimethyl Sulphoxide. *J. Chem. Soc.* **1965**, 4296.

(12) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 63rd ed.; CRC Press: Boca Raton, FL, 1982−1983.

(13) Perry, R. H.; Green, D. W.; Malone, J. O. *Perry's Chemical Engineers Handbook*, 6th ed.; McGraw-Hill: New York, 1984.

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