Density, Viscosity, and Vapor Pressure of Dichlorophenylphosphine Sulfide

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The density and viscosity of dichlorophenylphosphine sulfide ($C_6H_5PSCl_2$) over a temperature range of (303.16 to 423.40) K were measured. The vapor pressure of dichlorophenylphosphine sulfide in the range of (417.83 to 448.12) K were measured by a static method. The density data were fitted to a second-order polynomial, the viscosity data were fitted to the Andrade equation, and the results of vapor pressure data were fitted to the Antoine equation. The density data and vapor pressure data of dichlorophenylphosphine sulfide were compared with literature values.

Introduction

Dichlorophenylphosphine sulfide (DCPPS, $C_6H_5PSCl_2$) is an intermediate for the production of bis(4-carboxyphenyl)phenyl phosphine oxide, a halogen-free flame-retarding monomer that can be chemically incorporated into various macromolecules to produce flame-retarding polymers.[1] In general, DCPPS is widely used in the preparation of flame retardants, insecticides, and plasticizers.[2]

Although commercially available, the density, viscosity, and vapor pressure of DCPPS 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 value of DCPPS at 293.15 K ($\rho = 1.4042$ g·cm^{-3})[3] and 298.15 K ($\rho = 1.390$ g·cm^{-3})[2] were reported. The boiling temperatures of DCPPS at 3.47 kPa,[4] 0.67 kPa,[5] 0.27−0.40 kPa,[6,7] and 0.08 kPa[3] were reported in the literature.

In this paper, the density and viscosity of DCPPS are presented in the range of (303.16 to 423.40) K, respectively, and the results of density were compared with the literature values. The vapor pressure of DCPPS in the range of (417.83 to 448.12) K, were measured by a static method and correlated to the Antoine equation. A comparison was made with reported values as mentioned above.

Experimental Section

Chemicals. DCPPS was synthesized from PCl_3, benzene, and sulfur in our laboratory following the procedure described by Wang et al.[2] Then it was distilled under reduced pressure (2.67 kPa). The purity of DCPPS after distillation was 99.9 % (mass) determined by a gas chromatography test. The refractive index value was obtained at 20 °C on an Abbe model refractometer with an uncertainty of ± 0.0001 n_D. The measured value was $n_D^{20} = 1.6179$, which agrees with the values in the literature ($n_D^{20} = 1.6227$,[8,9] $n_D^{20} = 1.6176$[5]). Ethylene glycol purchased from Beijing Chemical Reagent Company was an analytical reagent.

Density Measurements. A 10 cm^3 picnometer calibrated with deionized and double-distilled water was used for the measurements in the range of (303.16 to 353.19) K. The same picnometer calibrated with ethylene glycol was used for the measurements in the range of (363.25 to 423.40) K. The mass was determined on an electronic balance with a precision of ± 0.1 mg. The picnometer was then immersed in a thermostat bath with temperature control precision of ± 0.01 K. The measured densities of DCPPS are listed in Table 1. The densities of pure water and ethylene glycol are obtained from the literature.[10] The estimated uncertainty in density was ± 5 × 10^{-4} g·cm^{-3}.

Table 1. Density of DCPPS

T/K	ρ/g·cm^{-3}	100 δ^a	T/K	ρ/g·cm^{-3}	100 δ^a
303.16	1.3818	−0.234	374.75	1.2841	−0.588
313.12	1.3742	−0.002	383.20	1.2760	−0.173
323.25	1.3593	−0.238	393.26	1.2609	−0.051
332.85	1.3565	0.424	403.85	1.2370	−0.501
343.00	1.3443	0.499	412.65	1.2324	0.410
353.19	1.3291	0.411	423.40	1.2106	0.278
363.25	1.3084	−0.056			

[a] $100\ \delta = 100(\rho - \rho_{calc})/\rho$.

Viscosity Measurements. An Ubbelohde capillary viscometer was used to measure the viscosity. The capillary was calibrated (including a kinetic energy correction term) with pure water in the corresponding experimental temperature range. The kinematic viscosity is expressed as a function of two constants (k_1, k_2) and the flow time t:

$$\upsilon = k_1 t - k_2/t \tag{1}$$

The kinematic viscosity υ for calibration was obtained from literature values of the absolute viscosity and density.[11] The capillary was 0.55 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 (± 0.33 % at the high end of temperature). The density values used to convert kinematic viscosity to absolute values were calculated from the fitted equation. The measured viscosities of DCPPS over a range of temperature are listed in Table 2. The measured flow time was in the range of (80.72 to 172.38) S; the estimated uncertainty in viscosity was within ± 0.5 %.

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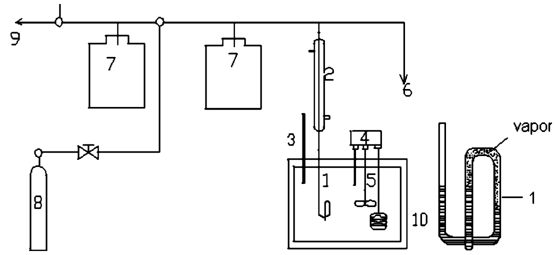

Figure 1. Apparatus for the measurement of vapor pressure: 1, equilibrium cell; 2, condenser; 3, temperature indicator; 4, thermoregulator; 5, agitator blade; 6, to mercury pressure gauge; 7, buffer bottle; 8, nitrogen cylinder; 9, to vacuum pump; 10, thermostat bath.

Table 2. Viscosity of DCPPS

T/K	η/mPa·s	100 δ^a	T/K	η/mPa·s	100 δ^a
303.16	3.634	3.849	374.75	1.199	−0.037
313.12	2.957	1.100	383.20	1.082	−0.358
323.25	2.439	−1.175	393.26	0.972	0.270
332.85	2.082	−1.892	403.85	0.872	0.766
343.00	1.791	−1.865	412.65	0.798	0.770
353.19	1.556	−1.651	423.40	0.729	2.171
363.25	1.356	−2.084			

[a] $100\ \delta = 100(\eta - \eta_{\text{calc}})/\eta$.

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 cell with a U-type tube construction for the judgment of pressure balance, as shown in Figure 1, containing the liquid sample was immersed in the thermostat silicon oil bath. The temperature of the oil bath was controlled automatically by a YCC-16 intelligent controller to ± 0.1 K. 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 a barometer. The accuracy of the pressure measurements was better than 0.013 kPa.

The apparatus setup had been tested by measuring the vapor pressure of pure water from (293.15 to 353.15) K and by comparing the results with literature values.[10] The deviations between the experimental results and the literature values were within ± 0.2 %, which showed the apparatus to be reliable.

The equilibrium cell was made of thin-walled glass to aid the sample to reach rapid temperature equilibrium with the surrounding silicon oil bath. Before setting the equilibrium cell in the thermostat bath, it was necessary to degas the sample thoroughly. The liquid sample was degassed by repeated freeze−evacuate−thaw cycles. After degassing, the equilibrium cell was immersed in the thermostat bath and connected to the vacuum system with a condenser in between. Along with the evacuation process, the space in the U-type tube of the equilibrium cell was filled with pure vapor of the liquid sample. At each selected temperature, evacuation was conducted continuously until the liquid sample in the equilibrium cell began to boil, then the nitrogen gas was filled into the vacuum system carefully to adjust the system pressure to equal the vapor pressure of the sample by observing the liquid levels in the U-type tube of the equilibrium cell. The temperature and the pressure were recorded and corrected correspondingly. The operation was repeated seven to eight times at each temperature, and an averaged value was adopted. The maximum deviation between the individual measured values for each temperature was within ± 0.05 %. The vapor pressure measurement versus temperature was performed in every (2−5) K intervals. The experimental vapor pressure data for DCPPS in the range of (417.83 to 448.12) K are listed in Table 3.

Table 3. Vapor Pressure Data of DCPPS

T/K	p/kPa	100 δ^a	T/K	p/kPa	100 δ^a
417.8	2.77	0.60	435.4	5.97	−1.81
420.0	3.15	−2.64	438.1	6.45	1.47
423.1	3.47	0.99	440.8	7.34	−0.71
425.1	3.90	−2.08	443.3	8.10	−0.76
427.9	4.26	0.90	445.9	8.95	−0.40
430.4	4.65	2.65	448.1	9.77	−0.48
433.1	5.21	2.44			

[a] $100\ \delta = 100(p - p_{\text{calc}})/p$.

Table 4. Antoine Constants for DCPPS

Antoine constants			temperature range	
A	B	C	K	100 AAD
9.198	4011	40.45	417.8−448.1	1.38

DCPPS is a slightly yellowish transparent liquid at ambient temperature. When the temperature was raised to 448.12 K, the color of the sample began to change and became yellowish brown. This phenomenon indicates that the DCPPS will decompose above this temperature.

Results and Discussion

Results. The measured data of the density, viscosity, and vapor pressure of DCPPS were fitted to the following equations. Density versus temperature was fitted to a second-order polynomial:

$$\rho/\text{g·cm}^{-3} = 1.372 + 1.130 \times 10^{-3}(T/\text{K}) - 3.590 \times 10^{-6}(T/\text{K})^2 \quad (2)$$

Viscosity versus temperature was fitted to the Andrade equation:

$$\ln(\eta/\text{mPa·S}) = -4.346 + 1697/(T/\text{K}) \quad (3)$$

Vapor pressure versus temperature was fitted to the Antoine equation:

$$\log(p/\text{kPa}) = A - \frac{B}{C + T/\text{K}} \quad (4)$$

where p is the vapor pressure; T is the temperature; and A, B, and C are the Antoine constants.

The Antoine constants A, B, and C determined from least-squares fitting and the absolute average deviation are listed in Table 4. A comparison of the vapor pressure obtained from the fitted equation and the measured data and the literature values is shown in Figure 2.

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

$$\text{AAD}(\rho) = \frac{1}{N}\sum|\rho_i - \rho_{i,\text{calc}}|/\rho_i \quad (5)$$

$$\text{AAD}(\eta) = \frac{1}{N}\sum|\eta_i - \eta_{i,\text{calc}}|/\eta_i \quad (6)$$

$$\text{AAD}(p) = \frac{1}{N}\sum|p_i - p_{i,\text{calc}}|/p_i \quad (7)$$

where the suffix calc stands for the calculated values from fitted equations. The absolute average deviation of density, viscosity,

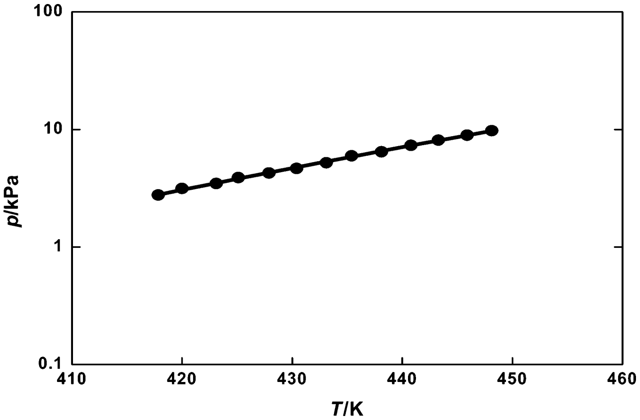

Figure 2. Experimental and calculated vapor pressure data for DCPPS: ●, experimental data; —, calculated by eq 4.

and vapor pressure fitting for DCPPS are (0.3, 1.4, and 1.38) %, respectively.

Discussion

The densities of DCPPS calculated from eq 2 at (293.15 and 298.15) K are (1.3947 and 1.3898) g·cm^{-3}, which are in good agreement with the literature values of 1.4042 g·cm^{-3} at 293.15 K[3] and 1.390 g·cm^{-3} at 298.15 K.[2] While the viscosity data over a temperature range of (303.16 to 423.40) K were fitted to the Andrade equation, no literature values are available.

Welton[4] reported the boiling temperature of 150 °C at 3.47 kPa. Compared with the data of this work, 423.10 K(150.10 °C) at 3.47 kPa, they are in fairly good agreement. In addition, Giichi et al.,[5] Warren,[6] and Kabachnik and Godovikov[3] reported the boiling temperatures of 115 °C at 0.67 kPa, (95 to 110) °C at (0.27 to 0.40) kPa, and (76 to 77) °C at 0.08 kPa, respectively, which are beyond the temperature range of these experimental measurements. The boiling temperatures calculated from eq 6 are 114.55 °C at 0.67 kPa, 97.12 °C at 0.27 kPa, and 76.04 °C at 0.08 kPa, respectively, which could be regarded as a useful reference.

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