

Vapor Pressure of Dimethyl Phosphite and Dimethyl Methylphosphonate

Chuan-Lei Fan and Li-Sheng Wang*

School of Chemical Engineering & the Environment, Beijing Institute of Technology, Beijing 100081, People's Republic of China

The vapor pressures of dimethyl phosphite in the range of (352.9 to 443.4) K and dimethyl methylphosphonate in the range of (358.2 to 453.5) K were measured by a static method. The vapor pressure data were fitted to the Antoine equation. The vapor pressure data of dimethyl phosphite and dimethyl methylphosphonate were compared with literature values. The average relative deviations of vapor pressure fitting for dimethyl phosphite and dimethyl methylphosphonate are 0.52 % and 0.68 %, respectively.

Introduction

Dimethyl methylphosphonate (DMMP) is useful as a flame retardant.¹ Dimethyl phosphite is a byproduct during the synthesis of DMMP. The vapor pressure data of the two components can be used in their separation and purification process. However, these data have not been reported systematically in the literature. The vapor pressure of dimethyl phosphite in the range of (243.2 to 443.2) K^{2–9} and the vapor pressure of DMMP in the range of (258.2 to 454.4) K^{9–16} were reported. In this paper, the vapor pressures of dimethyl phosphite and DMMP are presented in a range of (352.9 to 443.4) K and (358.2 to 453.5) K, respectively. The vapor pressures were correlated with the Antoine equation. The obtained experimental results were compared with the literature values. The average relative deviations of vapor pressure fitting for dimethyl phosphite and DMMP are (0.52 and 0.68) %, respectively.

Experimental Section

Chemicals. Dimethyl phosphite was purchased from Rizhao Lideshi Chemical Company, and the specified purity is above 98 %, with a refractive index value at 293.15 K of $n_{D,293.15K} = 1.4035$ (lit.⁴ 1.4038). DMMP was purchased from Tsingtao Haida Chemical Company, and the specified purity is above 98 %, with a refractive index value at 298.15 K of $n_{D,298.15K} = 1.4111$ (lit.¹⁷ 1.4111). To improve the purity, both of the substances were distilled twice before using. Density values at 293.15 K were determined with $\rho = 1.1821 \text{ g}\cdot\text{cm}^{-3}$ (for dimethyl phosphite, lit.¹⁹ 1.1941) and $\rho = 1.1542 \text{ g}\cdot\text{cm}^{-3}$ (for DMMP, lit.²⁰ 1.16). The final purity is above 99 %.

Vapor Pressure Measurements. The vapor pressure was measured by a static method. The apparatus setup is schematically shown in Figure 1. 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. The deviation between the experimental results and the literature values was within 0.2 %, which showed the apparatus to be reliable. The vapor pressure measurement versus temperature was performed in (3 to 6) K intervals. The measurement procedure was the same as that given in our previous paper.¹⁸ 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

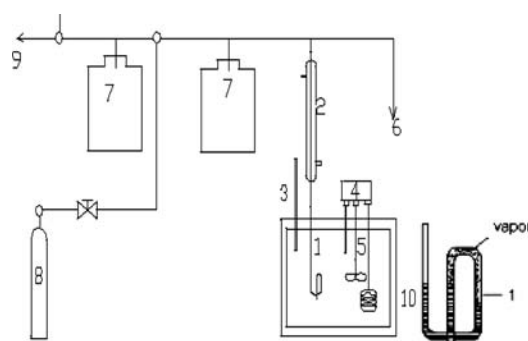


Figure 1. Apparatus for the measurement of vapor pressure: 1, equilibrium cell; 2, condenser; 3, temperature indicator; 4, thermoregulator; 5, agitator blade; 6, mercury pressure gauge; 7, buffer bottle; 8, nitrogen cylinder; 9, to vacuum pump; 10, thermostat bath.

Table 1. Experimental Vapor Pressure Data of Dimethyl Phosphite Obtained in this Work

<i>T</i> /K	<i>p</i> /kPa	100δ ^a	<i>T</i> /K	<i>p</i> /kPa	100δ ^a
352.9	4.10	0.79	398.8	25.46	0.45
354.1	4.33	0.78	403.0	29.32	0.04
356.9	4.87	-0.10	408.1	34.77	-0.09
357.4	4.93	-1.02	413.5	41.60	0.15
360.9	5.80	-0.11	416.8	46.60	0.93
364.2	6.70	-0.07	422.5	55.24	0.08
367.1	7.47	-1.23	423.9	57.79	0.16
371.0	8.60	0.90	428.0	65.89	0.77
372.5	9.39	-0.53	430.9	71.50	0.53
376.1	10.96	0.47	434.8	79.35	-0.64
378.9	12.16	-0.09	437.1	86.14	1.09
382.4	14.01	0.31	438.6	89.11	0.09
387.7	16.94	-0.34	440.4	93.10	-0.52
391.8	19.85	0.47	441.9	96.63	-1.03
396.8	23.33	-1.29	443.4	101.33	-0.46
397.6	24.17	-0.56			

$$^a \delta = (p - p_{\text{calcd}})/p.$$

temperature was within ± 0.05 %. The vapor pressure measurement was estimated to have an uncertainty within 0.5 %.

Results and Discussion

The experimental vapor pressure data for dimethyl phosphite in the range of (352.9 to 443.4) K are listed in Table 1 and for DMMP in the range of (358.2 to 453.5) K are listed in Table 2. The measured vapor pressure data of DMMP and dimethyl phosphite in this work were fitted to the Antoine equation

* Corresponding author. E-mail: lishengwang@btamail.net.cn. Fax: +86-10-68911040. Tel: +86-10-68912660.

$$\log(p/\text{kPa}) = A - \frac{B}{C + T/\text{K}} \quad (1)$$

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 average relative deviations of the experimental data obtained in this work from the fitted equations are listed in Table 3. The average relative deviation (ARD) of measured data from the fitted equation is defined

$$\text{ARD} = 100 \cdot \frac{1}{N} \sum |p_i - p_{i,\text{calcd}}|/p_i \quad (2)$$

where calcd stands for the calculated values from the fitted equations. The relative average deviations of vapor pressure fitting for dimethyl phosphite and for DMMP are (0.52 and 0.68) %, respectively, as listed in Table 3. Figures 2 and 3 show the fractional deviations of the experimental pressures from values obtained with the Antoine equation of dimethyl phosphite and DMMP, respectively.

A comparison of the vapor pressure obtained from the fitted equation with the measured data and the literature values is

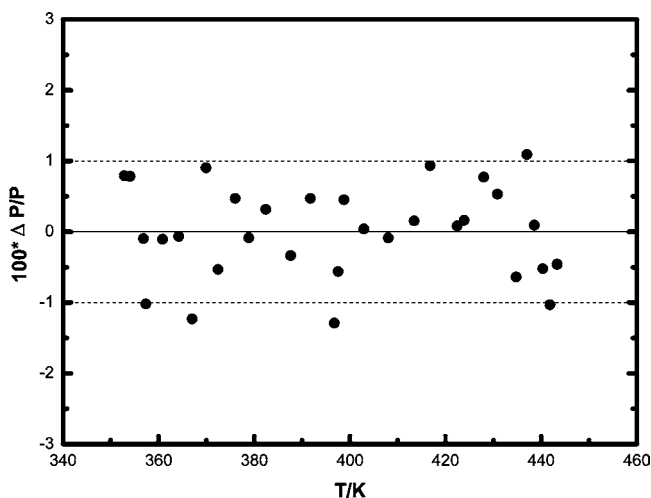


Figure 2. Fractional deviations $\Delta P = P(\text{exptl}) - P(\text{calcd})$ of the experimental pressures $P(\text{exptl})$ of dimethyl phosphite from values $P(\text{calcd})$ obtained with the Antoine equation.

Table 2. Experimental Vapor Pressure Data of DMMP Obtained in This Work

T/K	p/kPa	$100\delta^a$	T/K	p/kPa	$100\delta^a$
358.2	2.73	1.01	416.3	35.86	0.85
362.7	3.51	0.33	419.6	39.84	0.47
368.4	4.75	-0.38	423.3	44.26	-0.63
374.0	6.34	-0.21	427.1	50.30	0.46
380.8	8.76	-0.66	432.0	58.21	0.50
385.0	10.96	-1.78	434.7	63.24	1.00
390.3	13.41	-0.06	437.8	68.40	0.12
393.2	14.93	-1.42	442.3	77.79	0.69
397.5	18.07	0.36	446.3	84.92	-1.13
401.3	20.76	-0.45	448.7	91.51	0.16
403.9	23.13	0.62	450.9	96.47	-0.15
409.7	28.76	1.41	453.5	101.32	-1.72
412.5	31.41	0.51			

$$^a \delta = (p - p_{\text{calcd}})/p.$$

Table 3. Fitted Antoine Constants of Dimethyl Phosphite and DMMP Based on the Experimental Data of This Work

	Antoine constants			temperature range	ARD
	A	B	C	T/K	%
dimethyl phosphite	7.031	2088	-27.65	352.9 to 443.4	0.52
DMMP	4.887	771.0	-185.1	358.2 to 453.5	0.68

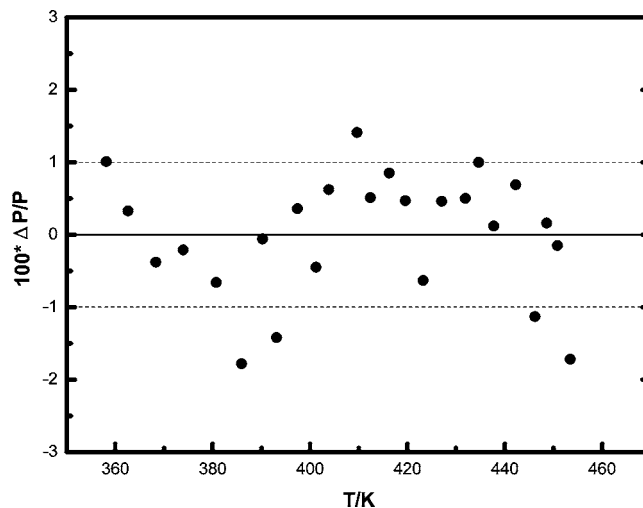


Figure 3. Fractional deviations $\Delta P = P(\text{exptl}) - P(\text{calcd})$ of the experimental pressures $P(\text{exptl})$ of DMMP from values $P(\text{calcd})$ obtained with the Antoine equation.

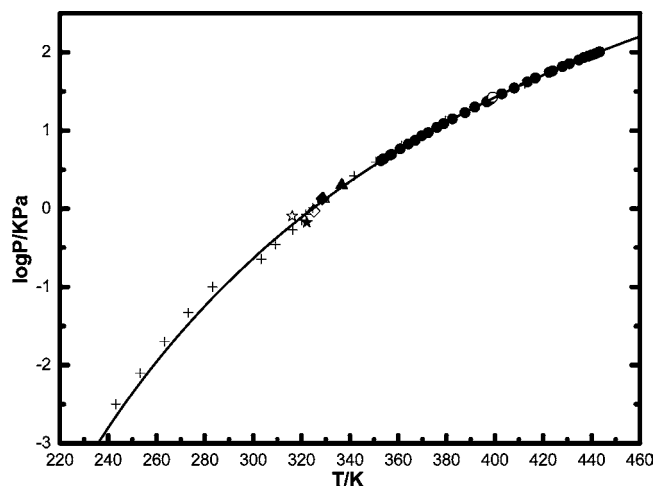


Figure 4. Experimental and calculated vapor pressure data for dimethyl phosphite: ●, experimental data; —, calculated by eq 1 including the experimental data measured in this work and the literature data. Literature data: ○, ref 2; ▲, ref 3; △, ref 4; ◆, ref 5; ◇, ref 6; ★, ref 7; ☆, ref 8; +, ref 9.

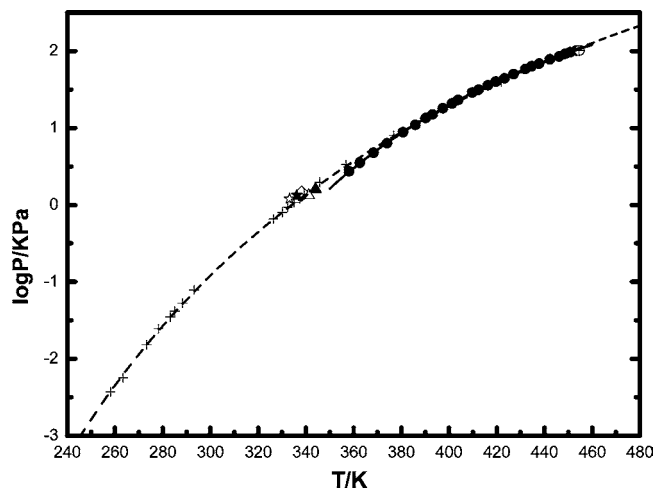


Figure 5. Experimental and calculated vapor pressure data for DMMP: ●, experimental data measured in this work; —, calculated by eq 1 for the experimental data measured in this work; - - -, calculated by eq 1 including the experimental data measured in this work and the reported data. Reported data: +, ref 9; ▲, ref 10; △, ref 11; ◇, ref 12; ◆, ref 13; ★, ref 14; ☆, ref 15; ○, ref 15.

shown in Figure 4 for dimethyl phosphite and in Figure 5 for DMMP. From Figure 4 it can be seen that the experimental data obtained in this work for dimethyl phosphate agree well with the literature data. In Figure 4, the Antoine equation fitted from the experimental data of this work was extrapolated to a temperature range of (243.2 to 443.2) K, and the calculated results agree well with the literature data. From Figure 5 it is obvious that the experimental data obtained in this work for DMMP in range of (374.0 to 453.5) K agree with the literature data as well. However, in a temperature range of (358.3 to 368.4) K, the experimental vapor pressures of DMMP obtained in this work are lower than the literature data. When the Antoine constants of DMMP were fitted including the experimental data of this work and the literature data, the results were shown by the dashed line in Figure 3. In this case, the Antoine constants $A = 7.093$, $B = 211.5$, and $C = -35.89$, and the obtained ARD is 1.38 %.

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