

Vapor Pressure of Dimethoxymethane and 1,1,1,3,3-Pentafluoropropane

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The vapor pressure of dimethoxymethane was measured at temperatures from (283 to 398) K with pressures from (27.7 to 935.5) kPa, together with the vapor pressure of 1,1,1,3,3-pentafluoropropane (HFC-245fa) measured at temperatures from (253 to 403) K, with pressures from (19 to 2348) kPa. The vapor pressure data was then correlated using Wagner-type and Wu-type vapor pressure equations. The uncertainties of the measurements for temperature and pressure were within ± 5 mK and ± 0.7 kPa, respectively.

Introduction

In recent research, it was found that by using dimethoxymethane ($\text{CH}_3\text{-O-CH}_2\text{-O-CH}_3$, also called methylal) as a fuel additive, a great improvement in diesel oil and petrol combustion properties together with a significant reduction in particle emission was achieved. The results indicated that a volume fraction of 30 % dimethoxymethane in diesel fuel caused in a reduction of particulate matter.¹ Furthermore, dimethoxymethane has a mass fraction of oxygen of 42 % and is miscible with diesel fuel;² hence, it is regarded as a good fuel additive and a potential alternative fuel in the future. In addition, dimethoxymethane is extensively used as a solvent in household and industrial sprays, as a blowing agent for polyurethane foams, and in the production of ion-exchange resins. High-purity dimethoxymethane is also used in cosmetics and pharmaceuticals. For those applications, the thermophysical property data of dimethoxymethane are important. In our previous work, the density, viscosity, and thermal conductivity of liquid dimethoxymethane was measured.^{3,4} In this work, the vapor pressures of dimethoxymethane were measured at temperatures from (283 to 398) K.

However, before the vapor pressures of dimethoxymethane were measured, the performance of the experimental system was checked with 1,1,1,3,3-pentafluoropropane (HFC-245fa) because of its importance as a promising replacement for chlorine-containing compounds, such as 1,1-dichloro-1-fluoroethane (HCFC-141b) and 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114) in high-temperature heat pumps and chemical blowing agents.

Experimental Section

Materials. The sample of 1,1,1,3,3-pentafluoropropane was provided by Zhejiang Fluoro-Chemical Technology Research Institute with stated mass fraction purity of 99.8 % and was degassed by repeatedly evacuating the sample container immersed in liquid nitrogen. The mass fraction purity of HFC-245fa was better than 99.99 %, as indicated by analysis with gas chromatograph (Agilent Technologies, model 6890N). A flame ionization detector (FID) and a capillary column (GS-GASPRO, Agilent model 113-4362) were used for the analysis

with the carrier gas hydrogen at 4.0 mL/min, and the oven temperature and the detector temperature were 423 K and 473 K, respectively.

The sample of dimethoxymethane was provided by Shanghai Yongfu Aerosol Manufacturing Co. Ltd. The sample was further purified with sodium and distillation.⁵ Finally, the mass fraction purity of dimethoxymethane was better than 99.98 %, as indicated by analysis with the Agilent 6890N gas chromatograph. A thermal conductivity detector (TCD) and a capillary column (DB-WAX, Agilent model 125-7032) were used on the analysis with the carrier gas hydrogen at 20.0 mL/min, and the oven temperature and the detector temperature were 473 K and 523 K, respectively.

Apparatus. The experimental apparatus used in this work is shown in Figure 1 and has been previously used to measure the vapor pressure of dimethyl ether.⁶ It consists of an optical sample cell, a thermostatic bath, a temperature measurement system, and a pressure measurement system. The optical sample cell (H) consists of a cylindrical vessel made of 304 type stainless steel, with two quartz glass windows for observation. This is immersed in a thermostatic bath. In the previous papers,^{7,8} the thermostatic bath, temperature measurement system, and pressure measurement system have been described in detail; hence, only a brief introduction is given here.

The temperature of the thermostatic bath was controlled by a computer with two heaters (HL and HS) and a cooler and was monitored continuously. To improve the performance of the thermostatic bath, a Fuzzy-PID algorithm was applied in the temperature control system. Ethanol was used as the bath fluid from (250 to 313) K, and silicone oil was used in the temperature range from (313 to 403) K. The temperature fluctuation in the bath was less than ± 4 mK \cdot h⁻¹.

The temperature measurement system consisted of an ASL F18 thermometry bridge and two 25 Ω standard platinum resistance thermometers (Beijing Const Technology Co. Ltd.). One thermometer (no. 68033) can be used from (83.8058 to 273.16) K, and another (no. 68115) can be used from (273.15 to 933.473) K. The thermometers were calibrated on ITS-90 at the National Institute of Metrology of China. The total standard uncertainty of temperature was better than ± 1.0 mK with a 100 Ω reference resistor.

When measuring pressure, four high-precision quartz pressure sensors (A, B, C, and D, Paroscientific Inc., models 223A-101, 2200A-101, 31K-101, and 42K-101) and two differential

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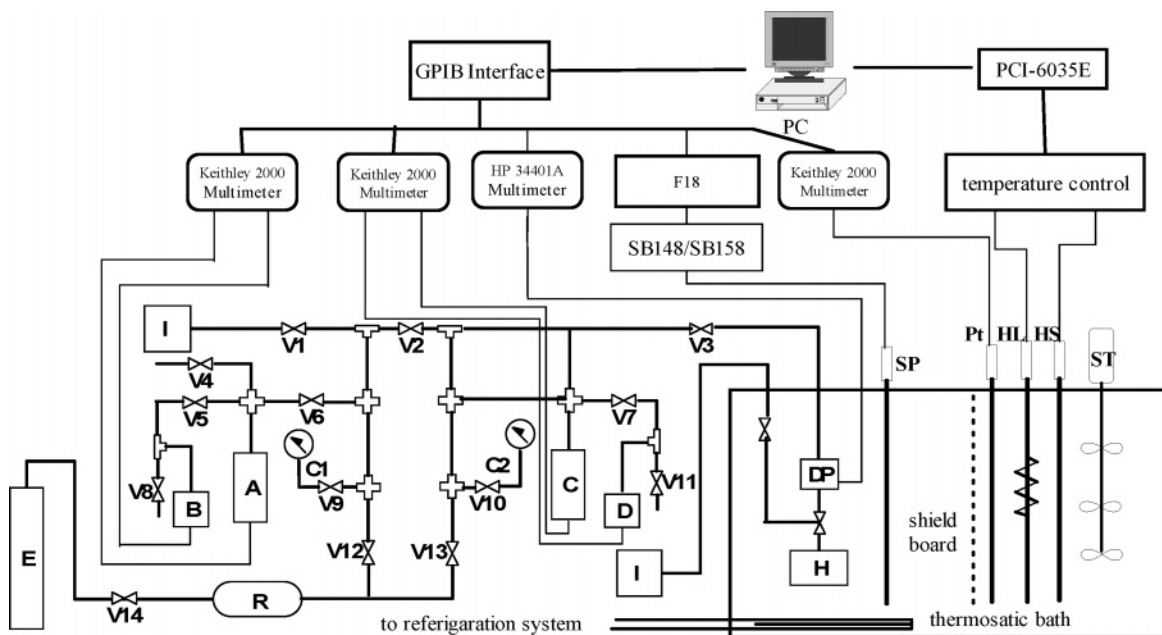


Figure 1. Schematic diagram of experiment system: A to D, pressure sensors; C1 and C2, pressure gauge (0–16 MPa); DP, pressure transducer; E, nitrogen gas; H, apparatus; HL, auxiliary heaters; HS, controlled heater; I, vacuum pump; Pt, platinum resistance thermometer; R, gas reservoir; SP, 25 Ω standard platinum resistance thermometer; ST, stirrer motor; V1 to V14, valves.

Table 1. Experimental Vapor Pressure (P) of 1,1,1,3,3-Pentafluoropropane

T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
253.125	19.34	295.077	131.93	323.164	343.03	358.161	893.28
258.159	25.37	298.058	147.46	325.164	364.63	363.158	1007.01
263.129	32.79	303.062	177.01	328.160	398.98	368.132	1130.31
268.120	41.88	305.051	190.20	330.162	423.22	373.132	1265.73
273.125	52.91	308.051	210.95	333.162	461.65	378.157	1413.62
278.118	66.17	310.091	225.91	338.164	531.78	383.152	1573.34
283.149	82.07	313.101	249.94	343.162	609.29	388.142	1745.43
285.144	89.11	315.078	266.801	345.161	642.58	393.136	1932.23
288.124	100.56	318.119	294.26	348.161	695.02	398.123	2133.20
293.092	122.20	320.166	312.44	353.160	789.45	403.075	2348.19

pressure transducers (DP, Rosemount, model 3051) were available for use. The pressure could be measured from (0 to 13.8) MPa with high accuracy. In this work, the model 31K-101 pressure sensor was used from (0 to 6.89) MPa with an uncertainty of $\pm 0.01\%$. The range of the differential pressure transmitter was from (–6.22 to +6.22) kPa, and the uncertainty was $\pm 0.075\%$. The total standard uncertainty of pressure was better than ± 0.7 kPa. On the basis of the above discussion, the standard uncertainties of the vapor pressure measurements are better than ± 5.0 mK for temperature and ± 0.7 kPa for pressure, respectively.

Results and Analysis

1,1,1,3,3-Pentafluoropropane (HFC-245fa). A total of 40 values were measured at temperatures from (253 to 403) K, with pressures from (19 to 2348) kPa. The vapor pressure measurements of HFC-245fa are given in Table 1, with temperatures given on the ITS-90 scale.

Using the vapor pressure data reported here, a Wagner-type vapor pressure equation for HFC-245fa was fitted:

$$\ln P_r = (a_1\tau + a_2\tau^{1.5} + a_3\tau^3 + a_4\tau^6)/T_r \quad (1)$$

where $T_r = T/T_c$ is the reduced temperature; T_c is the critical temperature, 427.2 K from ref 9 with an uncertainty of ± 0.02 K; $\tau = 1 - T_r$; $P_r = P/P_c$ is the reduced pressure; a_1 , a_2 , a_3 , and a_4 are the fitted parameters. The fitted values for a_1 , a_2 , a_3 ,

Table 2. Reported Vapor Pressures of HFC-245fa

no. of points	range		uncertainties		ref
	T/K	P/kPa	$\delta P/kPa$	$\delta T/mK$	
32	293–426	126–3595	± 5	± 20	10
51	264–351	353–761	± 0.7	± 15	11
79	255–393	21–1950	± 0.8	± 10	12
7	293–313	122–253	± 1.0	± 20	13, 14

and a_4 were -7.4259585 , 0.52277026 , -2.5776233 , and -8.391318 , respectively. P_c is the critical pressure of HFC-245fa, found to be 3635.98 kPa by fitting eq 1 to the present data, and the uncertainty of P_c was estimated to be less than ± 10 kPa. Furthermore, the P_c value is coincident with the value provided in ref 12. The maximum and absolute average deviations from the Wagner equation are 0.24 % and 0.068 %, respectively. Finally, the normal boiling point (T_b) and the Pitzer acentric factor (ω) of HFC-245fa derived from eq 1 are 288.3 K and 0.376, respectively.

To our knowledge, three sets^{10–12} of experimental data of vapor pressure of HFC-245fa were found in the published literatures. Bobbo et al.^{13,14} also reported several experimental values of vapor pressure of HFC-245fa at four different temperatures. The details about previous vapor pressure data of HFC-245fa are given in Table 2, and the comparisons of the present experimental data and the previous published data are shown in Figure 2 and Figure 3.

The data of Di Nicola¹¹ show good agreement with eq 1 to within 0.5 % (± 2.5 kPa) from (264 to 352) K, and particularly, most of the data agree relatively well within 0.1 %. The data of Wang and Duan¹² agree with eq 1 within 0.3 % at temperatures above about 280 K; however, below 280 K, the data depart rapidly from eq 1, and the deviation reaches about 1.1 % at 255 K but in the uncertainty of pressure ± 0.7 kPa. The relative deviations of Bobbo et al.^{13,14} results from eq 1 are less than 1.0 % except at 298.18 K and 313.22 K. The data of Sotani and Kubota¹⁰ exhibit relative deviations from 2.9 % to -0.8% and show considerable discrepancies up to ± 25 kPa from other data. The deviations of those calculated from NIST REFPROP 7.0¹⁵ are also shown in Figure 2, and the maximum deviation was less than 1.6 %.

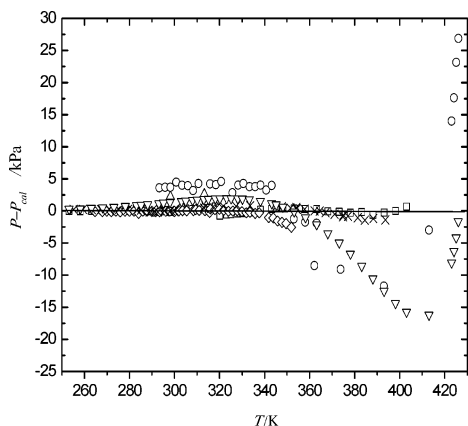


Figure 2. Absolute deviations of the vapor pressure data of HFC-245fa from eq 1: \square , this work; \circ , Sotani and Kubota;¹⁰ \diamond , Di Nicola;¹¹ \times , Wang and Duan;¹² \triangle , Bobbo et al.;^{13,14} ∇ , REFPROP 7.0.¹⁵

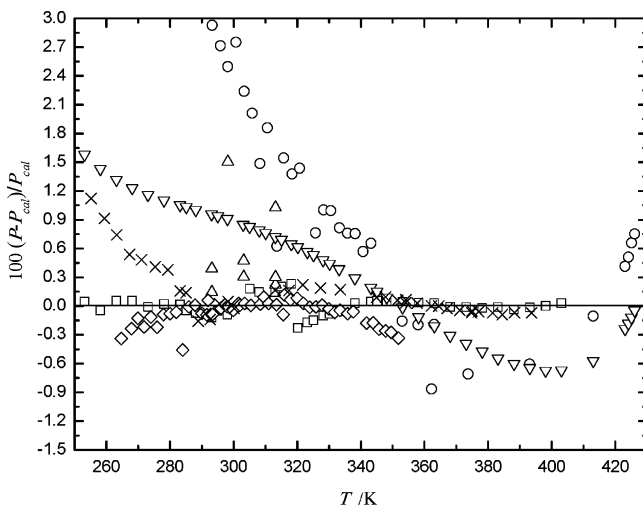


Figure 3. Relative deviations of the vapor pressure data of HFC-245fa from eq 1: \square , this work; \circ , Sotani and Kubota;¹⁰ \diamond , Di Nicola;¹¹ \times , Wang and Duan;¹² \triangle , Bobbo et al.;^{13,14} ∇ , REFPROP 7.0.¹⁵

In addition, the experimental data of this work were also correlated with the Wu type vapor pressure equation,¹⁶ which is a new vapor pressure equation with good extrapolation characteristics:

$$\ln P_r = \ln T_{rp} [a_0(1 - \tau)^{3.76} + a_1(1 - \tau)^{-0.56} + a_2\tau^{1.89}] \quad (2)$$

where $P_r = P/P_c$; $T_{rp} = (T - T_p)/(T_c - T_p)$; $\tau = 1 - T_{rp} = 1 - (T - T_p)/(T_c - T_p)$; $a_2 = -a_0/0.56$; and the three adjustable parameters (a_0 , a_1 , and T_p) were fitted as 0.5097734, 5.882596, and 57.5 K, respectively. The parametric determination of T_p consisted of repeating the nonlinear fit procedure for various fixed values of T_p to achieve a minimum sum of squared errors. P_c is the critical pressure of HFC-245fa, found to be 3641.53 kPa by fitting eq 2 to the present data, and the uncertainty of P_c was estimated to be less than ± 10 kPa. The maximum deviation and the absolute average deviation are 0.25 % and 0.072 %, respectively. The normal boiling point (T_b) and the Pitzer acentric factor (ω) derived from eq 2 were calculated to be 288.3 K and 0.376, respectively. It shows that the results of HFC-245fa derived from the Wu vapor pressure equation agrees well to that derived from the Wagner vapor pressure equation.

The maximum deviation and the absolute average deviation of Wagner-type and Wu-type vapor pressure equations are similar, and both can represent the data within the uncertainties of the experimental results. However, it is well-known that,

Table 3. Experimental Vapor Pressure (P) of Dimethoxymethane

T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
283.133	27.73	308.046	77.74	335.166	194.47	368.156	477.61
285.126	30.39	310.075	83.80	338.164	212.79	373.15	538.51
288.112	34.73	313.164	93.85	340.161	225.73	378.158	605.33
293.075	43.08	318.133	111.95	343.158	246.24	383.133	677.68
295.075	46.83	323.168	132.98	345.161	260.68	388.154	757.05
298.067	52.94	325.175	142.06	348.16	283.65	393.158	842.82
300.069	57.14	328.168	156.44	353.16	325.16	398.152	935.48
303.051	64.26	330.167	166.67	358.158	371.53		
305.046	69.42	333.167	182.96	363.159	421.82		

unless the true or recommended value of P_c is known and used directly, the critical pressure (P_c) fitted from eq 1 depends closely on the data set (i.e., if one or two experimental values are added or deleted from the data set in the fitting process, sometimes the P_c value will change very significantly). During the fitting process of the Wagner vapor pressure equation of HFC-245fa, the P_c value determined by using the data at temperatures from (250 to 375) K is 3635 kPa, but it is significantly different from 3860 kPa, which was determined by using the data at temperatures from (250 to 355) K. However, the Wu-type vapor pressure equation is independent of the data set and also can extrapolate well from a small amount of data points in the usual range to the entire vapor–liquid coexistence region both up to the critical temperature and down to the triple point. By using the data at temperatures from (250 to 375) K and (250 to 355) K, the P_c values determined by the Wu equation are 3661 kPa and 3694 kPa, respectively. The difference is very little. At the same time, the Wu vapor pressure equation will not cause the negative enthalpy of vaporization, which happens sometimes with the Wagner equation.¹⁶ On the basis of the above consideration, the Wu-type equation is recommended to calculate the vapor pressure of HFC-245fa.

Dimethoxymethane. The vapor pressures of dimethoxymethane were measured at temperatures from (283.133 to 398.152) K with pressures from (27.7 to 935.5) kPa. A total of 34 values are reported in Table 3.

The experimental data were correlated as the Wagner-type vapor pressure equation. The fitted parameters of the Wagner-type equation are $P_c = 5018.9$ kPa, $a_1 = -9.3754276$, $a_2 = 5.6709651$, $a_3 = -8.2535942$, and $a_4 = 6.3250031$. The critical temperature of dimethoxymethane $T_c = 491$ K was recommended by ref 17 with an uncertainty of ± 1.0 K, which was deduced from the experimental data published in ref 18. The maximum deviation is 0.25 %, and the absolute average deviation is 0.086 %. The normal boiling point (T_b) and the Pitzer acentric factor (ω) were calculated to be 315.3 K and 0.302, respectively.

To our knowledge, few vapor pressures of dimethoxymethane have been published in the literatures, except the data of McEachern and Kilpatrick¹⁹ at temperature from (281 to 299) K. The range of temperature was relatively limited. The deviations of the present experimental data and the published data from the Wagner-type vapor pressure equation of dimethoxymethane are shown in Figure 4 and Figure 5. As shown in Figure 4 and Figure 5, the maximum deviation was 0.88 %, and the difference of the present data and the data of McEachern and Kilpatrick¹⁹ was in the uncertainty of pressure measurement ± 0.7 kPa, but the value of the present data is lower than that of the data of McEachern and Kilpatrick at the corresponding temperature.

Similarly, the data was correlated with the Wu-type vapor pressure equation of dimethoxymethane with the following parameters: $P_c = 4303.056$ kPa, $a_0 = 0.4152705$, $a_1 = 5.341831$, and $T_b = 62.7$ K, where $T_c = 491$ K was used. The

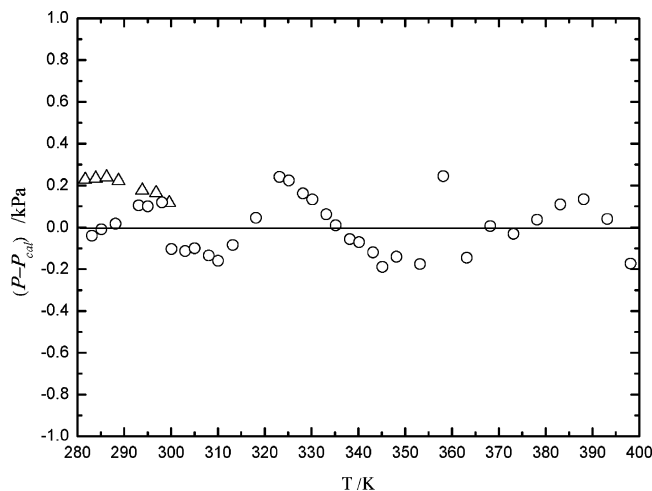


Figure 4. Absolute deviations of the vapor pressure data of dimethoxymethane from the Wagner-type vapor equation: \circ , this work; \triangle , McEachern and Kilpatrick.¹⁹

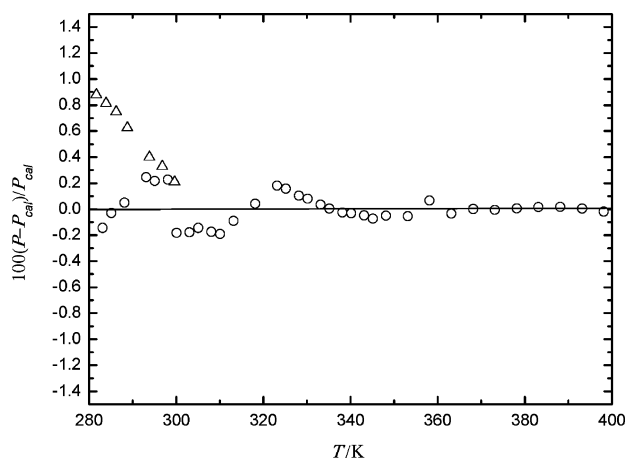


Figure 5. Relative deviations of the vapor pressure data of dimethoxymethane from the Wagner-type vapor equation: \circ , this work; \triangle , McEachern and Kilpatrick.¹⁹

maximum deviation and the absolute average deviation are 0.24 % and 0.10 %, respectively. The normal boiling point (T_b) and the Pitzer acentric factor (ω) were calculated to be 315.3 K and 0.236, respectively.

The calculated critical pressure show a large discrepancy (1058.9 kPa) from the recommended value of 3960 kPa^{17,20} and the value of 5018.9 kPa derived from the Wagner vapor pressure equation. However, it is easy to learn that the P_c difference of the recommended value and the derived value from the Wu vapor pressure equation is 343.1 kPa and much less. In addition, if the critical temperature $T_c = 480.6$ K recommended in ref 20 was used, the critical pressure is 3736 kPa and more close to the recommended value of 3960 kPa. Hence, the Wu-type equation is also recommended to calculate the vapor pressure of dimethoxymethane.

Conclusion

Vapor pressures of 1,1,1,3,3-pentafluoropropane were measured in a range of temperatures from (253 to 403) K, with pressure from (19 to 2348) kPa and of dimethoxymethane at temperature from (283 to 398) K with pressure from (27 to 935) kPa. The measurement standard uncertainties of temperature and pressure were ± 5.0 mK and ± 0.7 kPa, respectively. The data were correlated with the Wagner-type and the Wu-type vapor pressure equation. Considering the extrapolating characteristics,

the Wu-type vapor pressure equation was recommended. The maximum and absolute average deviations from Wu equation for dimethoxymethane were 0.24 % and 0.10 % and for HFC-245fa were 0.25 % and 0.072 %, respectively. The comparisons between the measurements and the published literature data were also made.

Literature Cited

- (1) Maricq, M. M.; Chase, R. E.; Podsiadlik, D. H.; Siegl, W. D.; Kaiser, E. W. The effect of dimethoxy methane additive on diesel vehicle particulate emissions. *SAE Pap.* **1998**, No. 982572.
- (2) Vertin, K. D.; Ohi, J. M.; Naegeli, D. W.; Childress, K. H.; Hagen, G. P.; McCarthy, C. I. Mehtylal and methylal-diesel blended fuels for use in compression-ignition engines. *SAE Pap.* **1999**, No. 1999-01-1508.
- (3) Pan, J.; Wu, J. T.; Liu, Z. G. Measurement of the thermal conductivity of liquid dimethoxymethane from 240 to 362 K. *Int. J. Thermophys.* **2004**, *25*, 701–707.
- (4) Wu, J. T.; Xu, Z. Y.; Liu, Z. G.; Wang, B. Density and viscosity of saturated liquid dimethoxymethane from (218.15 to 383.15) K. *J. Chem. Eng. Data* **2005**, *50*, 966–968.
- (5) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 4th ed.; World Publishing Co. Ltd.: Beijing, 2000.
- (6) Wu, J. T.; Liu, Z. G.; Pan, J.; Zhao, X. M. Vapor pressure measurements of dimethyl ether from (233 to 399) K. *J. Chem. Eng. Data* **2004**, *49*, 32–34.
- (7) Wu, J. T. Development of the new thermophysical properties measurement system and research of thermophysical properties of dimethyl ether. Ph.D. Dissertation, Xi'an Jiaotong University, Xi'an, People's Republic of China, 2003.
- (8) Wu, J. T.; Liu, Z. G.; Pan, J. Development of fluid thermophysical property measurement system with high accuracy. *J. Xi'an Jiaotong Univ.* **2004**, *38*, 937–942.
- (9) Schmidt, J. W.; Carrillo-Nava, E.; Moldover, M. R. Partially halogenated hydrocarbons CHFCl–CF₃, CF₃–CH₃, CF₃–CHF–CHF₂, CF₃–CH₂–CF₃, CHF₂–CF₂–CHF₂, CF₃–CH₂–CHF₂, CF₃–O–CHF₂: critical temperature, refractive indices, surface tension, and estimates of liquid, vapor and critical densities. *Fluid Phase Equilib.* **1996**, *122*, 187–206.
- (10) Sotani, T.; Kubota, H. Vapor pressures and PVT properties of 1,1,1,3,3-pentafluoropropane (HFC-245fa). *Fluid Phase Equilib.* **1999**, *161*, 325–335.
- (11) Di Nicola, G. Vapor pressure and gas-phase P – V – T data for 1,1,1,3,3-pentafluoropropane (R-245fa). *J. Chem. Eng. Data* **2001**, *46*, 1619–1622.
- (12) Wang, Z. W.; Duan, Y. Y. Vapor pressures of 1,1,1,3,3-pentafluoropropane (HFC-245fa) and 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea). *J. Chem. Eng. Data* **2004**, *49*, 1581–1585.
- (13) Bobbo, S.; Camporese, R.; Scalabrin, G. Isothermal vapour–liquid equilibrium measurements for the binary mixtures HFC-125 + HFC-245fa and HC-290 + HFC-245fa. *High Temp. – High Pressures* **2000**, *32*, 441–447.
- (14) Bobbo, S.; Fedele, L.; Scattolini, M.; Camporese, R. Isothermal VLE measurements for the binary mixtures HFC-134a + HFC-245fa and HC-600a + HFC-245fa. *Fluid Phase Equilib.* **2001**, *185*, 255–264.
- (15) Lemmon, E. W.; McLinden, M. O.; Huber, M. L. Reference fluid thermodynamic and transport properties. *NIST Standard Reference Database 23 (REFPROP) version 7.0*; National Institute of Standard and Technology: Boulder, CO, 2003.
- (16) Wu, J. T.; Liu, Z. G. An accurate vapor pressure equation with good extrapolating characteristics. *Int. J. Thermophys.* **2005**, *26*, 767–784.
- (17) Kudchadker, A. P.; Ambrose, D.; Tsonopoulos, C. Vapor–liquid critical properties of elements and compounds. 7. Oxygen compounds other than alkanols and cycloalkanols. *J. Chem. Eng. Data* **2001**, *46*, 457–479.
- (18) Morton, D. W.; Lui, M.; Young, C. L. The (gas+liquid) critical temperature of some ethers, esters and ketones. *J. Chem. Thermodyn.* **1999**, *31*, 675–684.
- (19) McEachern, D. M.; Kilpatrick, J. E. Entropy and related thermodynamics properties of dimethoxymethane. *J. Chem. Phys.* **1964**, *41*, 3127–3131.
- (20) Kobe, K. A.; Mathews, J. F. Critical properties and vapor pressures of some organic nitrogen and oxygen compounds. *J. Chem. Eng. Data* **1970**, *15*, 182–186.

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