[Review Paper]

Eight Constants in the Benedict-Webb-Rubin Equation of State for 1-Pentyne and Their Validity for Bubble Point Pressure with Propane or Dimethyl Ether

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Saturated vapor pressure was measured for pentane and 1-pentyne using a static apparatus at temperatures in the range 273.15 to 463.58 K. The P-V-T relationship was measured for 1-pentyne by a constant volume method up to 4.0919 MPa at 485.00 K, where the inner volume of the cell was calibrated with the mass and pressure of gaseous pentane at the same temperature. Bubble point pressures were also investigated for two binaries, propane or dimethyl ether with 1-pentyne, using the static apparatus at 303.15 K and 313.15 K. The eight constants of the Benedict-Webb-Rubin (BWR) equation of state were determined for 1-pentyne by assuming functions where the critical pressure and the acentric factor depend on the critical temperature. The average relative deviations for saturated vapor pressure and P-V-T relationship were −5.813 % and 3.321 %, respectively. Using mixing rules with a binary parameter in the BWR equation, the average relative deviation was 0.231 % for the bubble point pressures of the two binaries.

1. Introduction

Dimethyl ether (DME) is directly/indirectly synthesized from syngas in industry[1]~[3], and is a potential alternative or supplement for liquefied petroleum gas (LPG) because the molecular weight and the saturated vapor pressure are close to those of propane[4]~[7]. We previously reported the phase equilibrium data of dimethyl ether (DME) and mixtures with light hydrocarbons[6],[7]. The P-V-T relationship and saturated vapor pressure were reported for DME[6], and the eight constants of the Benedict-Webb-Rubin (BWR) equation of state[8] were determined using experimental data of the P-V-T relationship. Vapor-liquid equilibrium (VLE) and saturated liquid density have been also reported for binary and ternary mixtures of propane, DME and butane[7]. The BWR equation provided excellent predictions for the saturated vapor pressure and VLE.

The Helmholtz type equation of state, REFPROP, has been widely used for the prediction of the physical properties of refrigerants and light hydrocarbons. However, the validity of REFPROP is now under investigation for the VLE of multicomponent systems. Cubic equations of state, such as the Soave-Redlich-Kwong (SRK)[9] and Peng-Robinson (PR)[10] equations, have been widely used in process simulators for VLE prediction. However, these equations do not always provide good reproducibility for the volume properties of both the liquids and the high pressure vapors. Predictions using the BWR equation are not better that those using the REFPROP, but better reproducibility can be expected than by using cubic equations. Otherwise, the BWR equation shows reproducibility equal to that of cubic equations for the VLE of light hydrocarbon mixtures.

Recently various alkynes, alkenes and alkadienes were proposed as new types of sulfur-free odorants for LPG[11],[12]. Of those, 1-pentyne is one of the most likely sulfur-free odorants. Therefore, a previous study[13] measured the bubble point for propane–1-pentyne and

Table 1 Chemical Reagents Used in This Study

	CAS No.	Supplier	Grade	Molecular weight M_w [-]	Purity
Propane	74-98-6	Takachiho Chemical Industrial Co., Ltd., Japan	Research	44.10	99.9 vol%[a]
DME	115-10-6	Mitsubishi Gas Chemical Co., Inc., Japan	Propellant use	46.07	99.9 vol%[b]
Pentane	109-66-0	Wako Pure Chemical Industries, Ltd., Japan	Special	72.15	98 mass%[a]
1-Pentyne	627-19-0	Sigma-Aldrich, U. S.		68.12	99 mass%[a]

a) Stated by supplier. b) Analyzed by supplier.

Table 2 Devices for Temperature, Pressure Measurements, Constant Temperature Baths and Their Experimental Temperature Ranges

Thermometer [a]	Pressure sensor	Constant temperature bath	
		TRL-101FEZ	T-305
	Saturated vapor pressure		
D641	PHS-2KA [b]	273.15-313.44	
F250 MkII	PHS-50KA [c]		331.66-463.58
	P-V-T relationship		
F250 MkII	PHS-50KA [c]		485.00
	Bubble point pressure		
D641	PG-10KU [d], PG-100KU [e]	303.15, 313.15	

a) $u(T) = 0.05$ K.   b) $u(p) = 0.50$ kPa.   c) $u(p) = 6.0$ kPa.   d) $u(p) = 2.5$ kPa.
e) $u(p) = 15.0$ kPa.

four other binaries with propane at 303.15 K. However, the correlation was carried out only using the PR equation. The present study measured saturated vapor pressure for 1-pentyne at 273.15-463.58 K. The P-V-T relationship was measured in the pressure range 3.2660-4.0919 MPa at 485.00 K, and the bubble point pressure for the two binaries propane–1-pentyne and DME–1-pentyne at 303.15 K and 313.15 K. By applying the corresponding state theory, the eight constants of the BWR equation were determined for 1-pentyne. The validity of the BWR equation was investigated using the bubble point pressure data of the two binaries.

2. Experimental Section

2. 1. Materials

Table 1 lists the chemicals used in this study. Pentane was used as a standard/reference to validate the saturated vapor pressure and P-V-T relationship measurements. All chemicals were used without further purifications.

2. 2. Measurement of Saturated Vapor Pressure for Pentane and 1-Pentyne

The previous study measured the saturated vapor pressure for 1-pentyne only at 303.15 K and 313.51 K[13]. Confirmation of the validity of the BWR equation preferably requires data over a wide range of temperatures. Therefore, the saturated vapor pressure was measured for 1-pentyne in the range of 273.15-463.04 K. Saturated vapor pressure was also measured for pentane in the range of 273.15-463.58 K to validate the reliability of the experimental data. Two apparatus were em-

ployed for the saturated vapor pressure measurements, both based on a static method for low temperature range (273.15-313.44) K, and high temperature range (331.66-463.58) K. **Table 2** lists the equipment used for the temperature and pressure measurements, as well as the constant temperature baths.

Figure 1 shows a schematic diagram of the static apparatus used in the low temperature range. The equipment was described in the previous study[13]. The cell was made of Pyrex glass with inner volume of about 37 cm³, and maximum safe pressure up to 4.5 MPa. The cell incorporated a magnetic stirrer bar. The valve was connected to the glass with a specially designed assemblies[13]. The cell was previous used for saturated vapor and bubble point pressure measurements[6),13)~18]. Pentane or 1-pentyne liquid was loaded into the cell, and the valve was closed. The cell was heated in the hot water bath up to 333 K. The pressure was increased up to about 200 kPa, and then the valve was opened to expel the air remaining in the cell. After confirming the boiling condition, the valve was closed again. This procedure removed dissolved air from the liquid sample together with the saturated vapor. The cell (part 4 in **Fig. 1**) was set in a constant temperature bath (part 3, TRL-101FEZ, Thomas Kagaku Co., Ltd., Tokyo). The apparatus was equipped with two sensors. Generally, the pressure sensor with large capacity should be closest to the cell. Therefore, part 8 was a pressure gauge (PG-10KU, Kyowa Electronic Instruments Co., Ltd., Tokyo) with capacity of 1 MPa, and part 9 was the absolute pressure sensor (PHS-2KA, Kyowa Electronic Instruments Co.,
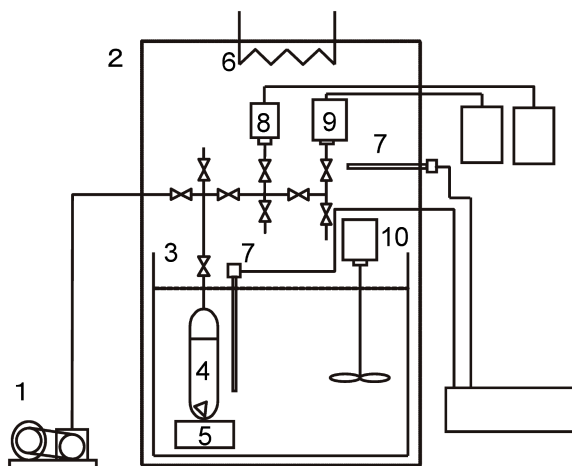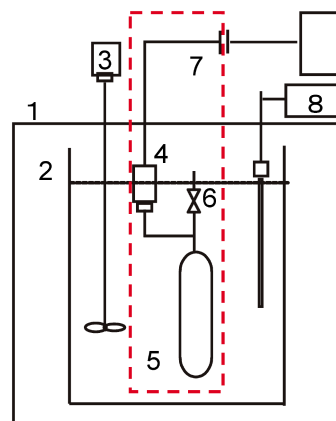
1: vacuum pump; 2: air chamber; 3: constant temperature bath; 4: glass cell; 5: water-proof magnetic stirrer; 6: heater; 7: thermistor thermometer; 8: pressure sensor (large capacity); 9: pressure sensor (small capacity); 10: agitator.

Fig. 1 Static Apparatus for Saturated Vapor Pressure at 273.11-313.44 K and Bubble Point Pressure Measurement at 303.15 K and 313.15 K

1: air chamber; 2: constant temperature bath; 3: agitator; 4: absolute pressure sensor; 5: high pressure cell; 6: sample inlet valve 7: cable connector; 8: Pt resistance thermometer

Fig. 2 Static Apparatus for Measurement of Saturated Vapor Pressure at 331.66-463.58 K and P-V-T Relationship at 485.00 K

Ltd., Tokyo) with a capacity of 200 kPa. Only the latter was used for the saturated vapor measurements. The temperature was measured with a thermistor thermometer (part 7, D641, Technoseven Co., Ltd., Yokohama, Japan). The uncertainties for the pressure and temperature measurements were $u(p) = 0.50$ kPa and $u(T) = 0.05$ K, respectively.

Figure 2 shows a schematic diagram of the static apparatus used for the high temperature range. The cell consisted of a double-ended sample cylinder (304-HDF-2-40, Swagelok, Solon, U. S.) made of stainless steel 304 with inner volume of about 40 cm^3, and safe pressure up to 12.4 MPa. The liquid sample was prepared in the cell by the same procedure as that at 273.15-313.44 K. The cell (part 5 in **Fig. 2**) was then placed in the bath (part 2, T-305, Thomas Kagaku Co., Ltd., Tokyo) filled with silicone oil (TSF433, GE Tohshiba Co., Ltd., Tokyo). The experimental temperature and pressure were measured by a platinum resistance thermometer (part 8, F250 MK II, ASL, Cambridge, U. K.) and an absolute pressure sensor (part 4, PHS-50KA, Kyowa Electronic Instruments Co., Ltd., Tokyo), respectively. The capacity of the pressure sensor was up to 5 MPa. As shown in **Fig. 2**, the cell and the pressure sensor were soaked in silicone oil to avoid condensation of sample gas in the tubing. This method seems to cause some problems in the pressure sensor, but nothing actually occurred as described in the previous study[6]. No facilities to agitate the sample solution were included, so the cell and the pressure sensor were sometimes shaken in the bath. The uncertainties for the pressure and temperature measurement

were $u(p) = 6.0$ kPa and $u(T) = 0.05$ K, respectively.

2. 3. Measurement of P-V-T Relationship for Pentane and 1-Pentyne

Figure 2 shows the apparatus for establishing the P-V-T relationships for pentane and 1-pentyne at 485.00 K. **Table 2** also lists the devices and the bath for the measurements. The apparatus was the same as that for saturated vapor pressure measurements at 331.66-463.58 K, but used a different cell. The cell consisted of a single-ended sample cylinder (SS-4CS-TW-50, Swagelok, Solon, U. S.) with volume of 50 cm^3. The cell was directly connected to the valve by Swagelok assemblies. The inner volume of the cell must be calibrated for measurement of the P-V-T relationship. Details will be described later, but the inner volume was calibrated with pentane using standard data provided by the National Institute of Standards and Technology (NIST)[19]. The procedure of measurements was also different from those for the saturated vapor pressure. The sample amount was accurately measured as follows. After loading of the sample liquid, the cell was heated up to 333 K. The procedure was the same as that for the saturated vapor pressure measurements. The weight of the cell (part 5), together with the pressure sensor and its cable, was measured by a direct-reading balance (AV 1581, Exact Co., Kamagaya, Japan). The weighed part is indicated as the inside of the dotted line in **Fig. 2**. The maximum capacity and sensitivity of the balance were 1 kg and 0.1 mg, respectively. After weighing the cell assembly, the cell was set in the constant temperature bath (part 6). After equilibrium was confirmed, the pressure and the temperature were measured by the platinum resistance thermometer (part 8) and the absolute pressure sensor (part 4), respectively. The uncertain-

Table 3 Saturated Vapor Pressure of Pentane

Measured		NIST standard data[19]		Antoine equation		BWR equation[8),22)]	
Temperature [a] T [K]	Pressure p^s [kPa]	Pressure p^s [kPa]	RD δp^s [%]	Pressure p^s [kPa]	RD δp^s [%]	Pressure p^s [kPa]	RD δp^s [%]
273.15	24.67[b]	24.45	0.908	27.22	10.35	20.12	−18.46
283.14	37.84[b]	37.82	0.056	40.89	8.066	33.11	−12.51
293.15	56.59[b]	56.56	0.057	59.76	5.593	51.76	−8.539
303.15	81.92[b]	81.99	−0.089	85.09	3.874	77.41	−5.508
313.44	115.36[b]	116.78	−1.216	119.53	3.613	112.70	−2.302
331.66	206.8[c]	205.5	0.638	207.0	0.092	202.7	−1.970
345.63	304.5[c]	302.9	0.532	303.1	−0.476	301.1	−1.124
357.71	412.4[c]	412.3	0.015	411.2	−0.280	410.9	−0.358
365.73	498.0[c]	499.9	−0.378	498.0	−0.003	498.4	0.072
375.80	624.6[c]	628.7	−0.654	625.9	0.203	626.4	0.292
392.70	901.1[c]	898.5	0.287	894.3	−0.754	893.0	−0.895
419.76	1513.9[c]	1498.7	1.014	1490.6	−1.541	1481.5	−2.139
437.57	1985.2[c]	2032.0	−2.303	2014.8	1.489	2002.3	0.860
448.63	2392.0[c]	2430.2	−1.572	2400.0	0.333	2391.1	−0.038
463.58	3012.4[c]	3067.8	−1.806	2999.7	−0.421	3015.4	0.101
		average	−0.301	average	2.010	average	−3.501

a) $u(T) = 0.05$ K.   b) $u(p) = 0.50$ kPa.   c) $u(p) = 6.0$ kPa.

ties for the pressure and temperature measurements were $u(p) = 6.0$ kPa and $u(T) = 0.05$ K, respectively. The uncertainty for the weight was estimated to be $u(w) = 20.0$ mg.

2. 4. Measurement of Bubble Point Pressure for Propane–1-pentyne and DME–1-pentyne

Bubble point pressures were measured for the two binaries, propane–1-pentyne and DME–1-pentyne at 303.15 K and 313.15 K. **Table 2** also lists the equipment used for the measurements.

Figure 1 shows the schematic diagram of the apparatus for bubble point pressure measurement at 303.15 K and 313.15 K. The apparatus was the same as that for saturated vapor pressure measurement at 273.15-313.44 K, except that the absolute pressure sensor, PHS-2KA, was exchanged for the pressure gauge, PG-10KU, Kyowa Electronic Instruments Co., Ltd., Tokyo (part 9) and the other pressure gauge, PG-100KU, Kyowa Electronic Instruments Co., Ltd., Tokyo, was connected to the tubing (part 4). Therefore, the pressure gauge, PG-10 KU was mainly used for the measurements. Only pressures higher than 1 MPa were measured with PG-100KU. The cell was also the same as that for the saturated vapor pressure measurements at 273.15-313.44 K. The sample preparation procedure has been already reported[13]. Propane or DME was loaded into the cell from the gas cylinder. Then, the cell was cooled with methanol with added dry ice. The weight of the cell after loading was measured with the direct reading balance, AV1581. Subsequently, 1-pentyne was loaded into the cell through a HPLC pump (PU713, GL Sciences Inc., Tokyo). The weight was measured again to determine the overall mole fraction. The cell was placed in a constant temperature bath. The mole fraction in the liquid phase was as-sumed to be the overall mole fraction because the density of the vapor was far lower than that of the liquid phase. The temperature and pressure were measured with the pressure gauge and the thermistor thermometer, respectively. Uncertainties for the pressure measurement were $u(p) = 2.5$ kPa and 15.0 kPa for the PG-10KU and the PG-100KU, respectively. Uncertainties for the temperature and mole fraction were $u(T) = 0.05$ K and $u(x_1) = 0.0004$, respectively.

## 3. Experimental Results

3. 1. Saturated Vapor Pressure for Pentane and 1-Pentyne

The saturated vapor pressure was measured for pentane to confirm the reliability of the experimental data, **Table 3** lists the experimental data, and **Fig. 3** compares the experimental data and its standard values provided by NIST[19]. The standard values are also listed in **Table 3**. Previously reported values[13] are also shown in **Fig. 3**. **Table 4** lists the critical point by Yaws[20], as also shown in **Fig. 3**. Two different apparatus were employed for the measurements in different temperature ranges, but the experimental data agreed well with the NIST data. **Table 3** and **Fig. 4** show the relative deviation (RD) from the standard values. The RDs were calculated by:

$$\delta p^s = \frac{p^s - p^s_{exp}}{p^s_{exp}} \times 100 \qquad (1)$$

The average RD was −0.301 % over the whole range of experimental temperature, and was regarded as an indicator for the reliability of the saturated vapor pressure data.

Table 5 lists the experimental data of saturated vapor
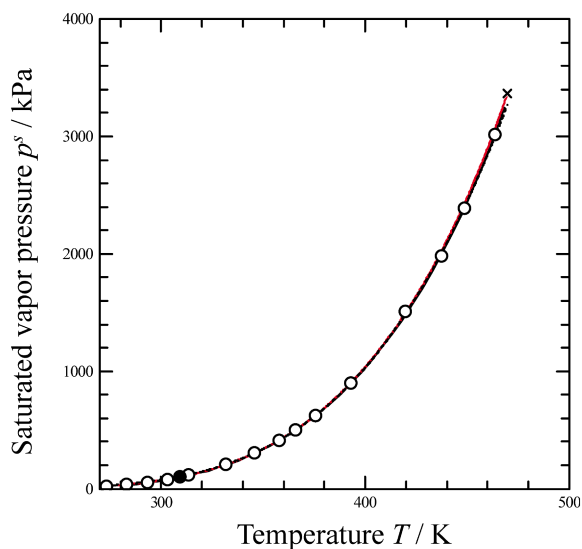
(○): this study; (●): Tsuji *et al.*[13]; (✕): critical point[20]; (—·—): NIST standard data[19]; (- - -): Antoine equation; (——): BWR equation.

Fig. 3 Saturated Vapor Pressure of Pentane

Table 4 Critical Properties for Butane, Pentane and 1-Pentyne

|	Critical temperature T_c [K]	Critical pressure p_c [MPa]	Acentric factor ω [-]
Butane	425.16[a]	3.796[a]	0.199[b]
Pentane	469.65[a]	3.369[a]	0.251[b]
1-Pentyne	476.35	3.550	0.267

a) Yaws[20]. b) Reid *et al.*[23].

pressure of 1-pentyne, and **Fig. 5** compares the experimental data in this and the previous study[13]. The two values, 62.9 kPa and 101.09 kPa, were reported using the same apparatus at 303.15 K, and by an ebulliometer at 313.51 K, respectively[13]. The saturated vapor pressure of 1-pentyne showed similar trends to that of pentane as shown in **Fig. 5**. Otherwise, careful examination of the data in **Tables 3** and **5** found the volatilities were slightly smaller than those of pentane.

3. 2. P-V-T Relationship for Pentane and 1-Pentyne at 485. 00 K

The cell was newly prepared for the measurements of P-V-T relationship, so its inner volume must be calibrated before starting the measurements. In this study, the inner volume was determined from the pressure and the loading weights of pentane. **Table 6** lists the loading weight of pentane, *w*, and the pressure, *p*, in the measurement of P-V-T relationship at 485.00 K. Assuming the absence of any pressure dependence in the inner volume, the compressibility factor, *Z*, is given by:

$$Z = \frac{p}{\rho RT} = \frac{p M_w}{w RT} V \qquad (2)$$

where ρ and M_w are the molar density and molecular
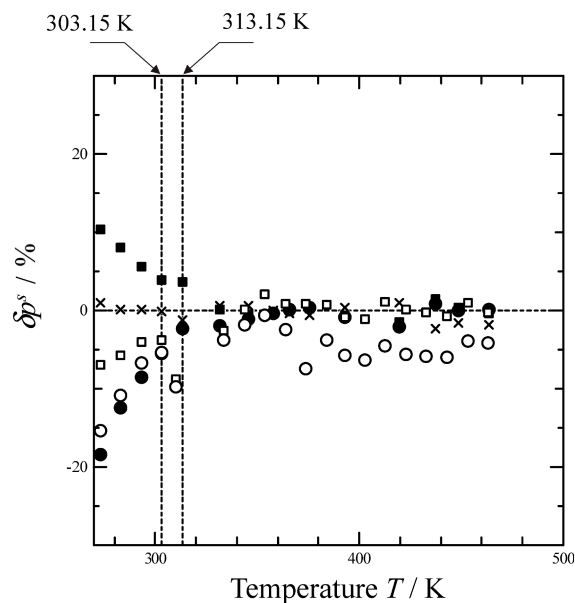
(✕): NIST standard data[19], pentane; (■): Antoine equation, pentane; (●): BWR equation, pentane; (□): Antoine equation, 1-pentyne; (○): BWR equation, 1-pentyne.

Fig. 4 RDs from Experimental Saturated Vapor Pressure Data

weight, respectively. The inner volume, *V*, was determined by fitting with the NIST standard data of the compressibility factor of pentane as listed in **Table 6**[19]. The calibrated inner volume was $V = 49.237$ cm^3. **Table 6** lists the compressibility factors as recalculated using the calibrated inner volume and the experimental data, and the RD for the NIST standard data. The RD for the experimental compressibility factor was evaluated by:

$$\delta Z = \frac{Z - Z_{exp}}{Z_{exp}} \times 100 \qquad (3)$$

Figures 6 and **7** show the compressibility factor and the RDs, respectively. The compressibility factor indicated a slight inflexion point around 3.6 MPa as shown in **Fig. 6**. The compressibility factor became more sensitive in the pressure range higher than the inflexion point. Therefore, the RD rapidly increased. However, in the range lower than 3.850 MPa, the RDs were smaller than 1.720 %. This deviation apparently depended on pressure dependence in the inner volume, but this study made no associated corrections.

Table 7 lists the experimental data of the P-V-T relationship for 1-pentyne using the calibrated volume of the cell at 485.00 K. Considering the uncertainty of the inner volume of the cell, the uncertainty of the compressibility factor was estimated to be $u(Z) = 0.020$. **Figure 8** shows the pressure dependence of the compressibility factor. Only three data points could be obtained through the measurements, which must be finished within three hours, as the pressure seemed to

Table 5 Saturated Vapor Pressure of 1-Pentyne

Measured		Antoine equation		BWR equation[8]	
Temperature [a] T [K]	Pressure p^s [kPa]	Pressure p^s [kPa]	RD δp^s [%]	Pressure p^s [kPa]	RD δp^s [%]
273.15	19.30[b]	17.94	−7.036	16.32	−15.422
283.14	30.74[b]	28.95	−5.807	27.39	−10.893
293.27	47.06[b]	45.16	−4.029	43.87	−6.771
303.15	69.99[b]	67.30	−3.846	66.24	−5.353
310.15	96.10[b]	87.63	−8.813	86.65	−9.831
333.67	198.2[c]	193.2	−2.545	190.6	−3.851
343.63	259.5[c]	259.7	0.081	254.8	−1.804
353.69	336.6[c]	343.3	1.996	334.5	−0.620
363.73	441.8[c]	445.5	0.833	431.1	−2.413
373.75	563.8[c]	568.4	0.818	521.8	−7.456
383.82	710.6[c]	715.4	0.676	683.4	−3.824
392.84	876.9[c]	869.0	−0.907	826.2	−5.784
402.79	1075.9[c]	1064.4	−1.074	1007.8	−6.326
412.75	1275.5[c]	1289.4	1.086	1217.7	−4.536
422.73	1545.0[c]	1546.4	0.091	1458.9	−5.576
432.77	1844.3[c]	1838.9	−0.294	1736.2	−5.864
442.78	2182.9[c]	2166.2	−0.765	2051.1	−6.037
453.11	2520.0[c]	2543.2	0.920	2421.7	−3.902
463.04	2952.0[c]	2944.7	−0.246	2828.3	−4.191
		average	−1.519	average	−5.813

a) $u(T) = 0.05$ K. b) $u(p) = 0.50$ kPa. c) $u(p) = 6.0$ kPa.
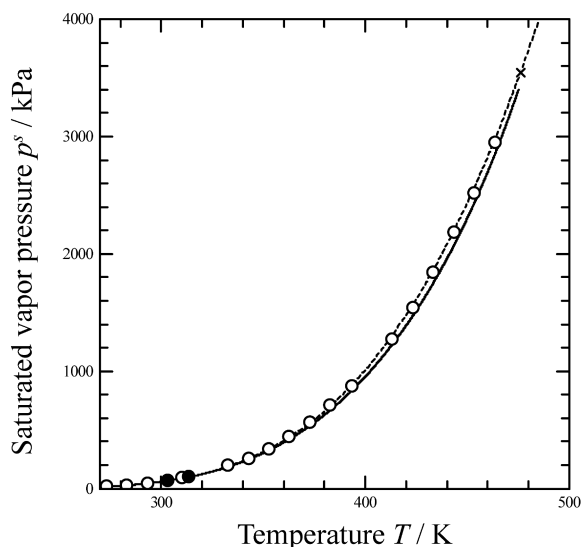
(○): this study; (●): Tsuji et al.[13]; (✕): critical point; (- - -): Antoine equation; (——): BWR equation.

Fig. 5 Saturated Vapor Pressure of 1-Pentyne

gradually decrease after three hours.   The inside of the cell was rinsed with acetone after the measurements. Then, the acetone became slightly yellow, suggesting that dimerization of 1-pentyne had occurred in the cell. The reliability was less than that for pentane, but the data were obtained in the vapor phase.   The experimental temperature, 485.00 K, was thought to be slightly higher than the critical temperature of 1-pentyne. In the previous study[13], the critical temperature was as-

sumed to be 493.39 K to evaluate the two constants in the PR equation[10].   Otherwise, the critical temperature was also reported as 498.40 K[21], and 481.20 K[20]. Considering the experimental data, the actual critical temperature was thought to be close to 481.20 K[20].

3. 3. Bubble Point Pressure for Propane(1)–1-pentyne(2) and DME(1)–1-pentyne(2)

Table 8 lists the experimental data of the bubble point pressure for propane(1)-1-pentyne(2) and DME(1)-1-pentyne(2) at 303.15 K and 313.15 K. **Figure 9** shows the experimental data of the present and the previous study[13].   Data for propane(1)-1-pentyne(2) at 303.15 K were measured with the same apparatus, and the findings agreed well.   The bubble point pressures were linearly increased with mole fraction of DME as shown in **Fig. 9**.   The pressure range was extended by about 1.5 times, but a similar linearity was obtained for propane(1)-1-pentyne(2) at 313.15 K. Considering these results, an approximation of the ideal solution was thought to be acceptable for the two binaries.

### 4. Eight Constants of the BWR Equation for 1-Pentyne

The BWR equation of state is given by:

$$p = RT\rho + (B_0 RT - A_0 - \frac{C_0}{T^2})\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \quad (4)$$

Table 6 Pressure of Gaseous Pentane in Constant Volume Cell at 485.00 K

| Measured			NIST standard data[19]		BWR equation[8),22)]	
Loading mass[a] $w \times 10^3$ [kg]	Pressure[b] p [MPa]	Compressibility factor[c] Z [-]	Compressibility factor Z [-]	RD δZ [%]	Compressibility factor Z [-]	RD δZ [%]
2.0172	1.8375	0.8025	0.8057	0.401	0.8254	2.854
3.0326	2.4732	0.7185	0.7206	0.292	0.7152	−0.456
3.5836	2.7365	0.6728	0.6806	1.152	0.6728	−0.006
4.4177	3.0761	0.6135	0.6232	1.579	0.6093	−0.680
6.1156	3.5615	0.5131	0.5219	1.720	0.4825	−5.962
7.8560	3.8065	0.4269	0.4543	6.423	0.3654	−14.413
9.4112	3.9513	0.3699	0.4047	9.407	0.2878	−22.199
10.3531	4.0187	0.3420	0.3790	10.807	0.2679	−21.663
10.4887	4.0334	0.3388	0.3732	10.158	0.2645	−21.921
			average	4.660	average	−9.383

a) $u(w) = 20.0$ mg. b) $u(T) = 0.05$ K, $u(p) = 6.0$ kPa. c) Calculated with $V = 49.237$ cm³.
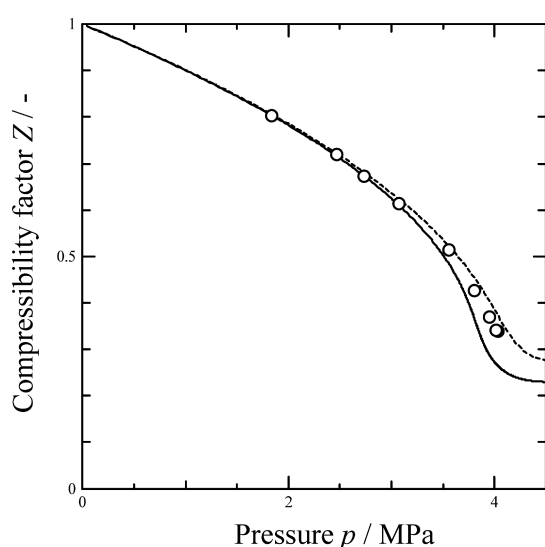
(○): this study; (- - -): NIST standard data table[19]; (——): BWR equation.

Fig. 6 Compressibility Factor of Pentane at 485.00 K
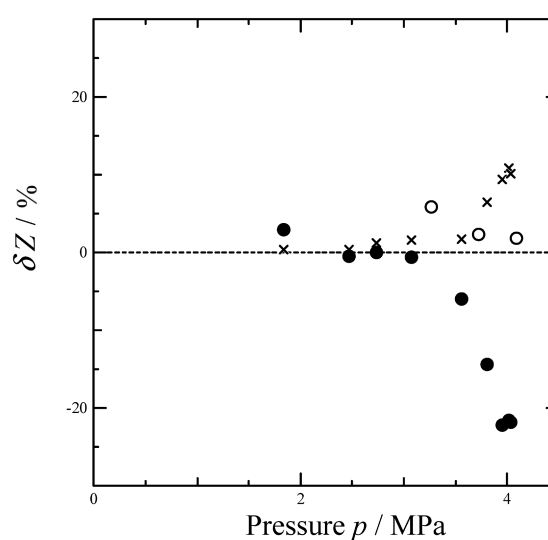
(✕): NIST data table[19], pentane; (●): BWR equation, pentane; (○): BWR equation, 1-pentyne.

Fig. 7 RDs from Experimental Compressibility Factor Data

Table 7 P-V-T Relationship for 1-Pentyne at 485.00 K

Measured		BWR equation[8]	
Pressure[a] p [MPa]	Compressibility factor[b] Z [-]	Compressibility factor Z [-]	RD δZ [%]
3.2660	0.5328	0.5638	5.818
3.7268	0.3976	0.4067	2.289
4.0919	0.2531	0.2578	1.857
		average	3.321

a) $u(T) = 0.05$ K, $u(p) = 6.0$ kPa. b) $u(Z) = 0.020$.

where the eight constants, A_0, B_0, C_0, a, b, c, α and γ, were previously reported for light hydrocarbons[22] and for DME in the previous study[6]. **Table 9** lists the constants for propane, butane, pentane and DME[6),22)]. **Figures 6** and **7** show the calculation results of the compressibility factor for pentane at 485.00 K and its RDs, respectively. The calculation for pentane is also listed in **Table 6**. The calculation agreed well with the experimental data despite some discrepancies at pressures higher than 3.5615 MPa. Discrepancies were also observed even for the NIST standard data[19], so were thought to originate in the function form of the BWR equation[8] or the literature constants[22]. Otherwise, the eight constants for 1-pentyne had not been reported. Therefore, these constants were determined by a method based on corresponding state theory and the saturated vapor pressure data for 1-pentyne. The corresponding state theory was partly the same as that adopted in the previous report[6]. Applying the corresponding state theory, Eq. (4) is converted to the following non-dimensional form[22]:

$$p_r = \frac{T_r}{v_r} + \left(B_{0r}T_r - A_{0r} - \frac{C_{0r}}{T_r^2}\right)\frac{1}{v_r^2}$$
$$+ (b_r T_r - a_r)\frac{1}{v_r^3} + \frac{a_r\alpha_r}{v_r^6} \tag{5}$$
$$+ \frac{c_r}{T_r^2 v_r^3}\left(1 + \frac{\gamma_r}{v_r^2}\right)\exp\left(-\frac{\gamma_r}{v_r^2}\right)$$

where P_r, T_r and v_r are the reduced properties using the critical temperature and the critical pressure:

$$p_r = \frac{p}{p_c} \tag{6}$$

$$T_r = \frac{T}{T_c} \tag{7}$$

$$v_r = \frac{p_c}{\rho R T_c} \tag{8}$$

Comparing with Eq. (4), the non-dimensional constants in Eq. (5) are given by:

$$A_{0r} = A_0\frac{p_c}{R^2 T_c^2} \tag{9}$$

$$B_{0r} = B_0\frac{p_c}{R T_c} \tag{10}$$
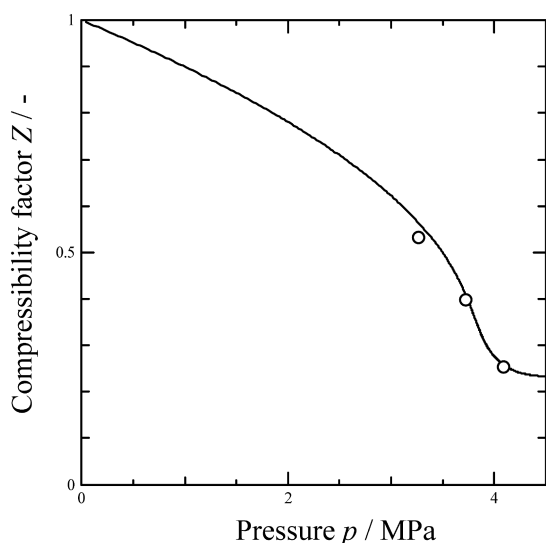
$$C_{0r} = C_0\frac{p_c}{R^2 T_c^4} \tag{11}$$

$$a_r = a\frac{p_c^2}{R^3 T_c^3} \tag{12}$$

$$b_r = b\frac{p_c^2}{R^2 T_c^2} \tag{13}$$

$$c_r = c\frac{p_c^2}{R^3 T_c^5} \tag{14}$$

$$\alpha_r = \alpha\frac{p_c^3}{R^3 T_c^3} \tag{15}$$

$$\gamma_r = \gamma\frac{p_c^2}{R^2 T_c^2} \tag{16}$$

(○): this study; (——): BWR equation.

Fig. 8 Compressibility Factor of 1-Pentyne at 485.00 K

Table 8 Bubble Point Pressure for Propane(1) + 1-Pentyne(2) and DME (1) + 1-Pentyne (2)

Mole fraction [b] x_1 [-]	303. 15 K [a]					313.15 K [a]				
	Measured	BWR equation [d), 8]				Measured	BWR equation [e), 8]			
	Pressure [c] p [kPa]	Mole fraction $x_{1,cal}$ [-]	RD δx_1 [%]	Pressure p_{cal} [kPa]	RD δp [%]	Pressure [c] p [kPa]	Mole fraction $x_{1,cal}$ [-]	RD δx_1 [%]	Pressure p_{cal} [kPa]	RD δp [%]
Propane(1) + 1-pentyne(2)										
0.1963	310.06	0.2012	2.472	304.56	−1.774	389.11	0.2051	4.471	377.17	−3.068
0.2873	405.34	0.2880	0.238	404.61	−0.180	510.41	0.2965	3.213	498.42	−2.349
0.3577	472.87	0.3530	−1.326	477.68	1.017	592.80	0.3611	0.961	588.48	−0.729
0.5100	617.43	0.5024	−1.489	624.44	1.135	774.92	0.5112	0.231	773.53	−0.179
0.6879	770.52	0.6735	−2.093	783.18	1.643	970.68	0.6802	−1.114	979.52	0.910
0.8366	904.72	0.8234	−1.582	917.10	1.368	1142.1 [f]	0.8254	−1.344	1155.99	1.216
		average	−0.623	average	0.535		average	1.070	average	−0.700
DME(1) + 1-pentyne(2)										
0.2859	219.4	0.2725	−4.704	227.31	3.606	288.91	0.2720	−4.855	299.27	3.587
0.4429	321.15	0.4415	−0.326	322.04	0.277	412.21	0.4327	−2.301	420.29	1.961
0.5461	385.23	0.5439	−0.399	386.61	0.358	501.92	0.5441	−0.372	503.60	0.334
0.6249	443.45	0.6347	1.576	437.08	−1.438	570.42	0.6264	0.243	569.14	−0.224
0.7763	545.93	0.7900	1.765	536.74	−1.684	704.57	0.7819	0.716	699.66	−0.696
		average	−0.418	average	0.224		average	−1.312	average	0.992

a) $u(T) = 0.05$ K.   b) $u(x_1) = 0.004$.   c) $u(p) = 2.5$ kPa (except for f).   d) Constants by Cooper and Goldfrank[22] for propene.
e) Constants by Tsuji et al.[6] for DME.   f) $u(p) = 15.0$ kPa.
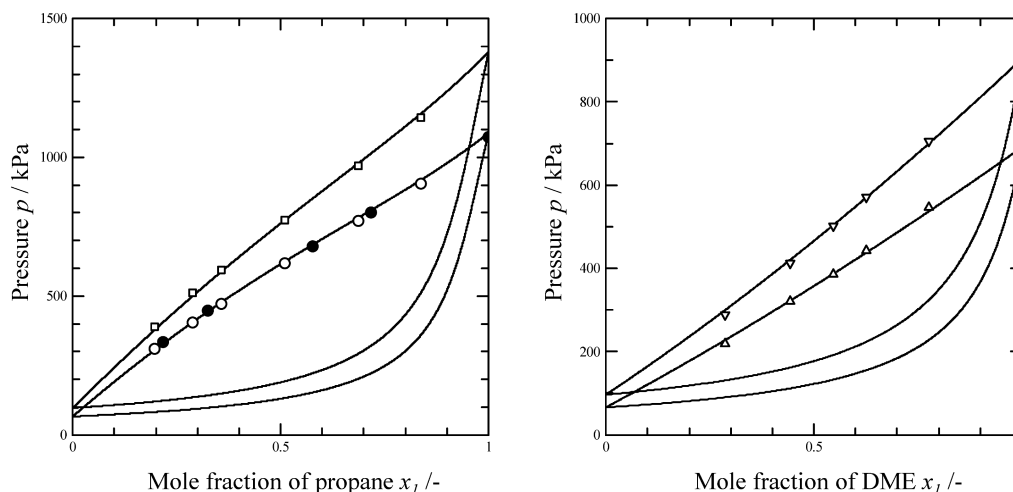
(○): this study, propane–1-pentyne at 303.15 K; (●): Tsuji et al.[13], propane–1-pentyne at 303.15 K; (□): this study, propane–1-pentyne at 313.15 K; (△): this study, DME–1-pentyne at 303.15 K; (▽): this study, DME–1-pentyne at 313.15 K.

Fig. 9   Bubble Point Pressure for Propane(1)–1-pentyne(2) and DME (1)–1-pentyne(2) at 303.15 K and 313.15 K

Table 9   Constants in BWR Equation[8]

	Propane [a]	Butane [a]	Pentane [a]	DME [b]	1-Pentyne
$A_0 \times 10^1$	6.96263	10.2173	12.3386	6.56761	11.5514
$B_0 \times 10^5$	9.730826	12.43549	15.67372	8.49172	15.16243
$C_0 \times 10^{-4}$	5.14940	10.0589	21.4894	5.715362	23.0121
$a \times 10^5$	9.59407	19.0697	41.2770	8.249236	41.3571
$b \times 10^8$	2.249781	3.999440	6.680028	1.826113	6.340970
$c \times 10^{-1}$	1.30690	3.20545	8.34870	1.26141	8.57595
$\alpha \times 10^{13}$	6.07068	11.0116	18.0953	3.491735	15.3408
$\gamma \times 10^8$	2.19979	3.3997	4.7492	1.60754	4.2645

a) Cooper and Goldfrank[22], original constants are in units, L, atm, mol and K.   b) Tsuji et al.[6].

Table 10   Constants in Antoine Equation

	Constants in Antoine equation		
	A_{ps} [-]	B_{ps} [K]	C_{ps} [K]
Pentane	6.35050	1317.12	−5.20
1-Pentyne	6.03103	1049.16	−53.53

In this study, the following Lee-Keslar equation was adopted for the eight non-dimensional constants:

$$Q_r = \frac{Q_{r,R1} - Q_{r,R2}}{\omega_{R1} - \omega_{R2}}(\omega - \omega_{R2}) + Q_{r,R2} \qquad (17)$$

where ω_{R1} and ω_{R2} are the acentric factors for the reference compounds.   In this study, butane and pentane was selected as the reference compounds.   **Table 9** lists the eight constants of the BWR equation for butane and pentane.   The critical temperature, critical pressure[20] and acentric factor[23] for pentane are also listed in **Table 4**.   However, values for 1-pentyne have not been published.   Therefore, these constants were evaluated as follows:
The critical temperature and the critical pressure

should occur at the end point of the saturated vapor pressure.   Therefore, the saturated vapor pressure data were correlated with the following Antoine equation:

$$\log_{10} p^s \text{ [kPa]} = A_{ps} - \frac{B_{ps}}{T \text{ [K]} + C_{ps}} \qquad (18)$$

Table 10 lists the three constants, A_{ps}, B_{ps}, and C_{ps}, fitted with the experimental data for 1-pentyne. **Table 10** also shows the three constants as determined for pentane.   The correlations for pentane and 1-pentyne are shown in **Figs. 3** and **5**, respectively.   In **Fig. 3**, the upper end of the saturated vapor pressure was set to 3269.2 kPa, which was calculated from the reported critical temperature of 469.65 K for pentane[20]. The calculated pressure was slightly smaller than the reported value of 3.369 MPa[20].   On the other hand, the upper point could not be decided for 1-pentyne because the critical point was not clarified.   Therefore, the highest experimental pressure data were extrapolated as shown in **Fig. 5**.   Determination of the critical point is described later.   The RDs for the Antoine equation are shown in **Fig. 4**, and are summarized in **Tables 3** and **5**.   Similar results were obtained in **Figs. 3** and **5**.

Otherwise, the absolute values of RD rapidly increased at temperatures lower than 313.44 K for pentane and 333.67 K for 1-pentyne. The average RDs were 2.010 % and -1.510 % for pentane and 1-pentyne, respectively. The critical temperature and the critical pressure for pentane were found using the extrapolation of Eq. (18) as shown in **Fig. 3**. Therefore, the following relationship was assumed between the critical temperature and the critical pressure for 1-pentyne:

$$\log_{10} p_c \text{ [kPa]} = A_{ps} - \frac{B_{ps}}{T_c \text{ [K]} + C_{ps}} \qquad (19)$$

Otherwise, the acentric factor is defined by[23]:

$$\omega = -\log_{10} \left. \frac{p^s}{p_c} \right|_{T/T_c=0.7} - 1.000 \qquad (20)$$

where the antilogarithm can be evaluated from Eqs. (18) and (19).

In this study, the critical temperature was assumed for 1-pentyne. The critical pressure and the acentric factor were calculated from Eqs. (18)-(20). Then, the eight non-dimensional constants of the BWR equation were evaluated by Eq. (17), and converted to the eight constants of the original BWR equation by Eqs. (9)-(16). The procedure was repeated until the calculated compressibility factors agreed with the experimental data for 1-pentyne. The finally determined critical temperature, critical pressure and acentric factor for 1-pentyne are listed in **Table 4**. The evaluated critical temperature of 1-pentyne was 476.35 K. Comparing with the three previous studies[13),20),21)], the temperature was close to one of the reported values, 481.20 K[20)]. The eight constants of the BWR equation are listed in **Table 9**. The calculated compressibility factor for 1-pentyne is shown in **Fig. 8**. The RDs are shown in **Fig. 7**. The values are also summarized in **Table 7**. Compared with the calculation for pentane, the RDs tended to decrease in the pressure range higher than 3 MPa. Some refinement of these values will be possible by using the data in a wide range of temperature and pressure, but will not be discussed here.

5. Prediction of the Saturated Vapor Pressure and the Bubble Point Pressure Using the BWR Equation

5. 1. Prediction of Saturated Vapor Pressure

Prediction of the saturated vapor pressure using the BWR equation for 1-pentyne is shown in **Fig. 5**, and that for pentane is also shown in **Fig. 3** together with the calculation by the Antoine equation. The RDs are shown in **Fig. 4**. Values are summarized in **Tables 3** and **5**. The average RD for 1-pentyne was -5.813 %, worse than that for pentane, -3.501 %, because of the slightly poor prediction in the high temperature range for 1-pentyne. The eight constants of the BWR equa-

tion were estimated from those for butane and pentane using the Lee-Keslar equation with the critical point and the acentric factor assumed from the Antoine equation and its extrapolation. The constants were verified only using the P-V-T relationship data at 485.00 K. The constants were determined from limited experimental data, but the BWR equation predicted the physical properties in a wide temperature range for 1-pentyne with some reproducibility. The predictions had negative RDs for the saturated vapor pressure as shown in **Figs. 4** and **5**, and **Table 5**, but positive RDs for the compressibility factor as shown in **Figs. 7** and **8**, and **Table 7**. These results were thought to originate in an imperfection of the function form of the BWR equation. In other words, the eight constants were fitted with the compressibility factor data in the vapor phase, and the saturated vapor pressure was calculated from the fugacities in the liquid and vapor phase. **Figure 4** indicates the experimental temperatures for the bubble point pressure measurements, 303.15 K and 313.15 K. The RDs were estimated to be around -5 % for the saturated pressure of 1-pentyne at the two experimental temperatures.

5. 2. Correlation of Saturated Vapor Pressure for Propane(1)–1-pnetyne(2) and DME(1)–1-pentyne(2)

The eight constants for propane have been previously reported[22)], and widely used in research and industry. The eight constants for DME and 1-pentyne were determined in the previous[6)] and this study. The correlations were carried out to investigate the validities for DME and 1-pentyne. Calculation for binaries used the Stotler-Benedict type mixing rule[24)]:

$$A_0 = \sum_i \sum_j x_i x_j m_{ij} \left(A_{0i} A_{0j} \right)^{1/2} \qquad (21)$$

$$B_0 = \sum_i \sum_j x_i x_j \frac{B_{0i} + B_{0j}}{2} \qquad (22)$$

$$C_0 = \sum_i \sum_j x_i x_j \left(C_{0i} C_{0j} \right)^{1/2} \qquad (23)$$

$$a = \left(\sum_i x_i a_i^{1/3} \right)^3 \qquad (24)$$

$$b = \left(\sum_i x_i b_i^{1/3} \right)^3 \qquad (25)$$

$$c = \left(\sum_i x_i c_i^{1/3} \right)^3 \qquad (26)$$

$$\alpha = \left(\sum_i x_i \alpha_i^{1/3} \right)^3 \qquad (27)$$

$$\gamma = \left(\sum_i x_i \gamma_i^{1/2} \right)^2 \qquad (28)$$

Table 11 Binary Interaction Parameters for BWR Equation

	Binary interaction parameter m_{ij} [-]	
	303.15 K	313.15 K
Propane (1)–1-Pentyne(2)	0.942	0.950
DME (1)–1-Pentyne(2)	1.009	1.012

where m_{ij} is a binary interaction parameter. In this study, the binary parameters were determined from the experimental data of the bubble point pressure. The correlations for the binaries propane(1)-1-pentyne(2) and DME(1)-1-pentyne(2) are shown in **Fig. 9**. **Table 11** lists the binary interaction parameters fitted with the experimental data. The RDs for the mole fraction and the pressure were calculated as follows:

$$\delta x_1 = \frac{x_1 - x_{1,\exp}}{x_{1,\exp}} \times 100 \quad (29)$$

$$\delta p = \frac{p - p_{\exp}}{p_{\exp}} \times 100 \quad (30)$$

The RDs for the mole fraction, δx_1, and the pressure, δp, are shown in **Fig. 10** and summarized in **Table 8**. δx_1 was plotted for the reduced pressure, p/p_1^s, in **Fig. 10**. p_1^s indicates the saturated vapor pressure of propane or DME calculated by the BWR equation. The values of p_1^s for propane were 1087.25 kPa and 1379.66 kPa at 303.15 K and 313.15 K, and for DME were 690.64 kPa and 903.37 kPa at 303.15 K and 313.15 K, respectively. For propane(1)-1-pentyne(2) at 303.15 K, the average RDs of the mole fraction and the pressure were -0.623 % and 0.535 %, respectively. For propane(1)-1-pentyne(2), those values were -0.418 % and 0.224 %. Otherwise, for propane(1)-1-pentyne(2) at 313.15 K, RDs of the mole fraction and the pressure were 1.070 % and -0.700 %, respectively. For DME(1)-1-pentyne(2), those were -1.312 % and 0.992 %. No difference was found between the two binaries at the two experimental temperatures. The smaller RDs than those for the saturated vapor pressure and the P-V-T relationship seems slightly in constituent. The results suggested that the errors were buffered within the binary interaction parameter.

6. Conclusion

The saturated vapor pressure was measured for 1-pentyne, which is a potential sulfur-free odorants for LPG. The measurement was also carried out for pentane, and the results validated by comparing with the NIST standard data. The P-V-T relationship was measured for 1-pentyne at 485.00 K using a constant volume cell, with the inner volume calibrated with pentane at the same temperature. The eight constants of the BWR equation were determined for 1-pentyne using the experimental data of saturated vapor pressure and

Fig. 10 RDs from Experimental Bubble Point Pressure Data
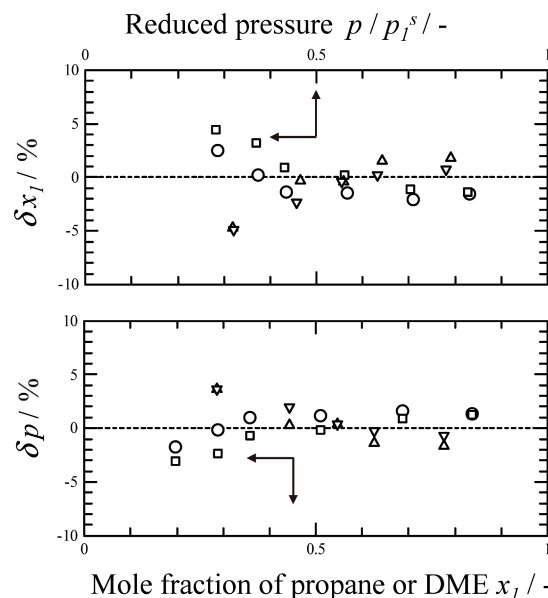
(◯): propane–1-pentyne at 303.15 K; (□): propane–1-pentyne at 313.15 K; (△): DME–1-pentyne at 303.15 K; (▽): DME–1-pentyne at 313.15 K.

P-V-T relationship. The critical temperature and the critical pressure were determined by extrapolation of the saturated vapor pressure, and the acentric factor was also assumed by the definition. Then, the eight constants in the BWR equation can be self-consistently evaluated by fitting the data of the P-V-T relationship. The eight constants, as obtained in this study, provided good reproducibility for experimental bubble point pressure for propane–1-pentyne and DME–1-pentyne. These methods and the data will contribute to develop new sulfur-free odorants for LPG.

Nomenclatures

A_0	: constant in the BWR equation
A_{0r}	: non-dimensional constant in the non-dimensional BWR equation
A_{ps}	: constant in the Antoine equation
a	: constant in the BWR equation
a_r	: non-dimensional constant in the non-dimensional BWR equation
B_0	: constant in the BWR equation
B_{0r}	: non-dimensional constant in the non-dimensional BWR

equation
B_{ps} : constant in the Antoine equation
b : constant in the BWR equation
b_r : non-dimensional constant in the non-dimensional BWR equation
C_0 : constant in the BWR equation
C_{0r} : non-dimensional constant in the non-dimensional BWR equation
C_{ps} : constant in the Antoine equation
c : constant in the BWR equation
c_r : non-dimensional constant in the non-dimensional BWR equation
m_{ij} : Binary interaction parameter for the BWR constant, B_0
p : pressure
p_c : critical pressure
p_r : reduced pressure
p^s : saturated vapor pressure
p_1^s : saturated vapor pressure of propane or DME
δp : relative deviation for pressure
δp^s : relative deviation for saturated vapor pressure
Q_r : generalized non-dimensional constant in the non-dimensional BWR equation
R : gas constant
T : temperature
T_c : critical temperature
T_r : reduced temperature
$u(X)$: uncertainty for physical properties X
V : inner volume of the cell
v_r : reduced molar volume
w : weight of cell
Z : compressibility factor
＜Greeks＞
α : constant in the BWR equation
α_r : non-dimensional constant in the non-dimensional BWR equation
γ : constant in the BWR equation
γ_r : non-dimensional constant in the non-dimensional BWR equation
ρ : density
ω : acentric factor
＜subscripts＞
cal : calculation
exp : experimental datum
R1, R2 : reference 1, 2
1, 2 : component 1, 2

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要　　旨

1- ペンチンに対する BWR 状態方程式の 8 定数の決定とプロパンまたはジメチルエーテルを加えた
2 成分系沸点データによるその妥当性の検討

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ペンタンと 1- ペンチンの飽和蒸気圧を温度 273.15 ～ 463.58 K の間で測定した。また，定容セル内のペンタン質量とその気体圧力から内容積を検定し，1- ペンチンの P-V-T 関係を 485.00 K において測定した。液化石油ガスであるプロパンまたはその代替物であるジメチルエーテルに 1- ペンチンを加えた 2 成分系の 303.15 K および 313.15 K における沸点も調べた。1- ペンチンの飽和蒸気圧から，臨界圧力と偏心因子を臨界温度の関数とした独自の方法と対応状態原理を組み合わせて，1- ペンチンに対する Benedict-Webb-Rubin 状態方程式の 8 定数を定めた。この定数を用いた飽和蒸気圧，P-V-T 関係の推算精度は平均相対偏差がそれぞれ −5.813 ％ および 3.321 ％ であった。2 成分系パラメーターを第 2 ビリアル係数に導入した混合則を適用したところ，沸点圧力の平均相対偏差が 0.231 ％ であった。

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