

Rapid Measurements of Thermodynamic Properties for Alternative Refrigerants with Vibrating-Tube Densimeter¹

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More than 2000 *PVT* data in the liquid phase, vapor phase, and at saturation boundaries have been obtained for pure compounds of several alternative refrigerants. In addition, more than 1000 liquid-density data have been obtained for several binary and ternary mixtures. The alternative refrigerants measured in the present study include CF_3OCH_3 (trifluoromethyl methyl ether) and $\text{CF}_3\text{CF}_2\text{OCH}_3$ (pentafluoroethyl methyl ether), which are hydrofluoroethers developed by RITE (the Research Institute of Innovative Technology for the Earth, Japan), and typical hydrocarbons, such as propane, *n*-butane, isobutene, and their binary and ternary mixtures. The measurement uncertainties are estimated to be 3 to 7 mK for temperature, 0.26 kPa or 0.022% whichever is greater for pressure, and $0.07 \text{ kg} \cdot \text{m}^{-3}$ or 0.024% whichever is greater for density. The present measurement system took only a few minutes to get one *PVT* datum, and one or two days to complete all the measurements for a single fluid at temperatures from 240 to 380 K and at pressures up to 7 MPa. In addition, an empirical equation of state (EoS) for the liquid phase was developed on the basis of the present data, and the EoS nicely reproduces not only the present data but also existing data reported by other researchers.

KEY WORDS: isobutane (R-600a); mixtures; *n*-butane (R-600); pentafluoroethyl methyl ether ($\text{CF}_3\text{CF}_2\text{OCH}_3$); propane (R-290); *PVT* properties; trifluoromethyl methylether (CF_3OCH_3); vibrating-tube densimeter.

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1. INTRODUCTION

The development and study of alternative refrigerants that have not only zero ozone depletion potential (ODP) but also low global warming potential (GWP) are a pressing need. In these circumstances, hydrofluoroethers and natural refrigerants are the substances of major attention. Hydrofluoroethers are new refrigerants developed by RITE (the Research Institute of Innovative Technology for the Earth, Japan). They have low GWP and their COP (coefficient of performance) is expected to be equal to conventional refrigerants, so they are promising as alternative refrigerants. However, because of the very short period to study them, their thermodynamic properties are not yet well known.

Natural refrigerants, such as HCs (hydrocarbons), ammonia, carbon dioxide, etc. are the most earth-friendly substances since they circulate through nature in large quantities and their circulation from generation to disappearance is already established. Not to mention that their ODP is zero, their GWP is also vanishingly small. Among some natural refrigerants with such features, HCs such as propane (R-290), *n*-butane (R-600), and isobutane (R-600a) are the most likely alternative refrigerants. However, very few data for their thermodynamic properties have been measured since the 1950s. Hence, it is considered that experimental and analytical studies for them are needed.

Based on such a situation, the present authors have measured a set of fundamental thermodynamic properties of alternative refrigerant candidates precisely and rapidly by means of an experimental instrument with a vibrating tube, which was originally developed by Kayukawa et al. [1]. The alternative refrigerants measured in the present study include CF_3OCH_3 (trifluoromethyl methyl ether) and $\text{CF}_3\text{CF}_2\text{OCH}_3$ (pentafluoroethyl methyl ether), which are hydrofluoroethers, and typical hydrocarbons, such as R-290, R-600, and R-600a, and their binary and ternary mixtures. For these alternative refrigerant candidates, we have successfully obtained more than 2000 *PVT* property data in the liquid phase, vapor phase, and at saturation boundaries for pure compounds, and more than 1000 data in the liquid phase for several binary and ternary mixtures. These results are introduced in the present paper.

2. A PRINCIPLE OF THE VIBRATING-TUBE DENSIMETER

The principle of a vibrating-tube densimeter involves the phenomenon in which the vibration period of a U-shaped tube changes with the density of the sample fluid enclosed in the tube. A vibrating-tube densimeter measures directly the vibration period, τ , of the U-shaped tube

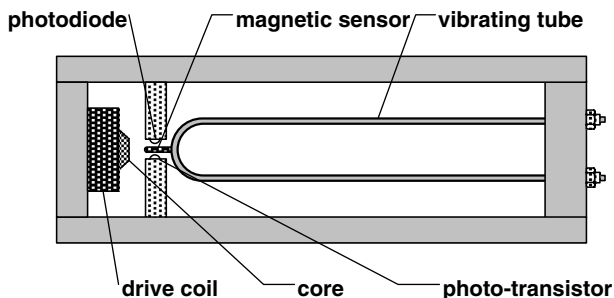


Fig. 1. Schematic diagram of a vibrating tube densimeter.

completely filled with the sample fluid, and then it is used to determine the densities, ρ , of the sample fluid by applying a fixed relation between τ and ρ . A diagram of a vibrating tube densimeter is shown in Fig. 1. When the U-shaped tube, completely filled with the sample fluid, is fixed by its ends as shown in Fig. 1 and is made to vibrate without twists in the direction perpendicular to the plane of the tube, the sample fluid is restrained by the pipe wall and vibrates as one body, so the influence of viscosity is considered to be sufficiently small because the relative displacement of the U-shaped tube is very small. Therefore, the mode of vibration can be regarded as a normal harmonic motion, and its vibration period, τ , is given by

$$\frac{1}{\tau} = \frac{1}{2\pi} \sqrt{k \left(\frac{1}{m} + \frac{1}{M} \right)} \quad (1)$$

$$m = m_0 + \rho V_0 \quad (2)$$

In Eq. (1), m , M , and k represent masses of the vibrating tube and a counter weight, and a spring constant of the vibrating tube, respectively. m is equivalent to the sum of the mass of the empty vibrating tube, m_0 , and fluid inside the tube, ρV_0 (ρ : sample density), as shown in Eq. (2). Then Eq. (1) is rewritten as Eq. (3) by introducing a periodic parameter, x , a proportionality constant, A , and a mass ratio, μ , as defined in the following equations.

$$\rho = A \frac{(1 + \mu)x}{1 - \mu x} \quad (3)$$

$$x = \left(\tau^2 / \tau_0^2 \right) - 1 \quad (4)$$

$$A = m_0 / V_0 \quad (5)$$

$$\mu = m_0/M \quad (6)$$

$$\tau_0 = 2\pi\sqrt{m_0/\{k(\mu + 1)\}} \quad (7)$$

The parameter τ_0 defined in Eq. (7) is equivalent to the vibration period when $\rho = 0$, so that τ_0 is simply obtained by measuring the natural frequency of the evacuated tube. As for the parameters A and μ given in Eqs. (5) and (6), they must be determined by measuring some reference fluids whose densities are well known.

3. MEASUREMENT SYSTEM

Figure 2 shows a schematic of the present *PVT* measurement system. The measurement equipment is roughly divided into a temperature-control measurement system and a pressure–density measurement system.

The pressure–density measurement unit consists of the vibrating-tube densimeter DMA512 [Anton Paar, K.G.] with resolution of 10 ns for the vibration period, which corresponds to about $0.037 \text{ kg} \cdot \text{m}^{-3}$ for density, a quartz pressure transducer with repeatability of 0.01%, and a variable volume vessel with metallic bellows. The pressure and density of the sample are regulated by changing the system inner volume with the variable volume vessel, and then they are measured with the densimeter and the pressure transducer. The sample pressure is directly measured by use of the pressure transducer, which is calibrated with a dead-weight piston gauge with uncertainty of 0.005%, so that the data can be recorded automatically and continuously on a computer. Since the vibration period is also directly measured by the densimeter connected to the computer, the operator can immediately confirm the behavior of the pressure–density ($P\rho$) locus on the computer screen. Just after changing the sample pressure, the sample density steeply changes as well as the sample temperature changes slightly. Then a few minutes later, the operator can confirm on the computer that the density change falls within the resolution of the densimeter, and it means that the temperature is recovered to a target value by the control system described below. The pressure range covers up to 7 MPa, and its uncertainty according to the ISO guideline [2] was estimated as

$$U_P = 0.26 \text{ kPa} + 0.00022P \quad (8)$$

with a coverage factor $k = 2$.

For the temperature-control measurement unit, it is considered that silicone oil which was used as a heat-transfer medium in a thermostatic bath and the sample are in a thermal equilibrium state so that the sample temperature can be measured indirectly by controlling the temperature of

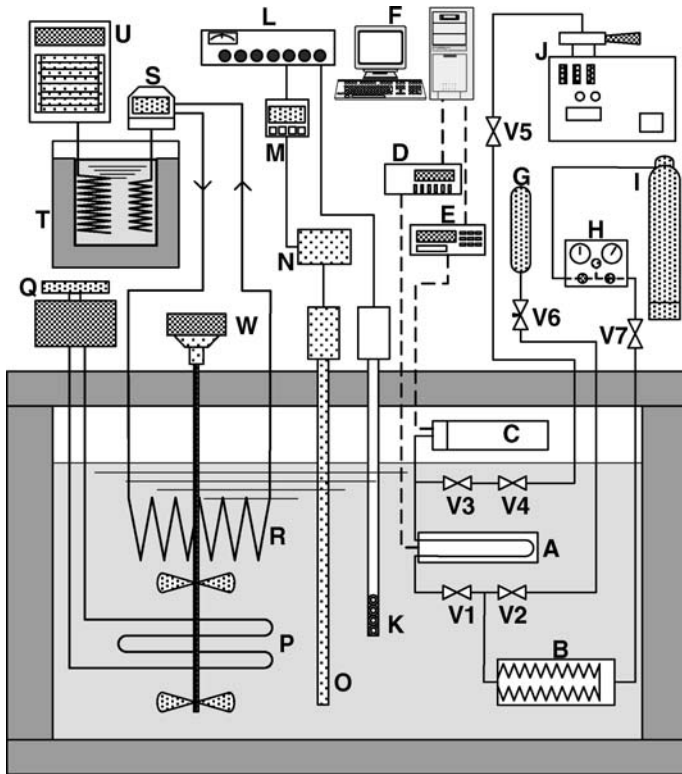


Fig. 2. Schematic diagram of the present experimental apparatus, (A) vibrating-tube densimeter; (B) variable volume vessel with metallic bellows; (C) quartz pressure transducer; (D) frequency counter; (E) pressure computer; (F) computer; (G) sample-supply cylinder; (H) pressure regulator; (I) nitrogen gas bottle; (J) vacuum pump; (K) standard platinum resistance thermometer; (L) thermometer bridge; (M) PID controller; (N) thyristor regulator; (O) trim heater; (P) main heater; (Q) slide transformer; (R) heat exchanger; (S) temperature regulator pump; (T) cooling bath; (U) immersion cooler; V1-V7, valves; (W) stirrer.

the silicone oil. The bath temperature is controlled to the target value by means of a PID controller and an associated electronic heater. The temperature is detected by use of a $25\ \Omega$ standard platinum resistance thermometer, which was calibrated on ITS-90 [3] at the National Metrology Institute of Japan (NMIJ), and a thermometer bridge with accuracy of 1 mK. The thermometer has been also calibrated its resistance at the triple point of water at least once a year, and the calibration uncertainty was estimated to be 1 mK. The present experimental temperature ranges from

240 to 380 K, and the temperature fluctuation is usually less than 1 mK, but increases to 3 mK at temperatures above 360 K. Thus, the temperature measurement uncertainty was estimated to be $3 < U_T/\text{mK} < 7$, when the coverage factor, k , is equal to 2.

4. RESULTS OF CALIBRATION FOR VIBRATING-TUBE DENSIMETER

To calculate the density of a sample, the three parameters, A , μ , and τ_0 , given in Eqs. (5) through (7), are required. A series of vibration periods under vacuum were simply obtained at different temperatures by evacuating the measurement system. Taking the aging of the densimeter and sample adsorption into consideration, we have used the most recent τ_0 data for density calculation.

The mass ratio, μ , given in Eq. (6) can be defined by measuring a couple of fluids of known density with the present measurement system. In this study, water and iso-octane were selected for this purpose and they were measured at 293.15 K and 101.3 kPa with the present measurement system. Then μ was calculated by the following equation:

$$\mu = \frac{\rho_{\text{water}}x_{\text{iso-octane}} - \rho_{\text{iso-octane}}x_{\text{water}}}{x_{\text{water}}x_{\text{iso-octane}}(\rho_{\text{water}} - \rho_{\text{iso-octane}})} \quad (9)$$

The density of water, ρ_{water} , can be calculated by the IAPWS-95 formulation [4] and is $998.207 \pm 0.001 \text{ kg} \cdot \text{m}^{-3}$. The iso-octane is a density standard prepared by Kyoto Electronic Manufacturing, Co. [5] and is traceable to the density standard [6] of Japan; its density is $691.86 \pm 0.03 \text{ kg} \cdot \text{m}^{-3}$. From the experimental results, we have determined the mass ratio, μ , as follows.

$$\mu = 0.0030 \pm 0.0005 \quad (10)$$

Then the proportionality parameter, A , can be derived from Eq. (3) by measuring a density reference fluid with the present measurement system. In order to obtain the parameter A from Eq. (3), water was selected as the reference fluid as well as for μ . Since the parameter A is defined as the vibrating-tube mass divided by its inner volume, m_0/V_0 , it decreases under higher pressures or temperatures where the vibrating tube slightly expands according to the pressure deformation or thermal expansion. To correlate the temperature and pressure dependence of the parameter A , the following functional form was employed in the present calibration procedure:

$$A(T, P) = \sum_{i=0}^3 \sum_{j=0}^1 a_{ij} T^{*i} P^{*j} \quad (11)$$

$$P^* = (P/\text{kPa})/1000 \quad (12)$$

$$T^* = (T/\text{K})/100 \quad (13)$$

The parameters a_{ij} shown in Eq. (11) were defined in such a way that the data for water measured with the present measurement system were fitted with the data calculated from the IAPWS-95 formulation [4] by the least-squares method.

Figure 3 illustrates deviations of experimentally obtained values of the proportionality parameter, A , derived from the correlation, Eq. (11), on the basis of the present measurements for water. From Fig. 3, it is found that the relative deviation for the parameter A is not greater than $\pm 0.012\%$ for water except at 320 K which was excluded from the input data used to fit the correlation, Eq. (11). The standard deviation of these data was found to be extremely small, 65 ppm. In Fig. 3, the deviations of the parameter A experimentally obtained for methanol were also included. Although there is scatter of about $\pm 0.07\%$, it is smaller than the claimed uncertainty of the IUPAC thermodynamic table for methanol [7]. At lower temperatures, even below 273.15 K where data for water are not available, it is found that the present correlation represents the methanol data with the same level of performance as that in the higher temperature range. Therefore, it is shown that the correlation Eq. (11) possesses a high reproducibility within the present measurement range for temperature, 240 to 380 K.

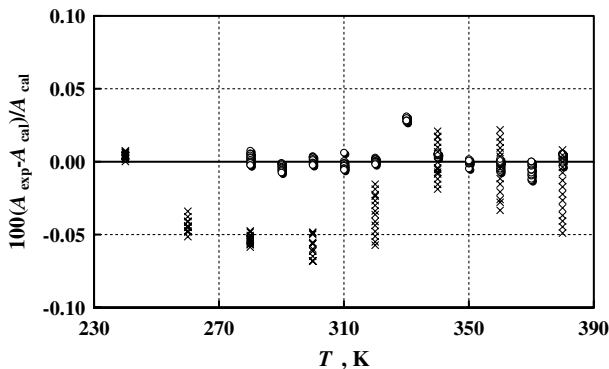


Fig. 3. Reproducibility of the fitted function, Eq. (11), \circ , water; \times , methanol.

By summing up the uncertainties of the parameters, A , μ , and τ_0 , we have estimated the density-measurement uncertainty of the present study as given in Eq. (14), where the coverage factor, k , is equal to 2.

$$U_\rho = 0.07 \text{ kg} \cdot \text{m}^{-3} + 0.00024\rho \quad (14)$$

More detailed information about the calibration can be found in Ref. 1.

5. MEASUREMENT RESULTS

We have conducted several series of measurements for some pure refrigerants; the hydrocarbons R-290, R-600, and R-600a, and the hydrofluoroethers, trifluoromethyl methyl ether and pentafluoroethyl methyl ether. Additionally, we have measured liquid phase PVT_x properties of all the possible binary and ternary combinations of R-290, R-600, and R-600a. In total, 2991 data points of PVT or PVT_x properties were obtained for the above samples. Table I summarizes the present experimental results. In addition, the present numerical data for the hydrofluoroethers are shown in Ref. 8, and those for the hydrocarbons will be reported elsewhere [9].

6. COMPARISON WITH EXISTING EQUATIONS OF STATE

The present paper will briefly discuss the experimental results for data in the liquid phase only. In order to examine comparisons of the

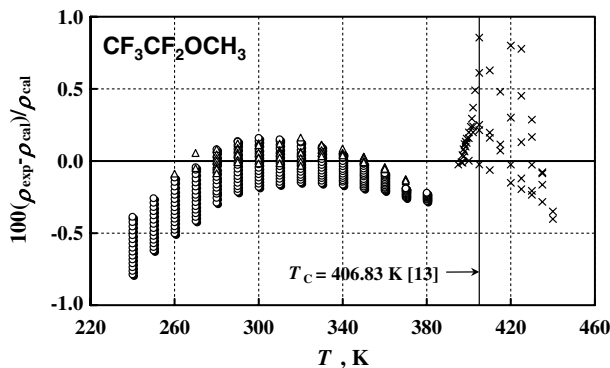


Fig. 4. Relative density deviations of the present measurements for pentafluoroethyl methyl ether from the EoS by Widiatmo and Watanabe [10], ○, This work; Δ, Ohta et al. (2001) [11]; ×, Widiatmo et al. (2001) [12].

Table I. Summary of Present Measurement Results

Substance	Purity (mol%)	Composition (mol%)	Phases ^a	Measurement		NO. of data
				<i>T</i> (K)	<i>P</i> (MPa)	
CF ₃ OCH ₃	99.98	–	Liquid	240–330	0.5–7.0	123
			Vapor	240–330	0.0–1.0	70
			VLE	240–330	0.1–1.3	15
CF ₃ CF ₂ OCH ₃	99.99	–	Liquid	240–380	0.5–7.0	202
			Vapor	290–380	0.0–1.5	98
			VLE	240–380	0.1–1.7	26
R-290	99.99	–	Liquid	240–380	0.5–7.0	503
			Vapor	240–380	0.0–3.4	134
			VLE	240–380	0.1–3.5	41
R-600	99.99	–	Liquid	240–380	0.5–7.0	115
			Vapor	300–380	0.1–1.5	27
			VLE	240–380	0.0–1.7	11
R-600a	99.99	–	Liquid	240–380	0.5–7.0	115
			Vapor	260–380	0.0–2.1	27
			VLE	240–380	0.0–2.3	11
R-290/600	–	25.0/75.0	Liquid	240–380	0.5–7.0	101
	–	50.0/50.0	Liquid	250–380	0.5–7.0	96
	–	75.0/25.0	Liquid	240–360	0.5–7.0	92
R-290/600a	–	25.0/75.0	Liquid	240–380	0.5–7.0	101
	–	50.0/50.0	Liquid	240–380	0.5–7.0	82
	–	75.0/25.0	Liquid	240–380	0.5–7.0	82
R-600/600a	–	25.0/75.0	Liquid	240–380	0.5–7.0	104
	–	50.0/50.0	Liquid	250–380	0.5–7.0	104
	–	75.0/25.0	Liquid	240–360	0.5–7.0	105
R-290/600/600a	–	34.0/33.0/33.0	Liquid	240–380	0.5–7.0	100
	–	60.0/20.0/20.0	Liquid	240–380	0.5–7.0	93
	–	20.0/60.0/20.0	Liquid	240–380	0.5–7.0	101

^aVLE = vapor-liquid equilibrium.

present measurements with available thermodynamic property models, density deviations have been calculated and analyzed.

For the hydrofluoroethers, Fig. 4 shows density deviations of the present measurements for pentafluoroethyl methyl ether from the EoS reported by Widiatmo and Watanabe [10]. The input data for these models are also included in this figure. Note that figure keys show only first author and reported year for simplicity. The present data for pentafluoroethyl methyl ether agree well with those by Ohta et al. [11] and the baseline EoS by Widiatmo and Watanabe [10] for temperatures above 260 K. Although the deviations are likely to increase below 260 K, this could be due to the limited range of validity of the EoS.

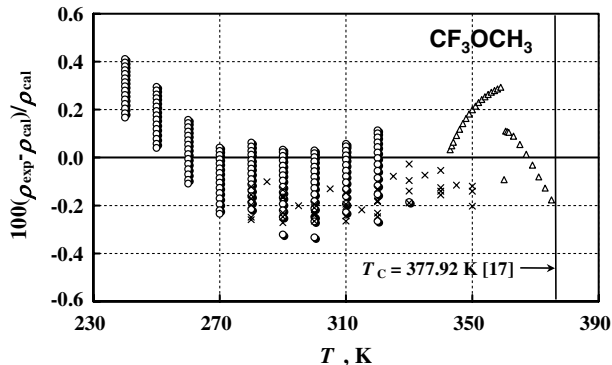


Fig. 5. Relative density deviations of the present measurements for trifluoromethyl methyl ether from the EoS by Widiatmo and Watanabe [14], \circ , This work; \times , Morimoto (2001) [15]; Δ , Yoneda (2001) [16].

For trifluoromethyl methyl ether, Fig. 5 shows density deviations of the present measurements from the EoS reported by Widiatmo and Watanabe [14]. The present data for trifluoromethyl methyl ether agree well with the EoS by Widiatmo and Watanabe [14] for temperatures above 260 K, and have similar behavior of the data by Morimoto [15] used to formulate the EoS. Considering that the present measurements have a similar systematic deviation to earlier measurements used to formulate the EoS by Widiatmo and Watanabe [10,14], the present measurements with lower uncertainty obtained over wider ranges of temperature and pressure than existing data should be a valuable contribution to improve the thermodynamic property model for these substances.

For pure hydrocarbons, the deviations for R-290 from the Helmholtz-type EoS by Miyamoto and Watanabe [18] are shown in Fig. 6. The data of other researchers are also included in the figure. It is found that the present measurements for R-290 agree well with the EoS within $\pm 0.4\%$ in density. The trend of the deviations for the present measurements generally resembles those by other researchers, but the uncertainties of the present *PVT* data are generally smaller than existing data which were measured many years ago, so that the present measurements may be considered to possess higher reliability than any other data shown in Fig. 6. For other hydrocarbon compounds, Figs. 7 and 8 show the density deviations of the present measurements for, respectively, R-600 and R-600a from the EoS by Miyamoto and Watanabe [24,25]. Both figures show that the present data

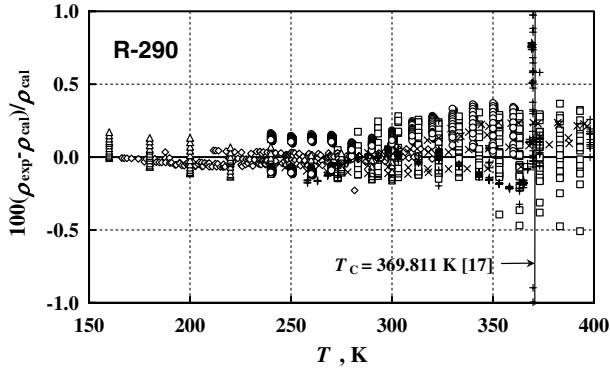


Fig. 6. Relative density deviations of the present measurements for R-290 from the EoS by Miyamoto and Watanabe [18], \circ , This work; \square , Dittmar et al. (1962) [19]; \diamond , Ely and Kobayashi (1978) [20]; Δ , Haynes (1983) [21]; \times , Kratzke and Müller (1984) [22]; $+$, Thomas and Harrison (1982) [23].

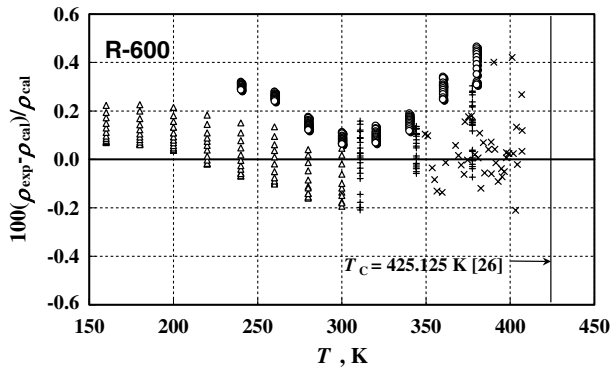


Fig. 7. Relative density deviations of the present measurements for R-600 from the EoS by Miyamoto and Watanabe [24], \circ , This work; Δ , Haynes (1983) [26]; \times , Kay (1940) [27]; $+$, Olds et al. (1944) [28].

agree with the EoS by Miyamoto and Watanabe [24,25] within $\pm 0.4\%$ in density except for a few points and have a similar systematic trend to the existing data.

Similar comparisons for the mixtures are now discussed. The density deviations of the present measurements for the R-290/600/600a system from the EoS by Miyamoto and Watanabe [32] are shown in Figs. 9–12. It is found from these figures that the present measurements

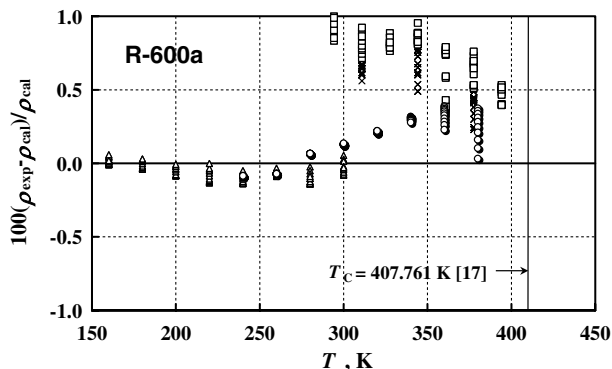


Fig. 8. Relative density deviations of the present measurements for R-600a from the EoS by Miyamoto and Watanabe [25], ○, This work; Δ, Haynes (1983) [29]; ×, Morris et al. (1939) [30]; □, Sage and Lacey (1938) [31].

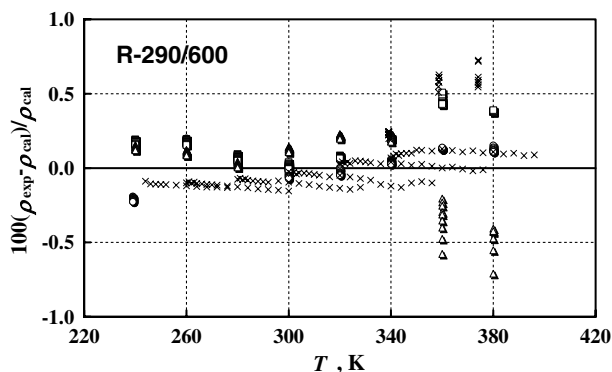


Fig. 9. Relative density deviations of the present measurements for the binary system R-290/600 from the EoS by Miyamoto and Watanabe [32], ○, This work (25/75 mol%); □, This work (50/50 mol%); Δ, This work (75/25 mol%); ×, Holcomb et al. (1995) [33].

for the R-290/600/600a system generally agree with the EoS within $\pm 0.6\%$ in density except for the data near the theoretical critical points. For hydrocarbon mixture systems of R-290, R-600, and R-600a, reported thermodynamic property data in the literature are limited to a few experimental studies over a narrow composition range, so the present measurements, which cover a wide range of composition, should be valuable to improve thermodynamic models for hydrocarbon mixtures.

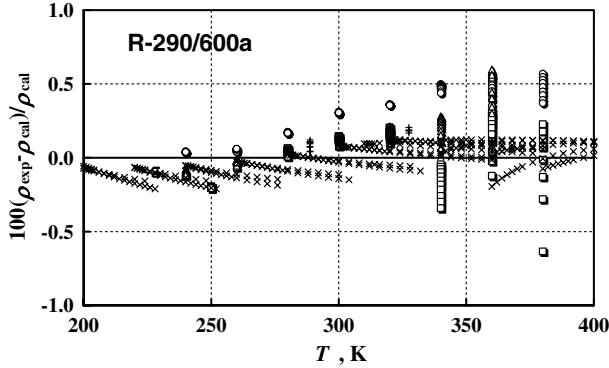


Fig. 10. Relative density deviations of the present measurements for the binary system R-290/600a from the EoS by Miyamoto and Watanabe [32], ○, This work (25/75 mol%); □, This work (50/50 mol%); Δ, This work (75/25 mol%); +, Kahre (1973) [34]; ×, Duarte-Garza and Magee (1999) [35]; -, Thompson, Jr. and Miller (1980) [36].

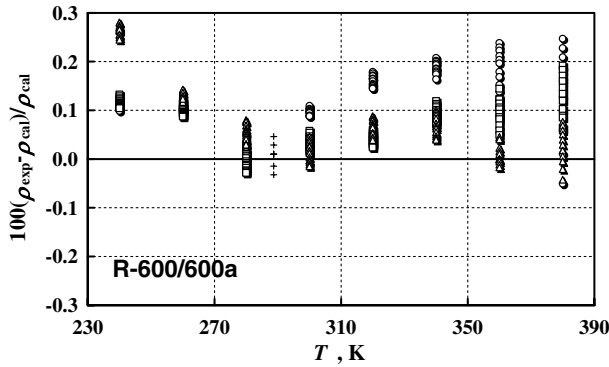


Fig. 11. Relative density deviations of the present measurements for the binary system R-600/600a from the EoS by Miyamoto and Watanabe [32], ○, This work (25/75 mol%); □, This work (50/50 mol%); Δ, This work (75/25 mol%); +, Kahre (1973) [34].

7. THERMODYNAMIC PROPERTY MODELING

To represent the thermodynamic properties in the liquid phase for the measured pure fluids, an empirical equation of state with a modified Tait

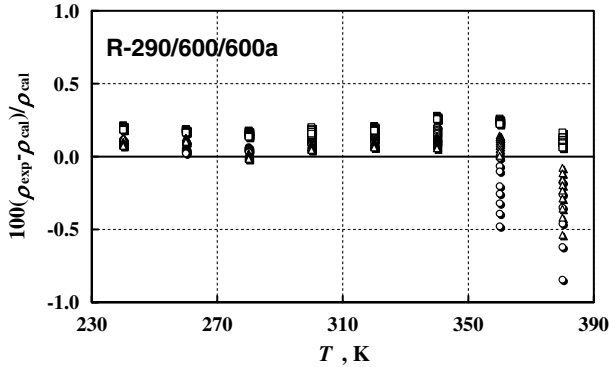


Fig. 12. Relative density deviations of the present measurements for the ternary system R-290/600/600a from the EoS by Miyamoto and Watanabe [32], \circ , This work (60/20/20 mol%); \square , This work (20/60/20 mol%); Δ , This work (34/33/33 mol%).

equation proposed by Sato [37] has been developed in the present study. The EoS can be derived from the van der Waals equation of state as shown below:

$$\rho_r = \frac{(P_r + B(T_r))^{C(T_r)}}{D(T_r)} \quad (15)$$

$$B(T_r) = \sum_{k=0}^2 b_i T_r^k \quad (16)$$

$$C(T_r) = \sum_{k=0}^2 c_i T_r^k \quad (17)$$

$$D(T_r) = \sum_{k=0}^2 d_i T_r^k \quad (18)$$

P_r , ρ_r , and T_r represent the reduced pressure, density, and temperature, and are given by $P_r = P/P_C$, $\rho_r = \rho/\rho_C$, and $T_r = T/T_C$, respectively. The critical parameters such as P_C , ρ_C , and T_C employed in the present study and fitting parameters, b_i , c_i , and d_i , which were determined by the least-squares method on the basis of the present data, are summarized in Table II. And note that the validity of the EoS shown in Eq. (15) is considered to extend to $T_r = 0.95$ in the liquid phase.

Table II. Numerical Constants for Eqs. (15)–(18).

Parameter	CF ₃ OCH ₃ [17]	CF ₃ CF ₂ OCH ₃ [13]	R-290 [17]	R-600 [26]	R-600a [17]
T _C (K)	377.92	406.83	369.811	425.125	407.761
P _C (kPa)	3640.2	2887.3	4245.8	3796	3629.3
ρ _c (kg·m ⁻³)	465	509	222	227.84	233
b ₀	-9.649 × 10 ⁻¹	-8.974 × 10 ⁻¹	-9.604 × 10 ⁻¹	-1.069 × 10 ⁰	-8.389 × 10 ⁻¹
b ₁	1.431 × 10 ¹	1.708 × 10 ¹	1.496 × 10 ¹	1.749 × 10 ¹	1.793 × 10 ¹
b ₂	3.668 × 10 ¹	3.704 × 10 ¹	4.071 × 10 ¹	4.454 × 10 ¹	1.901 × 10 ¹
c ₀	1.070 × 10 ⁻¹	1.133 × 10 ⁻¹	1.129 × 10 ⁻¹	1.117 × 10 ⁻¹	1.245 × 10 ⁻¹
c ₁	-1.999 × 10 ⁻¹	-2.070 × 10 ⁻¹	-7.913 × 10 ⁻²	-5.800 × 10 ⁻²	-1.621 × 10 ⁻¹
c ₂	2.682 × 10 ⁻¹	1.945 × 10 ⁻¹	6.055 × 10 ⁻²	-1.660 × 10 ⁻³	8.368 × 10 ⁻²
d ₀	5.613 × 10 ⁻¹	5.757 × 10 ⁻¹	5.650 × 10 ⁻¹	5.569 × 10 ⁻¹	5.941 × 10 ⁻¹
d ₁	-5.125 × 10 ⁻¹	-5.285 × 10 ⁻¹	-2.907 × 10 ⁻¹	-2.491 × 10 ⁻¹	-4.267 × 10 ⁻¹
d ₂	4.220 × 10 ⁻¹	3.426 × 10 ⁻¹	1.235 × 10 ⁻¹	2.039 × 10 ⁻²	1.579 × 10 ⁻¹

For the hydrofluoroethers, the density deviations of both the present data and the existing data for pentafluoroethyl methyl ether and trifluoromethyl methyl ether from the EoS of Eq. (15) are shown in Figs. 13 and 14, respectively. It is found from these figures that the present data for the hydrofluoroethers are excellently reproduced by the baseline of Eq. (15) within $\pm 0.05\%$ except for a few data. In addition, the existing data reported by other researchers are also well reproduced within $\pm 0.2\%$ except for a few data. These EoS, which possess the simple function form and accurate reproducibility, should be useful for formulating multi-property thermodynamic models such as Helmholtz-energy function EoS for these hydrofluoroethers.

For the hydrocarbons, the density deviations of both the present data and the existing data for R-290, R-600, and R600a from the EoS of Eq. (15) are shown in Figs. 15–17, respectively. It is found from Fig. 15 that Eq. (15) for R-290 reproduces the present data within $\pm 0.2\%$ in the range of $T_r < 0.95$. Although the existing data in the high-pressure region (larger than 50 MPa) reported by Dittmar et al. [19] are scattered more than $\pm 0.4\%$, the other existing data are almost represented within $\pm 0.3\%$ even in the lower temperature region (lower than 200 K) reported by Ely and Kobayashi [20] and Haynes [21]. For R-600 and R-600a, Figs. 16 and 17 indicate that the present data are nicely reproduced within $\pm 0.2\%$ by Eq. (15). Additionally, the existing data for R-600 and R-600a are also well reproduced within $\pm 0.3\%$ by Eq. (15) except for some data such as those

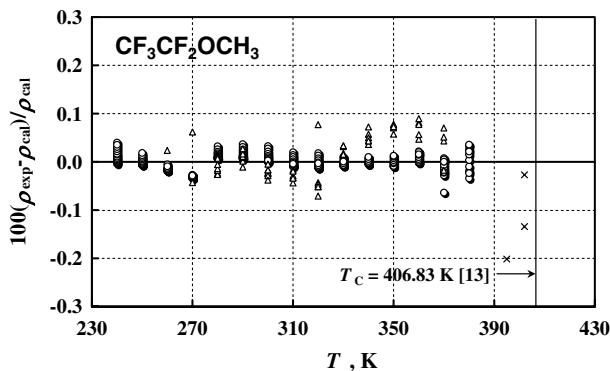


Fig. 13. Relative density deviations of the present measurements for pentafluoroethyl methyl ether from the Eq. (15), ○, This work; Δ, Ohta et al. (2001) [11]; ×, Widiatmo et al. (2001) [12].

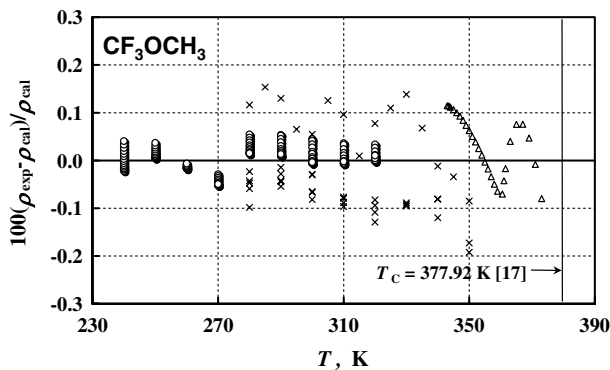


Fig. 14. Relative density deviations of the present measurements for trifluoromethyl methyl ether from the Eq. (15), ○, This work; ×, Morimoto (2001) [15]; Δ, Yoneda (2001) [16].

by Morris et al. [30] and Sage and Lacey [31], which also deviate systematically from the EoS by Miyamoto and Watanabe [25].

8. CONCLUSIONS

We have successfully achieved rapid and accurate density measurements with a vibrating-tube densimeter. The required time was reduced to a few minutes for a single *PVT* datum or about 2 hours for an isothermal measurement series. By using this system, we have measured *PVT* properties for five pure substances including trifluoromethyl methyl ether,

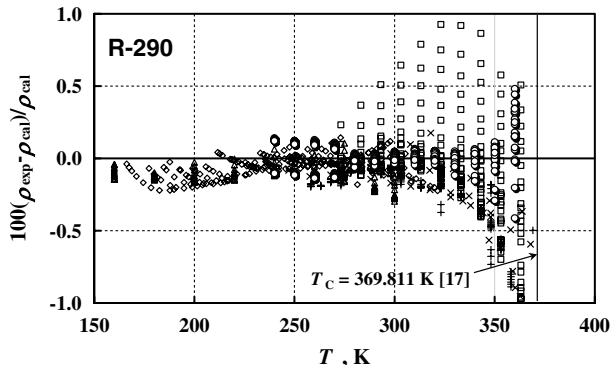


Fig. 15. Relative density deviations of the present measurements for R-290 from the Eq. (15), ○, This work; □, Dittmar et al. (1962) [19]; ◇, Ely and Kobayashi (1978) [20]; Δ, Haynes (1983) [21]; ×, Kratzke and Müller (1984) [22]; +, Thomas and Harrison (1982) [23].

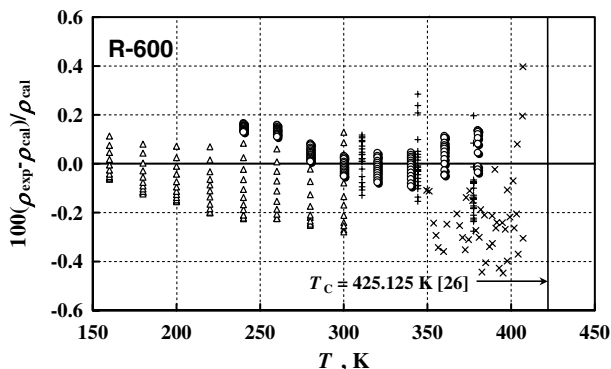


Fig. 16. Relative density deviations of the present measurements for R-600 from the Eq. (15), ○, This work; Δ, Haynes (1983) [26]; ×, Kay (1940) [27]; +, Olds et al. (1944) [28].

pentafluoroethyl methyl ether, R-290, R-600, and R-600a, and 12 mixtures for the R-290/600/600a system. As a result, about 3000 points of PVT or PVT_x data were obtained within a very short period. The present data were compared with available thermodynamic models, and on the basis of them, an empirical equation of state for the liquid phase was developed. The EoS well reproduces not only the present data but also the existing data reported by other researchers, and it should be valuable to improve

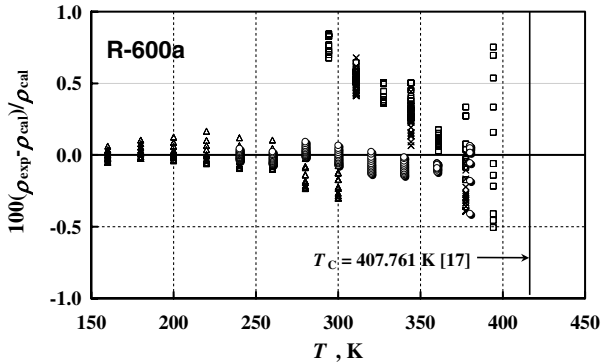


Fig. 17. Relative density deviations of the present measurements for R-600a from the Eq. (15), ○, This work; Δ, Haynes (1983) [29]; ×, Morris et al. (1939) [30]; □, Sage and Lacey (1938) [31].

multi-property thermodynamic models for these important substances used for future thermal-energy conversion systems.

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