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An Experimental Study of the *pVTx* Properties for Binary Mixtures of HFC-32 and HFC-125 from 258 to 354 K at Pressures up to 16.9 MPa[1]

T. Miyazaki[2] and K. Oguchi[2,3]

An experimental study of the *pVTx* properties for binary mixtures of HFC-32 (CH_2F_2) and HFC-125 (C_2HF_5) was conducted in the range of temperatures from 258 to 354 K, pressures up to 16.9 MPa, densities from 900 to 1400 kg·m^{-3}, and compositions from 0 to 1 mole fraction of HFC-32, within the uncertainties of 4.8 mK of temperatures, 1.8 kPa of pressures, 0.022% of densities, and 0.0022 mole fraction of compositions. The present results were determined with the use of a constant-volume apparatus consisting of a cylindrical vessel of approximately 173 cm^3 internal volume. The available data including the present measurements are critically compared with the equation of state developed by Tillner-Roth et al., and it is found that, in the liquid region for the range of compositions from 0.1 to 0.4 mole fraction of HFC-32, this equation of state is less reliable because of the lack of experimental data.

KEY WORDS: experimental; HFC-32; HFC-125; mixtures; *pVTx* properties.

1. INTRODUCTION

The alternative refrigerant R410A is a mixture of 50 mass% HFC-32 (CH_2F_2) and 50 mass% HFC-125 (C_2HF_5) used in air-conditioning systems. However, in the condenser and evaporator of these systems, the composition of this refrigerant varies because of the vapor–liquid equilibrium behavior. Therefore, the thermodynamic properties of refrigerant mixtures should be measured over a wide range of temperatures, pressures, and compositions.

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[2] Department of Mechanical Engineering, Faculty of Engineering, Kanagawa Institute of Technology, 1030 Shimo-Ogino, Atsugi-shi, Kanagawa 243-0292, Japan.

[3] To whom correspondence should be addressed. E-mail: oguchi@kait.jp

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This paper reports experimental data for the pressure–volume–temperature-composition ($pVTx$) properties for binary mixtures of HFC-32 and HFC-125 conducted in the range of temperatures from 258 to 354 K, pressures from 1.6 to 16.9 MPa, densities from 900 to 1400 $kg{\cdot}m^{-3}$, and compositions from 0 to 1 mol fraction of HFC-32. The experimental $pVTx$ data of this mixture have been already measured in the supercritical region for the range of compositions from 0.05 to 0.9 mol fraction of HFC-32 [1]. The available experimental data, including the present measured data, were compared with the equation of state developed by Tillner-Roth et al. [2] for HFC-32, HFC-125, and their mixtures.

2. SURVEY OF AVAILABLE DATA OF *pVTx* PROPERTIES

2.1. Pure Substances of HFC-32 and HFC-125

Pressure–volume–temperature (pVT) property data for HFC-32 have been measured, since 1993, in the range of temperatures from 142 to 424 K, pressures from 0.07 to 34.8 MPa, and densities from 2.6 to 1419 $kg{\cdot}m^{-3}$ by Qian et al. [3], Defibaugh et al. [4], Sato et al. [5], Fu et al. [6], Fukushima et al. [7], Magee [8], and Zhang et al. [9].

Pressure–volume–temperature property data for HFC-125 are available in the range of temperatures from 178 to 473 K, pressures from 0.1 to 35.4 MPa, and densities from 0.26 to 1683 $kg \cdot m^{-3}$, measured, since 1992, by Defibaugh and Morrison [10], Baroncini et al. [11], Sagawa et al. [12], Boyes and Weber [13], Fukushima et al. [7], Tsvetkov et al. [14], Ye et al. [15], Magee [8], Oguchi et al. [16], and Zhang et al. [9].

2.2. Binary Mixtures of HFC-32 and HFC-125

The $pVTx$ properties for binary mixtures of HFC-32 and HFC-125 are available in the range of temperatures from 200 to 440 K, pressures from 0.09 to 35.3 MPa, densities from 2.6 to 1497 $kg{\cdot}m^{-3}$, and compositions from 0.05 to 0.9 mol fraction of HFC-32, as shown in Table I. Most $pVTx$ property data of binary mixtures of HFC-32 and HFC-125 have been measured in the range of temperatures above 300 K and densities below 200 $kg{\cdot}m^{-3}$.

3. EXPERIMENTAL METHOD AND UNCERTAINTIES

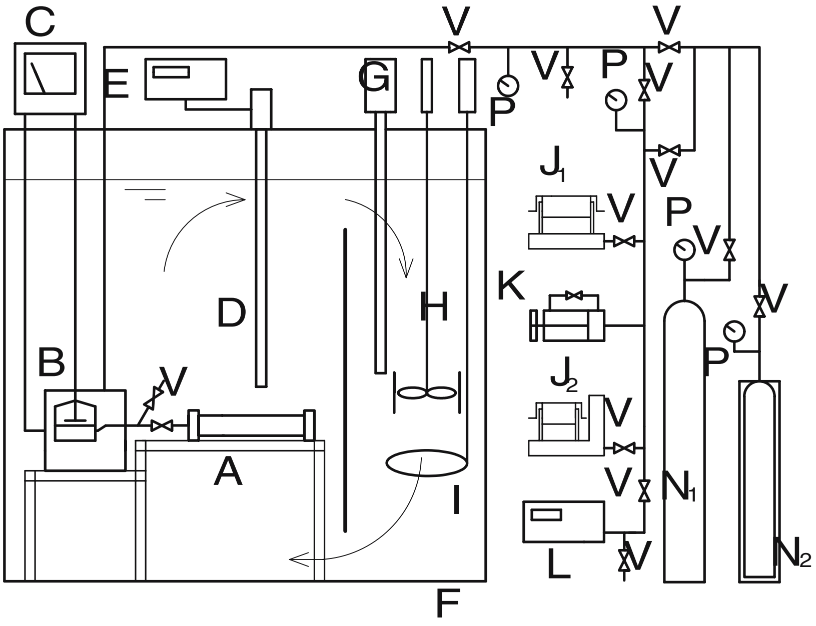
A constant-volume apparatus with a cylindrical vessel of approximately 173 cm^3 internal volume was used for the present measurements of the $pVTx$ properties, as shown in Fig.1. The sample of the binary

Table I. Experimental Studies of *pVTx* Properties for Binary Mixtures of HFC-32 and HFC-125

First Author	Temp. Range (K)	Pressure Range (MPa)	Density Range ($kg \cdot m^{-3}$)	Mole Frac. HFC-32	Data Points	Ref. No.
Widiatmo	280–310	0.88–2.3	940–1254	0.2–0.9	24	17
Weber	338–373	0.3–4.2	8.8–158.1	0.5	17	18
Bivens	280–373	0.49–4.8	13.7–206	0.65–0.78	111	19
Zhelezny	280–338	0.67–3.6	20–184	0.26–0.75	136	20
Kiyoura	320–440	1.7–5.2	67.7–158	0.37–0.61	104	21
Sato	320–440	1.72–5.3	50.4–125.1	0.70–0.90	156	22
Zhang	300–380	0.09–4.6	2.6–151.7	0.50–0.70	124	9
Magee	200–399	4.27–35.3	91.5–1497	0.5	228	23
Miyazaki	343–423	4.0–15.6	485–491	0.05–0.90	79	1

mixture of HFC-32 and HFC-125 was prepared as follows. After having weighed precisely the masses of the piezometer, namely the cylindrical vessel, and the sample supply cylinder in vacuum, HFC-32 was charged into the sample supply cylinder and HFC-125 also charged into the piezometer while controlling the mass of each charged sample. Both the sample supply cylinder with HFC-32 and the piezometer with HFC-125 were weighed carefully and precisely by the balance. Then, HFC-32 in the sample supply cylinder was charged into the piezometer of HFC-125 frozen by liquid nitrogen, and finally the mass of the mixture of HFC-32 and HFC-125 was weighed precisely by the balance.

This experimental method was described in other references [1, 16, 24, 25]. Normally, density and composition distributions caused by gravity exist in the vessel. For minimizing this effect for the *pVTx* measurements, a small inner diameter cylindrical vessel was used. The inner volume of this vessel was calibrated, for obtaining the average inner and outer diameters of this cylindrical vessel at 273.15 K, in the range of temperatures from 298 to 313 K and pressures up to 17 MPa with the use of doubly distilled ordinary water. The temperature was measured with the use of a platinum resistance thermometer calibrated within 2 mK at the National Physical Laboratory in the United Kingdom, based on the International Temperature Scale (1990). A Ruska Series 6000 quartz Bourdon type pressure gage, calibrated with the aid of two air piston gages, was used for the measurements of pressure. The density was determined by means of the mass of the sample divided by the internal volume of the vessel. The composition was calculated with the aid of each mass of the sample of HFC-32 and HFC-125. Uncertainties of the present data were within 4.8 mK of temperature, 1.8 kPa of pressure, 0.022% of density, and 0.0022 mol



A: Piezometer

B: Diaphragm type pressure balance detector

C: Null pressure indicator

D: Platinum resistance thermometer

E: Thermometer bridge

F: Thermostated bath

G: Cooler

H: Recirculation pump

I: Heater

$J_{1,2}$: Air piston pressure gage

K: Pressure controller

L: Ruska quartz Bourdon pressure gage

$N_{1,2}$: Nitrogen bottle

P: Bourdon type pressure gages

V: High pressure valves

←: Flow pattern of brine

Fig. 1. Schematic diagram of the *pVTx* apparatus. A: Piezometer; B: Diaphragm type pressure balance detector; C: Null pressure indicator; D: Platinum resistance thermometer; E: Thermometer bridge; F: Thermostated bath; G: Cooler; H: Recirculation pump; I: Heater; $J_{1,2}$: Air piston pressure gage; K: Pressure controller; L: Ruska quartz Bourdon pressure gage; $N_{1,2}$: Nitrogen bottle; P: Bourdon type pressure gages; V: High pressure valves; ←: Flow pattern of brine.

fraction of composition. The purities of the samples of HFC-32 and HFC-125 were 0.99983 and 0.9983 mol fraction, respectively.

4. RESULTS

Thermodynamic properties for refrigerators and air-conditioning equipment are required also in the range of temperatures below 273 K, but most available data for binary mixtures of HFC-32 and HFC-125 have been measured in the vapor region for the range of temperatures above 300 K. Therefore, the present experimental study was focused on the low-temperature liquid region.

One hundred and two data points of the *pVTx* properties for binary mixtures of HFC-32 and HFC-125 were measured in the range of temperatures from 258 to 354 K, pressures from 1.6 to 16.9 MPa, densities from 900 to 1400 $\mathrm{kg\cdot m^{-3}}$, and compositions from 0 to 1 mol fraction of HFC-32, as shown in Table II.

Table II. Experimental *pVTx* Properties for Binary Mixtures of HFC-32 and HFC-125

Mole Fraction of HFC-32	Temperature (K)	Pressure (MPa)	Density ($\mathrm{kg\cdot m^{-3}}$)
0.0000	258.157	4.5956	1403.78
0.0000	261.154	6.5798	1403.47
0.0000	262.143	7.2846	1403.36
0.0000	267.159	10.8092	1402.84
0.0000	270.192	13.0028	1402.53
0.0000	273.152	15.0759	1402.23
0.0000	275.154	16.5720	1402.04
0.0980	264.148	3.2352	1362.36
0.0980	267.160	5.3013	1362.04
0.0980	270.153	7.4144	1361.73
0.0980	273.151	9.5327	1361.42
0.0980	282.151	15.9775	1360.53
0.1000	313.146	2.8206	1097.54
0.1000	318.151	4.5285	1097.17
0.1000	323.159	6.2529	1096.79
0.1000	328.146	7.9860	1096.43
0.1000	333.168	9.7419	1096.06
0.1000	338.144	11.4891	1095.70
0.1000	343.127	13.2472	1095.35
0.1000	348.161	15.0221	1094.99
0.1000	353.138	16.7818	1094.64
0.3004	258.149	2.1770	1342.88
0.3004	259.150	2.9131	1342.77
0.3004	261.150	4.4749	1342.56

Table II. (*Continued*)

Mole Fraction of HFC-32	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
0.3004	263.153	6.1063	1342.34
0.3004	265.146	7.7670	1342.13
0.3004	267.158	9.3829	1341.92
0.3004	269.150	10.9833	1341.71
0.3004	273.148	14.2551	1341.32
0.3003	313.134	2.2175	1050.39
0.3003	318.183	3.9013	1050.03
0.3003	323.160	5.6459	1049.68
0.3003	328.150	7.4089	1049.33
0.3003	333.142	9.1884	1048.98
0.3003	338.134	10.9786	1048.63
0.3003	343.127	12.7725	1048.29
0.3003	348.168	14.5923	1047.95
0.3003	353.136	16.3860	1047.61
0.3003	354.135	16.7440	1047.54
0.4995	258.157	1.5544	1294.18
0.4995	259.150	2.4037	1294.07
0.4995	261.150	4.1183	1293.85
0.4995	263.147	5.8485	1293.64
0.4995	265.167	7.5859	1293.43
0.4995	267.146	9.2744	1293.23
0.4995	268.197	10.1515	1293.13
0.4995	269.138	10.9505	1293.04
0.4995	271.135	12.6474	1292.84
0.4995	273.080	14.3114	1292.65
0.4995	275.133	16.0655	1292.46
0.4993	318.207	3.3418	1000.30
0.4993	323.150	5.1293	999.96
0.4993	328.163	6.9697	999.62
0.4993	333.154	8.8145	999.29
0.4993	338.191	10.6899	998.95
0.4993	343.183	12.5499	998.62
0.4993	348.164	14.4227	998.30
0.4993	353.128	16.2902	997.98
0.4993	354.148	16.6721	997.91
0.6995	259.140	2.6583	1234.39
0.6995	261.150	4.5162	1234.17
0.6995	263.150	6.3629	1233.97
0.6995	264.151	7.2881	1233.88
0.6995	265.154	8.2136	1233.78
0.6995	267.147	10.0512	1233.58
0.6995	269.151	11.8944	1233.38
0.6995	271.156	13.7402	1233.20
0.6995	273.159	15.5793	1233.01
0.6995	274.162	16.4994	1232.92

Table II. (*Continued*)

Mole Fraction of HFC-32	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
0.6998	318.150	2.9218	949.66
0.6998	323.144	4.8670	949.34
0.6998	328.137	6.8399	949.01
0.6998	333.127	8.8340	948.69
0.6998	338.126	10.8431	948.37
0.6998	343.121	12.8603	948.05
0.6998	348.123	14.8870	947.74
0.6998	353.108	16.9168	947.43
0.8992	318.145	2.9590	900.95
0.8992	323.129	5.2123	900.63
0.8992	328.160	7.5092	900.31
0.8992	333.130	9.7934	900.01
0.8992	338.123	12.1003	899.70
0.8992	343.120	14.4191	899.40
0.8992	348.126	16.7457	899.10
0.8997	261.147	3.0611	1151.87
0.8997	262.144	4.0560	1151.77
0.8997	263.150	5.0583	1151.67
0.8997	264.150	6.0535	1151.57
0.8997	265.153	7.0509	1151.47
0.8997	267.153	9.0409	1151.28
0.8997	268.151	10.0319	1151.19
0.8997	269.158	11.0311	1151.09
0.8997	271.151	13.0075	1150.92
0.8997	273.155	14.9905	1150.74
0.8997	274.145	15.9693	1150.66
1.0000	313.158	3.3537	900.17
1.0000	316.153	4.9671	899.97
1.0000	319.149	6.5714	899.77
1.0000	322.151	8.1624	899.57
1.0000	328.156	11.3997	899.19
1.0000	334.149	14.7534	898.82
1.0000	337.153	16.5805	898.63

5. DISCUSSION

5.1. Pure Substances of HFC-32 and HFC-125

The deviations of available measured densities of HFC-32 from the equation of state [2] are shown in Fig. 2 for the range of densities from 648 to 1420 $kg \cdot m^{-3}$ [4, 5, 7, 8].

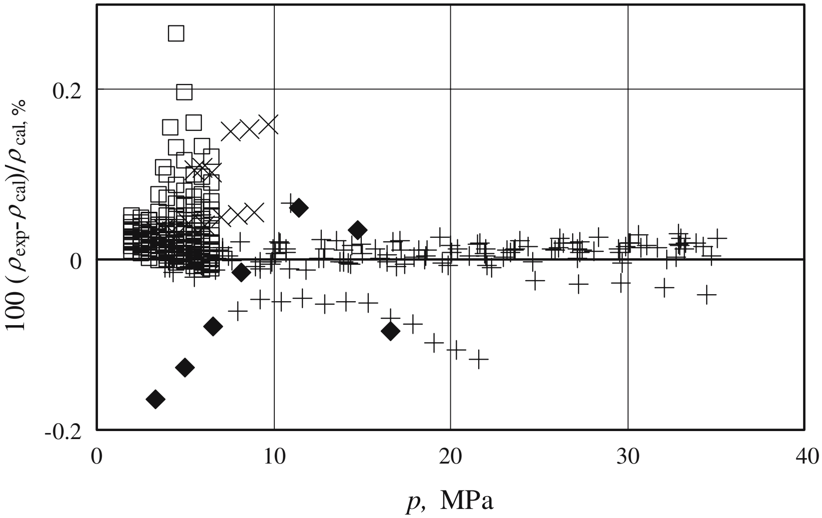


Fig. 2. Density deviations of the present results and available pVT properties of HFC-32 from the equation of state [2] (densities from 649 to 1420 kg · m^{-3}). (□) Defibaugh et al. [4]: $\rho = 737.44$–1157.22 kg · m^{-3}; (×) Sato et al. [5]: $\rho = 673.90$–850.15 kg · m^{-3}; (+) Magee [8]: $\rho = 708.00$–1419.50 kg· m^{-3}; (◆) This work: $\rho = 899.34$–901.64 kg· m^{-3}.

The data of Fukushima et al. [7] show deviations as large as 0.36–4.6% in density from the equation of state [2] and are out of the range of Fig. 2, while the other data including the present data are distributed within ±0.2%.

The deviations of available observed densities of HFC-125 from the equation of state [2] are shown in Fig. 3 for the range of densities from 817 to 1684 kg · m^{-3} [7, 8, 10, 12, 16]. The data of Sagawa et al. [12] show density deviations of −0.94 to −0.05%, while the data of Oguchi et al. [16] show deviations of 0.33–0.60% in density. The other data, including the present data, are distributed within ±0.2% in density, as shown in Fig. 3.

5.2. Binary Mixtures of HFC-32 and HFC-125

The deviations of available measured densities for binary mixtures of HFC-32 and HFC-125 from the equation of state [2] are shown in Fig. 4 for the range of densities from 888 to 1255 kg · m^{-3} [17, 23].

The data of Widiatmo et al. [17] show density deviations of −0.23 to 0.61%, the data of Magee and Haynes [23] show density deviations of −0.07 to 0.21%, and the present data show density deviations of −0.22 to 0.59%. In the range of compositions from 0.5 to 0.9 mol fraction of

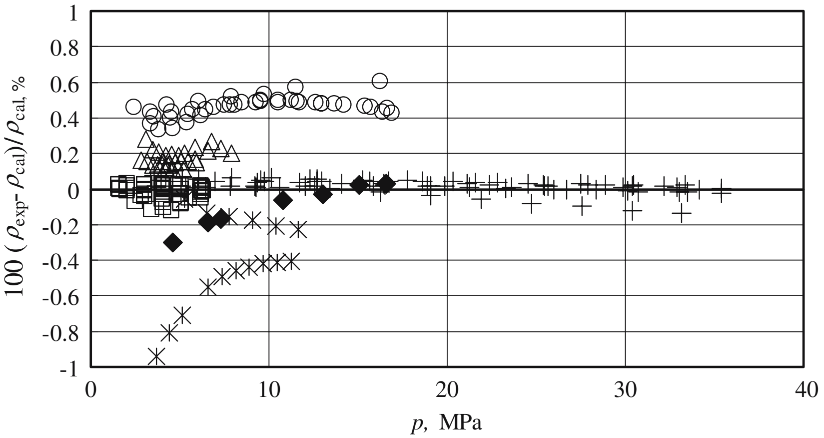


Fig. 3. Density deviations of the present results and available *pVT* properties of HFC-125 from the equation of state [2] (densities from 734 to 1684 $\mathrm{kg\cdot m^{-3}}$). (△) Fukushima et al. [7]: ρ = 804.8–997.4 $\mathrm{kg\cdot m^{-3}}$; (□) Defibaugh and Morrison [10]: ρ = 817.90–1348.40 $\mathrm{kg\cdot m^{-3}}$; (∗) Sagawa et al. [12]: ρ = 734.37–940.01 $\mathrm{kg\cdot m^{-3}}$; (+) Magee [8]: ρ = 1114.60–1683.70 $\mathrm{kg\cdot m^{-3}}$; (○) Oguchi et al. [16]: ρ = 845.08–1145.32 $\mathrm{kg\cdot m^{-3}}$; (◆) This work: ρ = 1402.04–1403.78 $\mathrm{kg\cdot m^{-3}}$.

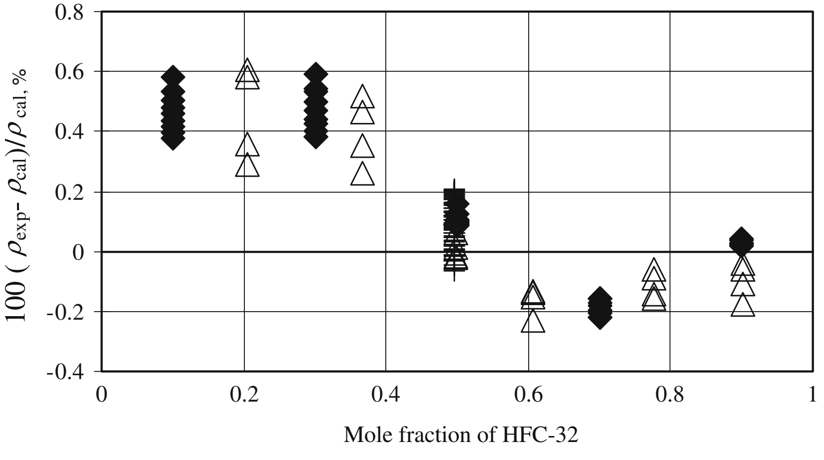


Fig. 4. Density deviations of the data of Widiatmo et al. [17], Magee and Haynes [23], and the present results from the equation of state [2] for binary mixtures of HFC-32 and HFC-125 (densities from 898 to 1255 $\mathrm{kg\cdot m^{-3}}$). (△) Widiatmo et al. [17]: ρ = 940.5 –1254.6 $\mathrm{kg\cdot m^{-3}}$; (+) Magee and Haynes [23]: ρ = 888.12–1033.11 $\mathrm{kg\cdot m^{-3}}$; (◆) This work: ρ = 898.71–1091.20 $\mathrm{kg\cdot m^{-3}}$.

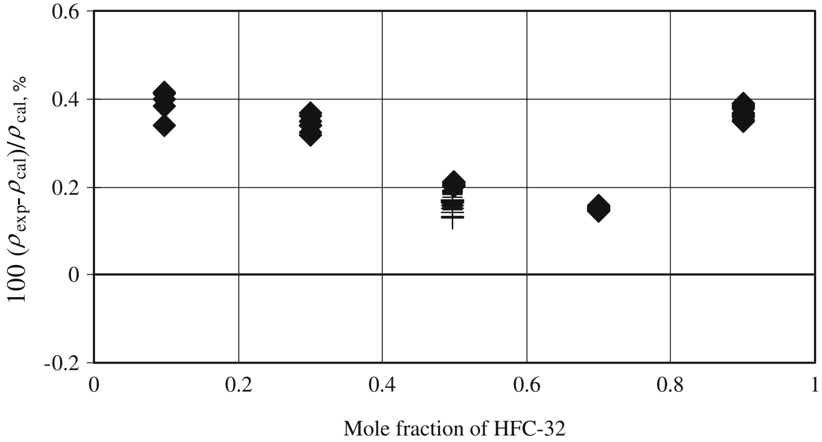


Fig. 5. Density deviations of the data of Magee and Haynes [23] and the present results from the equation of state [2] for binary mixtures of HFC-32 and HFC-125 (densities from 1150 to 1363 kg · m^{-3}). (+) Magee and Haynes [23]: $\rho = 940.5$–1254.6 kg · m^{-3}; (♦) This work: $\rho = 1270.99$–1334.96 kg · m^{-3}.

HFC-32, the density deviations of the available data including the present data are distributed from −0.2 to 0.4%, but in the range of compositions from 0.1 to 0.4 mol fraction of HFC-32, the data of Widiatmo et al. [17] and the present data show deviations of 0.2–0.6%.

In the range of densities from 888 to 1255 kg · m^{-3}, the present data agree with the data of Magee and Haynes [23] within ±0.1% in density.

The density deviations from the equation of state [2] are shown in Fig. 5 for the range of densities from 940 to 1335 kg· m^{-3} [23] for the binary mixtures of HFC-32 and HFC-125. The present data exhibit density deviations of 0.14–0.41%, while the data of Magee and Haynes [23] show density deviations of 0.10–0.19%.

6. CONCLUSION

One hundred and two data points of *pVTx* properties for binary mixtures of HFC-32 and HFC-125 were measured with the use of a constant-volume apparatus in the range of temperatures from 258 to 354 K, pressures from 1.6 to 16.9 MPa, densities from 900 to 1400 kg · m^{-3}, and compositions from 0 to 1 mol fraction of HFC-32, as shown in Table II. The available data for this mixture are compared with the equation of state [2] as shown in Figs. 2–5, and it is found that, in the liquid region for the range of compositions from 0.1 to 0.4 mol fraction of HFC-32, the equation of state [2] is less reliable because of the lack of experimental data.

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