PVTx Properties of Difluoromethane + Pentafluoroethane (R-32 + 125) and Difluoromethane + Pentafluoroethane + 1,1,1,2-Tetrafluoroethane (R-32 + 125 + 134a)

Hideaki Kiyoura, Jiro Takebe, Hirokatsu Uchida,* Haruki Sato, and Koichi Watanabe

Department of Mechanical Engineering, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223, Japan

The experimental pressure–volume–temperature–composition (*PVTx*) properties of a binary refrigerant, a system of difluoromethane (R-32) + pentafluoroethane (R-125), R-32 + 125, and a ternary refrigerant, a system of R-32, R-125, and 1,1,1,2-tetrafluoroethane (R-134a), R-32 + 125 + 134a, have been measured by a constant-volume method coupled with expansion procedures in an extensive range of temperatures, pressures, and densities. Ninety-four *PVTx* property data of the R-32 + 125 system were measured in a range of temperatures from (330 to 440) K, of pressures from (1.8 to 5.2) MPa, and of densities from (67 to 158) kg·m⁻³, of the compositions of 20.089 and 39.977 mass % R-32. One hundred and five *PVTx* property data of the R-32 + 125 + 134a system were measured in a range of temperatures from (1.6 to 5.7) MPa, and of densities from (67 to 166) kg·m⁻³, at compositions of (22.993/25.026/51.981), (23.075/25.112/51.813), (30.018/10.059/59.924), (29.996/29.971/40.033), (33.408/33.257/33.335) mass %.

Introduction

Among our previous publications, we have reported the *PVTx* property measurements for several binary refrigerants: R-22+12 (Takaishi *et al.*, 1982a), R-22+114 (Hasegawa *et al.*, 1985), Halon 1301+R-114 (Hosotani *et al.*, 1988), R-152a+114 (Yada *et al.*, 1988), R-115+114 (Yada *et al.*, 1989a,b), R-22+142b (Kumagai *et al.*, 1991), R-152a+134 (Tamatsu *et al.*, 1992), R-32+134a (Sato *et al.*, 1994a), and R-32+125 (Sato *et al.*, 1996), where R-22 is chlorodifluoromethane, R-12 is dichlorodifluoromethane, R-114 is 1,2-dichlorotetrafluoroethane, Halon 1301 is bromotrifluoromethane, R-152a is 1,1-difluoroethane, R-115 is chloropentafluoroethane, R-142b is 1-chloro-1,1-difluoroethane, and R-134 is 1,1,2,2-tetrafluoroethane.

The binary refrigerant R-32+125 and ternary refrigerant R-32+125+134a have zero ODP (ozone depletion potential). Because of its flammable characteristics, pure R-32 is not considered a suitable working fluid for refrigeration systems. A mixture of R-32 with nonflammable refrigerants, such as R-125 and R-134a, however, may overcome such a drawback in practical application. The present work aims to provide precise *PVTx* property measurements for binary and ternary refrigerants that could meet the requirements to replace R-22.

The previous paper on R-32+125 (Sato *et al.*, 1996) has reported *PVTx* properties with compositions of 50.021, 60.004, and 79.988 mass % R-32; so this paper reports additional *PVTx* property measurements for the compositions of 20.089 and 39.977 mass % R-32 for R-32+125 mixtures and also presents results for five compositions of R-32+125+134a.

Sample Purity

The purities of the sample fluids used are 99.998 mass % and 99.98 mass % for R-32, 99.99 mass % for R-125, and 99.99 mass % and 99.95 mass % for R-134a according to the analysis of the suppliers. We did not purify or analyze the samples.

Experimental Section

The apparatus and procedure have been reported (Takaishi *et al.*, 1982b). In principle the *PVTx* measurements



Figure 1. Experimental apparatus: (A) sample cell; (B) expansion cell; (C) differential pressure detector; (D) main heater; (E) auxiliary heater; (F) stirrer; (G) platinum-resistance thermometer; (H) thermostated bath; (I) vacuum pump; (J) nitrogen cylinder; (K) electric resistance detector; (L) nitrogen-gas damper; (M) precise pressure-controller; (N) air-piston type dead-weight pressure gauge; (O) quartz pressure transducer; (P) digital quartz pressure-transducer computer; (Q) thermometer; (R) pen recorder; (S) PID controller; (T) dc power supply; V_1-V_{11} valves.

of this work were made by the isochoric method coupled with the isothermal expansion procedures at different compositions of mixtures. The apparatus shown in Figure 1 consists of a sample cell (A), an expansion cell (B), a diaphragm type differential pressure detector (C), a platinum resistance thermometer (G) calibrated on ITS-90, a thermostated bath (H), temperature control/measuring devices, and pressure measuring instruments.

The sample cell and the expansion cell are thick-walled spherical vessels made of 304 stainless steel, and their inner volumes were carefully calibrated with pure water; they were (283.368 ± 0.027) cm³ and (55.583 ± 0.007) cm³ at room temperature. These cells and the differential pressure detector are connected with high-pressure valves (V1, V2, V3) and connecting tubes. Their volumes were

also calibrated with pure water; it was (17.092 ± 0.007) cm³ at room temperature. A sample of the mixture is prepared as follows: pure components were carefully filled in the independent vessels which were previously evacuated. The mass of the pure component in each vessel was adjusted to the prescribed mass and weighed by a precise chemical balance. Then the pure components were charged one by one into the sample cell cooled by liquefied nitrogen. The charged mass and composition were determined by the mass difference of each vessel before and after charging the component into the sample cell.

Then the sample cell was connected as shown in Figure 1. After the space of the connecting tube between the sample cell, the expansion cell, and the differential pressure detector was evacuated, the valve V2 was closed, and the valve V1 was opened successively. The temperature in the thermostated bath filled with silicone oil was controlled within ± 2 mK. When thermal equilibrium was reached and with the pressure remaining unchanged over several hours, the temperature and the pressure of the sample fluid were measured.

When a series of pressure measurements along an isochore was completed, the expansion cell was evacuated, the valve V3 was closed, and the valve V2 was opened gradually to expand part of the sample fluid into the expansion cell in the single phase. Throughout the expansion procedure, the two cells were agitated by a rocking device to ensure uniform density and to promote homogeneity of the sample. The valve V1 was closed when the temperature and the pressure became stable. By using these procedures, the *PVTx* measurements and the isothermal expansion procedures are repeated for several isochores under the measured composition at a single charge of the sample in this work.

The mass density along the initial isochore, ρ_0 , was determined by the following equation:

$$\rho_0 = m_0 / (V_a + V_c) \tag{1}$$

where m_0 denotes the mass of the sample, V_a denotes the inner volume of the sample cell, and V_c denotes that of the connecting tube between the sample cell, the expansion cell, and the differential pressure detector. The density after the *N*th expansion, ρ_{N} , was determined as follows:

$$\rho_N = \prod_{i=1}^N k_i m_0 / (V_a + V_c)$$
 (2)

where k_i denotes the volume ratio defined by the following equation

$$k_{i} = V_{a} / (V_{a} + V_{b} + V_{c}) \tag{3}$$

where $V_{\rm b}$ denotes the inner volume of the expansion cell. The variations of the inner volumes $V_{\rm a}$, $V_{\rm b}$, and $V_{\rm c}$ due to thermal expansion and pressure deformation were included. The experimental error of the density after the *N*th expansion procedure is estimated as less than 0.2% after the third expansion, which is the largest *N* value in the present study: it consisted of 0.103% for the estimated uncertainties of the changed mass of the sample, 0.0097% for the volume $V_{\rm a} + V_{\rm b}$, and 0.026% for the k_i ratio.

The overall experimental errors of the present measurements are estimated to be not greater than ± 7 mK in temperature, ± 2 kPa in pressure, $\pm 0.2\%$ in density for each component, and ± 0.02 mass % (R-32 + 125) and ± 0.05 mass % (R-32 + 125 + 134a) in the composition.

Results

Ninety-four PVTx property data of the R-32 + 125 system were measured along eight isochores at tempera-

Table 1. PVTx Properties for the R-32 + 125 System

TK	$ ho/{ m kg} \cdot { m m}^{-3}$	P/MPa	Ζ	<i>T</i> /K	$ ho/{ m kg} \cdot { m m}^{-3}$	P/MPa	Ζ
(a) 20.089 mass % R-32 (36.708 mol % R-32)							
330.000	158.08	2.8820	0.6316	330.000	99.78	2.1673	0.7525
340.000	158.01	3.1009	0.6599	340.000	99.73	2.2882	0.7715
350.000	157.93	3.3126	0.6852	350.000	99.68	2.4048	0.7880
360.000	157.86	3.5189	0.7080	360.000	99.64	2.5200	0.8032
370.000	157.78	3.7203	0.7286	370.000	99.59	2.6333	0.8171
380.000	157.70	3.9194	0.7478	380.000	99.54	2.7449	0.8297
390.000	157.63	4.1141	0.7652	390.000	99.49	2.8553	0.8413
400.000	157.55	4.3064	0.7813	400.000	99.44	2.9639	0.8519
410.000	157.47	4.4954	0.7961	410.000	99.40	3.0719	0.8618
420.000	157.39	4.6836	0.8101	420.000	99.35	3.1790	0.8711
430.000	157.31	4.8688	0.8229	430.000	99.30	3.2851	0.8797
440.000	157.23	5.0529	0.8351	440.000	99.25	3.3904	0.8877
330.000	125.59	2.5261	0.6969	330.000	79.27	1.8280	0.7989
340.000	125.53	2.6874	0.7199	340.000	79.23	1.9178	0.8139
350.000	125.47	2.8451	0.7407	350.000	79.20	2.0072	0.8279
360.000	125.41	2,9983	0.7593	360.000	79.16	2.0931	0.8398
370.000	125.35	3.1507	0.7767	370.000	79.12	2.1787	0.8509
380.000	125.29	3,2986	0.7921	380.000	79.08	2.2628	0.8609
390,000	125 23	3 4 4 4 9	0 8064	390,000	79.04	2 3461	0 8701
400.000	125.17	3.5891	0.8196	400.000	79.01	2.4294	0.8789
410 000	125.11	3 7316	0.8317	410 000	78.97	2 5117	0.8870
420 000	125.04	3 8729	0.8431	420 000	78.93	2 5932	0.8944
430.000	124.98	4 0126	0.0401	420.000	78.89	2 6740	0.0011
440 000	124.00	4.0120	0.0000	440 000	78.85	2 7543	0.0010
410.000	(b) 20	4.1012 077 ma	0.0000	2 (60 576	mol % P	22)	0.0077
240.000	(D) 39. 125 72	977 111d3 99461	0 6660	240 000	95 67	02011	0 7760
340.000	135.73	3.2401	0.0009	250.000	05.07	2.3041	0.7700
260.000	133.07	3.4030 9.6709	0.0920	260.000	85.03	2.3011	0.7912
300.000	135.00	3.0/03	0.7144	300.000	83.39 85 55	2.0233	0.0072
370.000	133.34	3.0024	0.7540	370.000	80.00 95 51	2.1399	0.0207
300.000	133.47	4.0030	0.7521	300.000	65.51	2.0004	0.0320
390.000	135.41	4.2842	0.7692	390.000	85.47	2.9082	0.8443
400.000	135.34	4.4810	0.7848	400.000	85.43	3.0802	0.8547
410.000	135.27	4.6739	0.7990	410.000	80.38	3.1914	0.8043
420.000	135.20	4.8657	0.8124	420.000	85.34	3.3012	0.8/32
430.000	135.13	5.0548	0.8248	430.000	85.30	3.4098	0.8814
440.000	135.06	5.2427	0.8364	440.000	85.26	3.5178	0.8891
330.000	107.89	2.6473	0.7050	330.000	68.10	1.9000	0.8016
340.000	107.84	2.8102	0.7267	340.000	68.06	1.9956	0.8176
350.000	107.79	2.9701	0.7465	350.000	68.03	2.0869	0.8310
360.000	107.73	3.1263	0.7643	360.000	68.00	2.1764	0.8429
370.000	107.68	3.2815	0.7809	370.000	67.97	2.2651	0.8540
380.000	107.63	3.4349	0.7963	380.000	67.94	2.3526	0.8640
390.000	107.58	3.5845	0.8100	390.000	67.90	2.4382	0.8729
400.000	107.52	3.7310	0.8225	400.000	67.87	2.5233	0.8812
410.000	107.47	3.8766	0.8341	410.000	67.84	2.6075	0.8889
420.000	107.42	4.0225	0.8453	420.000	67.80	2.6915	0.8961
430.000	107.36	4.1666	0.8557	430.000	67.77	2.7743	0.9027
440.000	107.31	4.3085	0.8652	440.000	67.73	2.8574	0.9090

tures from (330 to 440) K, at densities from (67 to 158) kg·m⁻³, at pressures from (1.8 to 5.2) MPa, and at mass fractions of 20.089 mass % (36.708 mol %) and 39.977 mass % (60.576 mol %) R-32, as tabulated in Table 1. Figure 2 shows the distribution of the *PVTx* data on a pressure–temperature plane, where the vapor-pressure curves are calculated from the correlations of both pure components (Sato *et al.*, 1994a,b; Zhang *et al.*, 1995). Twenty-three sets of second and third virial coefficients were also determined from the present measurements and tabulated in Table 2.

One hundred and five *PVTx* property data of the R-32 + 125 + 134a system were measured along eight isochores at temperatures from (315 to 440) K, at densities from (67 to 166) kg·m⁻³, at pressures from (1.6 to 5.7) MPa, and at mass fractions of 22.993/25.026/51.981 mass % (38.102/ 17.977/43.921 mol %), 23.075/25.112/51.813 mass % (38.217/ 18.028/43.755 mol %), 30.108/10.059/59.924 mass % (46.230/ 6.715/47.055 mol %), 29.996/29.971/40.033 mass % (47.312/ 20.491/32.196 mol %), and 33.408/33.257/33.335 mass % (51.540/22.239/26.221 mol %), as tabulated in Table 3. Figure 3 shows the distribution of the *PVTx* data on a pressure–temperature plane, where the vapor-pressure curves are calculated from the correlations of each pure component (Sato *et al.*, 1994a,b; Zhang *et al.*, 1995; Piao *et al.*, 1988). Eleven sets of second and third virial coefficients



Figure 2. Distribution of the *PVTx* property measurements for the R-32/125 system on a pressure−temperature plane: (\diamond) 20.089 mass % R-32; (\times) 60.004 mass % R-32 (Sato *et al.*, 1994a); (\Box) 39.977 mass % R-32; (\bigcirc) 79.988 mass % R-32 (Sato *et al.*, 1994a); (△) 50.021 mass % R-32 (Sato *et al.*, 1994a); (-) R-32 (Sato *et al.*, 1994a); (-) R-32 (Sato *et al.*, 1994b); (- -) R-125 (Zhang *et al.*, 1995). C.P. critical point.

Table 2.Second and Third Virial Coefficients for theR-32 + 125 System

	<i>B</i> /	10 ⁻⁶ C/		<i>B</i> /	10 ⁻⁶ C/
<i>T</i> /K	cm³∙mol ^{−1}	dm ⁶ ∙mol ⁻²	<i>T</i> /K	cm³∙mol ^{−1}	dm ⁶ ∙mol ⁻²
		(a) 20.089 n	nass %	R-32	
330	-260.5	0.023 45	390	-169.7	0.017 02
340	-241.3	0.022 10	400	-158.6	0.016 17
350	-223.7	0.020 59	410	-148.3	0.015 26
360	-208.6	0.019 73	420	-138.9	0.014 66
370	-194.1	0.018 53	430	-130.1	0.014 01
380	-181.6	0.017 87	440	-121.9	0.013 51
		(b) 39.977 n	nass %	R-32	
340	-228.1	0.020 27	400	-149.9	0.014 32
350	-213.4	0.020 08	410	-140.2	0.013 50
360	-197.8	0.018 50	420	-131.2	0.012 81
370	-183.6	0.016 87	430	-123.1	0.012 29
380	-171.2	0.015 75	440	-115.3	0.011 68
390	-160.0	0.014 97			

at mass fractions of 22.993/25.026/51.981 mass % were also determined from the present measurements and tabulated in Table 4.

Discussion

The compressibility factors, Z, of the present binary R-32+125 mixtures with compositions of 20.089 and 39.977 mass % R-32 and the present ternary R-32 + 125 + 134a mixture with a composition of 22.993/25.026/51.981 mass % were derived in the superheated vapor region from the measurements by using the following relations:

and

$$Z = MP/\rho RT \tag{4}$$

$$M = \sum_{i=1}^{n} x_i M_i \tag{5}$$

where *P*, ρ , *R*, and *T* denote pressure, mass density, the universal gas constant and temperature, respectively. *M_i* and *x_i* are the molar mass and respective mole fraction of each component. Figure 4 shows a typical example of the compressibility factors thus derived from the present 22.993/25.026/51.981 mass % *PVTx* data. Note that the solid curves in Figure 4 are isotherms.

The present *PVTx* data were represented within the estimated experimental uncertainty by the following truncated virial expression involving the molar density ρ_m :

Table 3.*PVTx* Properties for the R-32 + 125 + 134aSystem

0							
<i>T</i> /K	$ ho/{ m kg}{ m \cdot}{ m m}^{-3}$	P/MPa	Ζ	<i>T</i> /K	$\rho/{\rm kg}{\cdot}{\rm m}^{-3}$	P/MPa	Ζ
(a) 22	2.993/25.02	26/51.98	1 mass	% (38.102	/17.977/43	.921 ma	ol %)
320.000	165.84	1.9456	0.3801	315.000	104.70	1.6650	0.5235
330.000	165.76	2.4200	0.4587	320.000	104.67	1.8616	0.5763
340.000	165.68	2.9708	0.5468	330.000	104.62	2.2573	0.6779
350.000	165.60	3.3409	0.5977	340.000	104.57	2.4077	0.7022
360.000	165.52	3.6014	0.6267	350.000	104.52	2.5547	0.7241
370.000	165.44	3.8544	0.6529	360.000	104.47	2.6985	0.7439
380.000	165.36	4.1004	0.6766	370.000	104.42	2.8391	0.7619
390.000	165.28	4.3395	0.6981	380.000	104.37	2.9786	0.7787
400.000	165.19	4.5753	0.7180	390.000	104.32	3.1150	0.7939
410.000	165.11	4.8082	0.7365	400.000	104.27	3.2477	0.8074
420,000	165.03	5.0370	0.7535	410.000	104.22	3.3788	0.8199
430.000	164.94	5.2634	0.7695	420,000	104.17	3.5081	0.8314
440 000	164 86	5 4874	0 7844	430 000	104 11	3 6361	0.8421
320 000	131 75	1 8898	0 4648	440 000	104.06	3 7629	0.8521
330.000	131.69	2 3459	0.5597	320.000	83.16	1 8107	0 7045
340.000	131.63	2 7/60	0.0007	330.000	83 12	1 9505	0.7040
350.000	131.56	2 9572	0.0004	340.000	83.08	2 0628	0.7572
360.000	131.50	2 1501	0.0000	350.000	83.00	2 1600	0.77/1
370.000	131.50	2 2 2 2 2 9 2	0.0300	360.000	83.04	2.1033	0.7741
200.000	101.44	2 5912	0.7117	270.000	83.00	2 2 2 2 2 2 0	0.7308
200.000	131.37	3.3213	0.7314	370.000	02.90	2.3039	0.0000
390.000	101.01	3.7003	0.7492	300.000	02.92	2.4000	0.0109
400.000	131.24	3.8/89	0.7661	390.000	82.88	2.5907	0.8311
410.000	131.18	4.0528	0.7813	400.000	82.84	2.6917	0.8423
420.000	131.11	4.2248	0.7955	410.000	82.80	2.7906	0.8524
430.000	131.05	4.3943	0.8086	420.000	82.76	2.8892	0.8619
440.000	130.98	4.5621	0.8208	430.000	82.72	2.9862	0.8705
				440.000	82.68	3.0823	0.8786
(b) 23	8.075/25.11	12/51.81	3 mass	% (38.217	/18.028/43	8.755 mo	ol %)
320.000	66.46	1.5743	0.7671	390.000	66.24	2.1491	0.8621
330.000	66.43	1.6617	0.7855	400.000	66.21	2.2264	0.8712
340.000	66.40	1.7463	0.8016	410.000	66.18	2.3058	0.8807
350.000	66.37	1.8352	0.8187	420.000	66.15	2.3814	0.8883
360.000	66.34	1.9165	0.8316	430.000	66.11	2.4554	0.8951
370.000	66.31	1.9966	0.8434	440.000	66.08	2.5307	0.9020
380.000	66.28	2.0751	0.8539				
(c) 3	0.018/10.0	59/59.92	24 mass	% (46.230	0/6.715/47.	055 mol	%)
320.000	165.93	1.9221	0.3488	390.000	165.36	4.5190	0.6752
330.000	165.85	2.4021	0.4229	400.000	165.28	4.7707	0.6954
340.000	165.77	2.9291	0.5008	410.000	165.20	5.0127	0.7132
350.000	165.69	3.4506	0.5734	420.000	165.12	5.2535	0.7300
360.000	165.61	3.7313	0.6031	430.000	165.03	5.4885	0.7453
370.000	165.53	4.0032	0.6299	440.000	164.95	5.7179	0.7592
380.000	165.45	4.2639	0.6536				
(d) 20).996/29.97	71/40.03	3 mass	% (47.312	2/20.492/32	2.196 ma	ol %)
320.000	165.64	2.1460	0.3996	390.000	165.07	4.5499	0.6975
330,000	165.56	2.6628	0.4810	400.000	164.99	4.8001	0.7178
340.000	165.48	3,2506	0.5702	410.000	164.91	5.0390	0.7355
350 000	165 40	3 5202	0.6002	420 000	164.83	5 2723	0 7516
360.000	165 32	3 7894	0.6284	430.000	164 74	5 5210	0.7692
370.000	165.24	4 0569	0.0204	440 000	164.66	5 7488	0.7831
380.000	165.16	4.3040	0.0343	440.000	104.00	5.7400	0.7051
(e) 33	20 40	07/33.33	o mass	% (51.540	/22.239/26	.221 mo	1%)
320.000	/9.46	1.9145	0.7268	390.000	/9.20	2.6/88	0.8372
330.000	79.42	2.0284	0.7471	400.000	79.16	2.7784	0.8470
340.000	79.39	2.1426	0.7663	410.000	79.12	2.8672	0.8532
350.000	79.35	2.2508	0.7823	420.000	79.08	2.9742	0.8644
360.000	79.31	2.3577	0.7971	430.000	79.04	3.0828	0.8756
370.000	79.27	2.4751	0.8146	440.000	79.00	3.1779	0.8825
380.000	79.23	2.5778	0.8264				
			4.1.1	D .	~		

$$(Z-1)/\rho_m = B + C\rho_m \tag{6}$$

One of the typical examples of the results represented by eq 6 is shown in Figure 5 for the R-32 + 125 + 134a (22.993/25.026/51.981 mass %) mixture, where the intersection with the ordinate corresponds to the second virial coefficient *B* and the slope of each isotherm represents the third virial coefficient *C*. The second and third virial coefficient values thus determined from the present measurements are listed in Tables 2 and 4. We have estimated that the uncertainty for the determined *B* and *C* values are not greater than $\pm 3\%$ and $\pm 30\%$ for the present mixtures.



Figure 3. Distribution of the *PVTx* property measurements for the R-32 + 125 + 134a system on a pressure−temperature plane: (◊) 22.993/25.026/51.981 mass %; (*) 23.075/25.112/51.813 mass %; (×) 29.996/29.971/40.033 mass %; (△) 30.018/10.059/59.924 mass %; (○) 33.408/33.257/33.335 mass %; (─) R-32 (Sato *et al.*, 1994b); (---) R-125 (Zhang *et al.* 1995); (···) R-134a (Piao *et al.*, 1988). C.P. critical point.



Figure 4. Departure from the ideal gas for R-32 + 125 + 134a (22.993/25.026/51.981 mass %).

Table 4. Second and Third Virial Coefficients for the $R{-}32+125+134a$ (22.993/25.026/51.981 mass %) System

<i>T</i> /K	B/cm³⋅mol ⁻¹	10^{-6} C/dm ⁶ ·mol ⁻²
340	-275.3	0.024 36
350	-258.9	0.025 83
360	-239.9	0.023 77
370	-223.4	0.022 26
380	-207.5	0.020 35
390	-193.2	0.018 69
400	-180.4	0.017 41
410	-169.1	0.016 52
420	-158.4	0.015 54
430	-148.7	0.014 82
440	-139.8	0.014 20

Figures 6 and 7 show the temperature dependence of the *B* and *C* values determined for the binary R-32 + 125 mixtures with different compositions. For R-32, the reported *B* and *C* values (Sato *et al.*, 1994b) and *B* values (Zhang *et al.*, 1995) are included in Figures 6 and 7, while a similar comparison with the reported values for R-125 (Zhang *et al.*, 1995) and those for R-32 + 125 at mass fractions of 50.021, 60.004, and 79.988 mass % (Sato *et al.*, 1996) are also included.

Figures 8 and 9 show the temperature dependence of *B* and *C* values determined for the ternary R-32 + 125 + 134a mixtures with 22.993/25.026/51.981 mass % composition. For R-134a, the reported *B* and *C* values (Goodwin and Moldover, 1990) are included in Figures 8 and 9.



Figure 5. Relation of $(Z - 1)/\rho$ vs ρ for R-32 + 125 + 134a (22.993/25.026/51.981 mass %).



Figure 6. Temperature dependence of second virial coefficients for R-32 + 125: (□) 20.089 mass % R-32; (○) 60.004 mass % R-32 (Sato *et al.*, 1994a); (△) 39.977 mass % R-32; (×) 79.988 mass % R-32 (Sato *et al.*, 1994a); (◇) 50.021 mass % R-32 (Sato *et al.*, 1994a); (●) R-32 (Sato *et al.*, 1994b); (▲) R-32 (Zhang *et al.*, 1995); (■) R-125 (Zhang *et al.*, 1995); (−, …) Kiyoura *et al.*, 1996.



Figure 7. Temperature dependence of third virial coefficients for R-32 + 125: (*) 20.089 mass % R-32; (△) 60.004 mass % R-32 (Sato *et al.*, 1994a); (◇) 39.977 mass % R-32; (○) 79.988 mass % R-32 (Sato *et al.*, 1994a); (□) 50.021 mass % R-32 (Sato *et al.*, 1994a); (●) R-32 (Sato *et al.*, 1994b); (−, …) Kiyoura *et al.*, 1996.

Note that the solid and the dashed curves in Figures 6–9 are the calculated results by our own correlations (Kiyoura *et al.*, 1996) developed for each mixture and pure component. The solid curves denote the correlations for the pure components, and the dashed curves, those for the mixture components. These correlations express the *PVTx* measurements of this work within $\pm 0.2\%$ and the virial coefficient values of this work within $\pm 0.7\%$ for *B* and $\pm 10\%$ for *C* for R-32 + 125 mixtures, whereas the *PVTx*



Figure 8. Temperature dependence of second virial coefficients for R-32 + 125 + 134a: (○) 22.993/25.026/51.981 mass %; (●) R-32 (Sato *et al.*, 1994b); (▲) R-32 (Zhang *et al.*, 1995); (■) R-125 (Zhang *et al.*, 1995); (●) R-134a (Goodwin and Moldover, 1990); (−, …) Kiyoura *et al.*, 1996.



Figure 9. Temperature dependence of determined third virial coefficients for R-32/125/134a: (▲) 22.993/25.026/51.981 mass %; (●) R-32 (Sato *et al.*, 1994b); (*) R-134a (Goodwin and Moldover, 1990); (-, ...) Kiyoura *et al.*, 1996.

measurements are within $\pm 1.2\%$, $\pm 1.6\%$ for *B*, and $\pm 4.8\%$ for *C* for R-32 + 125 + 134a mixtures.

The *PVTx* measurements in our work also agree within $\pm 0.3\%$ with a recent model for R-32 + 125 mixtures (Zhang *et al.*, 1996), while the second virial efficients agree within $\pm 1.1\%$ and the third virial efficients within $\pm 11\%$ with their model.

Conclusion

Ninety-four *PVTx* property data of the binary R-32 + 125 mixture were measured along eight isochores. One hundred and five *PVTx* property data of the ternary R-32 + 125 + 134a mixture were measured along eight isochores. Twenty-three sets of second and third virial coefficients were determined for this binary mixture with compositions of 20.089 and 39.977 mass % R-32, and eleven sets of second and third virial coefficients were also determined for the R-32 + 125 + 134a mixture with a composition of

22.993/25.026/51.981 mass %.

Acknowledgment

We are indebted to Showa Denko Co. Ltd., Asahi Glass Co. Ltd., and Daikin Industries, Ltd., for kindly furnishing the sample refrigerants and to the National Research Laboratory of Metrology, Tsukuba, for the calibration of the thermometer.

Literature Cited

- Goodwin, A. R. H.; Moldover, M. R. Thermodynamic properties of gaseous refrigerants from speed of sound measurements. I. Apparatus, model and results for 1,1,1,2-tetrafluoroethane R134a. J. Chem. Phys. 1990, 93, 2741–2753.
- Hasegawa, N.; Uematsu, M.; Watanabe, K. Mesurements of PVTx Properties for the R22 + R114 System. J. Chem. Eng. Data **1985**, 30, 32-38.
- Hosotani, S.; Maezawa, Y.; Uematsu, M.; Watanabe, K. Measurements of PVTx Properties for the R13B1 + R114 System. *J. Chem. Eng. Data* **1988**, *33*, 20–23.
- Kiyoura, H.; Takebe, J.; Uchida, H.; Sato, H.; Watanabe, K. Measurements of PVTx Property and Development of Virial Equation of State for Ternary Mixtures R-32 + R-125 + R-134a System. Proc. Jpn. Joint Conf. Air-conditioning and Refrig., 30th 1996, 30, 125– 128 [in Japanese].
- Kumagai, K.; Yada, N.; Sato, H.; Watanabe, K. Measurements of PVTx Properties for the Binary Refrigerant HCFC-142b + HCFC-22 System. J. Chem. Eng. Data 1991, 36, 236-240.
 Piao, C.-C.; Sato, H.; Watanabe, K. A Study of Thermodynamic
- Piao, C.-C.; Sato, H.; Watanabe, K. A Study of Thermodynamic Properties of CFC Alternative R134a. *Proc. Jpn. Symp. Thermophys. Prop., 9th* **1988**, 235–238 [in Japanese].
- Sato, T.; Kiyoura, H.; Sato, H.; Watanabe, K. PVTx Properties of the Binary Difluoromethane + 1,1,1,2-Tetrafluoroethane System. J. Chem. Eng. Data 1994a, 39, 855–858.
- Sato, T.; Sato, H.; Watanabe, K. PVT Property Measurements for Difluoromethane. J. Chem. Eng. Data 1994b, 39, 851-854.
- Sato, T.; Kiyoura, H.; Sato, H.; Watanabe, K. Measurements of PVTx Properties of Refrigerant Mixture HFC-32 + HFC-125 in Gaseous Phase. Int. J. Thermophys. **1996**, *17*, 43–54.
- Takaishi, Y.; Kagawa, N.; Uematsu, M.; Watanabe, K. Volumetric Properties of The Binary Mixtures Dichlorodifluoromethane + Chlorodifluoromethane. Proc. ASME Symp. Thermophys. Prop., 8th 1982a, 2, 387–395.
- Takaishi, Y.; Uematsu, M.; Watanabe, K. Measurements of the PVTx Properties of Binary Refrigerant R12 + R22 System (1st. report, A mixture of 80 wt% R12 + 20 wt% R22) Bull. JSME 1982b, 25, 944– 951.
- Tamatsu, T.; Sato, T.; Sato, H.; Watanabe, K. PVTx Properties of the Binary 1,1-Difluoroethane + 1,1,2,2-Tetrafluoroethane System. *J. Chem. Eng. Data* **1992**, *37*, 512–515.
- Yada, N.; Uematsu, M.; Watanabe, K. Study of the PVTx Properties for Binary R152a + R114 System. *Trans. Jpn. Assoc. Refrig.* 1988, 5, 107–116 [in Japanese].
- Yada, N.; Uematsu, M.; Watanabe, K. Analysis of PVTx Measurements for Binary Mixtures of R115 and R114. *Int. J. Thermophys.* 1989a, 10, 639–648.
- Yada, N.; Uematsu, M.; Watanabe, K. PVTx Properties of the Binary System R115 + R114 and Its Thermodynamic Behavior. *J. Chem. Eng. Data* **1989b**, *34*, 431–434.
- Zhang, H.-L.; Sato, H.; Watanabe, K. Second Virial Coefficients for R-32, R-125, R-134a, R-143a, R-152a, and Their Binary Mixtures. Proc. Int. Congr. Refrig., 19th 1995, IVa, 622–629.
- Zhang, H.-L.; Sato, H.; Watanabe, K. Gas Phase PVT Properties for Difluoroethane + Pentafluoroethane (R-32 + 125) System. *J. Chem. Eng. Data* **1996**, *41*, 1401–1408.

Received for review March 11, 1996. Accepted August 13, $1996.^{\circ}$ The Ministry of Education, Science, and Culture, Japan, has partially supported this study as Grant-in-Aid 04402025.

JE960095D

[®] Abstract published in Advance ACS Abstracts, September 15, 1996.