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PVTx Properties of the Binary Difluoromethane + 1,1,1,2-Tetrafluoroethane System

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Pressure–volume–temperature–composition (*PVTx*) properties of the binary refrigerant difluoromethane (HFC-32) + 1,1,1,2-tetrafluoroethane (HFC-134a) have been measured by means of a constant-volume apparatus coupled with an expansion procedure. Two hundred sixty *PVTx* values were measured in a range of temperatures from 320 to 440 K, pressures from 1.5 to 6.2 MPa, and densities from 61 to 183 kg·m^{-3}.

Introduction

In our previous publications, we reported the *PVTx* measurements for several binary refrigerants: HCFC-22 (chlorodifluoromethane) + CFC-12 (dichlorodifluoromethane) (*1*), HCFC-22 + CFC-114 (1,2-dichlorotetrafluoroethane) (*2*), Halon 1301 (bromotrifluoromethane) + CFC-114 (*3*), HFC-152a (1,1-difluoroethane) + CFC-114 (*4*), CFC-115 (chloropentafluoroethane) + CFC-114 (*5, 6*), HCFC-22 + HCFC-142b (1-chloro-1,1-difluoroethane) (*7*), HFC-152a + HFC-134 (1,1,2,2-tetrafluoroethane) (*8*).

The binary refrigerant HFC-32 + HFC-134a has zero ozone-depletion potential (ODP). Because of its flammable characteristics, however, HFC-32 is not considered as a suitable working fluid for air-conditioning systems. The mixture of HFC-32 with a nonflammable refrigerant, such as HFC-134a, therefore, may overcome this drawback for practical application. This mixture may be a suitable replacement for the refrigerant HCFC-22, which is currently being used in air-conditioning and heat-pumping equipment but expected to be phased out by the year 2020.

Since there exist no single set of measurements on this data, the present work is aimed at providing precise *PVTx* measurements.

Sample and Sample Purification

The purities of the sample fluids used are 99.998 mass % for HFC-32 and 99.99 mass % for HFC-134a according to the analysis of the suppliers. We did not purify nor analyze the samples ourselves.

Experimental Section

The apparatus and procedure have been reported by Takaishi et al. (*9, 10*) and also discussed in detail in our earlier publications (*1–8, 11*). The isochoric method coupled with expansion procedures was applied for measuring the dew-point pressures and *PVT* properties at different compositions. The apparatus shown in Figure 1 consists of a sample cell (A), an expansion cell (B), a differential pressure detector (C), a platinum resistance thermometer (F) calibrated on ITS-90, a thermostated bath (G), temperature control/measuring devices, and pressure measuring instruments.

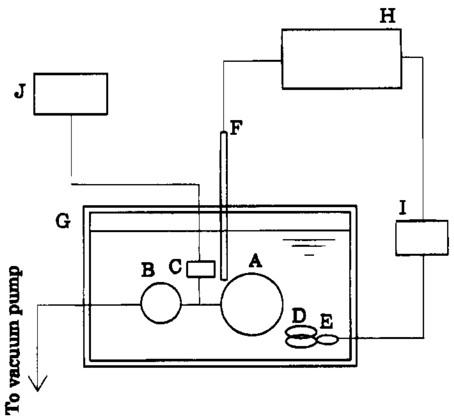

Figure 1. Experimental apparatus: (A) sample cell, (B) expansion cell, (C) differential pressure detector, (D) main heater, (E) auxiliary heater, (F) platinum-resistance thermometer, (G) thermostated bath, (H) thermometer, (I) PID controller, (J) pressure gauge.

The inner volumes of the sample cell and expansion cell were carefully calibrated with pure water; they were 283.368 ± 0.0027 cm^3 and 55.583 ± 0.007 cm^3 at room temperature, respectively. The temperature in the thermostated bath filled with silicone oil was controlled to within ±2 mK. After confirming thermal equilibrium and that the pressure remained constant over several hours, the temperature and the pressure were measured.

When a series of pressure measurements along an isochore was completed, we expanded part of the sample fluid into the expansion cell in the single phase to obtain another isochore, with composition unchanged. The valves between the sample cell and expansion cell were closed when the temperature and the pressure became stable.

The experimental errors of the present measurements are estimated to be not greater than ±7 mK in temperature, ±2 kPa in pressure, ±0.20% in density, and ±0.02 mass % in each composition.

Results

Two hundred and sixty density values were measured along 20 isochores at temperatures from 320 to 440 K, pressures from 1.5 to 6.2 MPa, and mass fractions w of 0.20 (mole fraction $x = 0.329\ 09$), 0.25 ($x = 0.395\ 34$), 0.40 ($x = 0.566\ 88$), 0.60 ($x = 0.746\ 42$), and 0.80 ($x = 0.887\ 13$) HFC-32, as tabulated in Table 1. For distinguishing the data under vapor–liquid equilibrium from those in the single phase region, we have graphically analyzed the

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Table 1. Density ϱ for HFC-32 (1) + HFC-134a (2)

T/K	P/MPa	ϱ/(kg·m^{-3})	T/K	P/MPa	ϱ/(kg·m^{-3})	T/K	P/MPa	ϱ/(kg·m^{-3})	T/K	P/MPa	ϱ/(kg·m^{-3})
					$w_1 = 0.20$						
320.000	1.6500	182.18^a	320.000	1.6216	144.74^a	320.000	1.5927	114.99^a	320.000	1.5595	91.35^a
330.000	2.0696	182.10^a	330.000	2.0306	144.67^a	330.000	1.9947	114.93^a	330.000	1.9522	91.31^a
340.000	2.5605	182.01^a	340.000	2.5149	144.60^a	340.000	2.4587	114.88^a	340.000	2.1449	91.27
350.000	3.1391	181.92^a	350.000	2.9820	114.82	350.000	2.6365	144.53	350.000	2.2745	91.22
360.000	3.5837	181.83	360.000	3.2109	114.77	360.000	2.8041	144.46	360.000	2.4003	91.18
370.000	3.8828	181.74	370.000	3.4315	144.39	370.000	2.9679	114.71	370.000	2.5215	91.14
380.000	4.1705	181.65	380.000	3.6454	114.66	380.000	3.1274	144.32	380.000	2.6416	91.09
390.000	4.4513	181.56	390.000	3.8543	144.25	390.000	3.2831	114.60	390.000	2.7587	91.05
400.000	4.7253	181.47	400.000	4.0590	144.18	400.000	3.4364	114.55	400.000	2.8741	91.18
410.000	4.9936	181.38	410.000	4.2605	144.10	410.000	3.5879	114.49	410.000	2.9884	90.96
420.000	5.2591	181.29	420.000	4.4588	144.03	420.000	3.7369	114.43	420.000	3.1003	90.91
430.000	5.5202	181.20	430.000	4.6546	143.96	430.000	3.8839	114.37	430.000	3.2119	90.87
440.000	5.7779	181.10	440.000	4.8473	143.89	440.000	4.0293	114.32	440.000	3.3221	90.82
					$w_1 = 0.25$						
320.000	1.7411	165.08^a	320.000	1.7074	131.15^a	320.000	1.6727	104.19^a	320.000	1.6374	82.78^a
330.000	2.1750	164.10^a	330.000	2.1298	131.08^a	330.000	2.0878	104.14^a	330.000	1.9683	82.74
340.000	2.6814	164.92^a	340.000	2.6254	131.02^a	340.000	2.4207	104.09	340.000	2.0905	82.70
350.000	3.2652	164.84^a	350.000	2.9497	130.96	350.000	2.5795	104.04	350.000	2.2074	82.66
360.000	3.5707	164.76	360.000	3.1587	130.90	360.00	2.7338	103.99	360.000	2.3223	82.62
370.000	3.8424	164.68	370.000	3.3600	130.83	370.000	2.8830	103.94	370.000	2.4343	82.58
380.000	4.1054	164.59	380.000	3.5567	130.77	380.000	3.0289	103.89	380.000	2.5448	82.54
390.000	4.3617	164.51	390.000	3.7480	130.70	390.000	3.1727	103.84	390.000	2.6529	82.50
400.000	4.6125	164.43	400.000	3.9351	130.64	400.000	3.3149	103.79	400.000	2.7590	82.62
410.000	4.8595	164.35	410.000	4.1211	130.57	410.000	3.4539	103.74	410.000	2.8646	82.42
420.000	5.1020	164.27	420.000	4.3033	130.51	420.000	3.5906	103.69	420.000	2.9685	82.38
430.000	5.3432	164.18	430.000	4.4832	130.44	430.000	3.7269	103.63	430.000	3.0707	82.34
440.000	5.5793	164.10	440.000	4.6616	130.38	440.000	3.8619	103.58	440.000	3.1733	82.29
					$w_1 = 0.40$						
320.000	2.0128	156.83^a	320.000	2.2020	124.57^a	320.000	1.9253	98.99^a	320.000	1.8708	78.64^a
330.000	2.5044	156.75^a	330.000	2.4433	124.54^a	330.000	2.3818	98.94^a	330.000	2.1127	78.60
340.000	3.0724	156.68^a	340.000	2.9653	124.48^a	340.000	2.6076	98.89	340.000	2.2416	78.57
350.000	3.5820	156.60	350.000	3.1897	124.42	350.000	2.7736	98.85	350.000	2.3634	78.53
360.000	3.8730	156.53	360.000	3.4052	124.36	360.000	2.9339	98.80	360.000	2.4840	78.49
370.000	4.1544	156.45	370.000	3.6159	124.30	370.000	3.0899	98.75	370.000	2.6011	78.46
380.000	4.4279	156.37	380.000	3.8202	124.24	380.000	3.2431	98.70	380.000	2.7162	78.42
390.000	4.6959	156.30	390.000	4.0206	124.18	390.000	3.3946	98.66	390.000	2.8300	78.38
400.000	4.9578	156.22	400.000	4.2160	124.11	400.000	3.5423	98.61	400.000	2.9428	78.34
410.000	5.2161	156.14	410.000	4.4111	124.05	410.000	3.6879	98.56	410.000	3.0536	78.30
420.000	5.4706	156.06	420.000	4.6021	123.99	420.000	3.8327	98.51	420.000	3.1626	78.26
430.000	5.7211	155.98	430.000	4.7903	123.93	430.000	3.9753	98.46	430.000	3.2714	78.22
440.000	5.9700	155.90	440.000	4.9769	123.86	440.000	4.1169	98.41	440.000	3.3788	78.18
					$w_1 = 0.60$						
320.000	2.3306	137.42^a	320.000	2.2896	109.17^a	320.000	2.2356	86.74^a	320.000	2.0531	68.91
330.000	2.8936	137.35^a	330.000	2.8318	109.12^a	330.000	2.5388	86.69	330.000	2.1792	68.88
340.000	3.5005	137.28^a	340.000	3.1146	109.07	340.000	2.7026	86.65	340.000	2.3022	68.84
350.000	3.7887	137.22	350.000	3.3279	109.02	350.000	2.8614	86.61	350.000	2.4209	68.81
360.000	4.0664	137.15	360.000	3.5349	108.97	360.000	3.0157	86.57	360.000	2.5375	68.78
370.000	4.3358	137.09	370.000	3.7359	108.91	370.000	3.1678	86.53	370.000	2.6513	68.75
380.000	4.5989	137.02	380.000	3.9330	108.86	380.000	3.3158	86.49	380.000	2.7633	68.71
390.000	4.8563	136.95	390.000	4.1265	108.81	390.00	3.4619	86.45	390.000	2.8739	68.68
400.000	5.1092	136.88	400.000	4.3168	108.75	400.000	3.6057	86.40	400.000	2.9829	68.65
410.000	5.3582	136.81	410.000	4.5046	108.70	410.000	3.7474	86.36	410.000	3.0910	68.61
420.000	5.6037	136.75	420.000	4.6897	108.64	420.000	3.8889	86.32	420.000	3.1982	68.58
430.000	5.8468	136.68	430.000	4.8730	108.59	430.000	4.0268	86.27	430.000	3.3035	68.54
440.000	6.0876	136.61	440.000	5.0548	108.53	440.000	4.1648	86.23	440.000	3.4087	68.51
					$w_1 = 0.80$						
320.000	2.6313	122.38^a	320.000	2.5989	97.23^a	320.000	2.4549	77.24	320.000	2.1079	61.37
330.000	3.2725	122.32^a	330.000	3.0111	97.18	330.000	2.6188	77.21	330.000	2.2304	61.34
340.000	3.6647	122.26	340.000	3.2249	97.14	340.000	2.7769	77.17	340.000	2.3496	61.31
350.000	3.9423	122.20	350.000	3.4309	97.09	350.000	2.9311	77.14	350.000	2.4664	61.28
360.000	4.2106	122.15	360.000	3.6314	97.04	360.000	3.0814	77.10	360.000	2.5783	61.25
370.000	4.4713	122.09	370.000	3.8282	96.10	370.000	3.2292	77.06	370.000	2.6904	61.22
380.000	4.7273	122.03	380.000	4.0198	96.95	380.000	3.3743	77.02	380.000	2.8006	61.19
390.000	4.9776	121.97	390.000	4.2085	96.90	390.000	3.5177	76.99	390.000	2.9087	61.16
400.000	5.2257	121.91	400.000	4.3949	96.85	400.000	3.6587	76.95	400.000	3.0171	61.13
410.000	5.4687	121.84	410.000	4.5798	96.81	410.000	3.7976	76.91	410.000	3.1224	61.10
420.000	5.7095	121.78	420.000	4.7608	96.76	420.000	3.9352	76.87	420.000	3.2285	61.07
430.000	5.9470	121.72	430.000	4.9405	96.71	430.000	4.0720	76.83	430.000	3.3323	61.04
440.000	6.1818	121.66	440.000	5.1181	96.66	440.000	4.2070	76.79	440.000	3.4363	61.01

[a] Under vapor–liquid equilibrium.

measured results along each isochore so as to identify the reflection point corresponding to the saturation conditions. 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 (*11*, *12*).

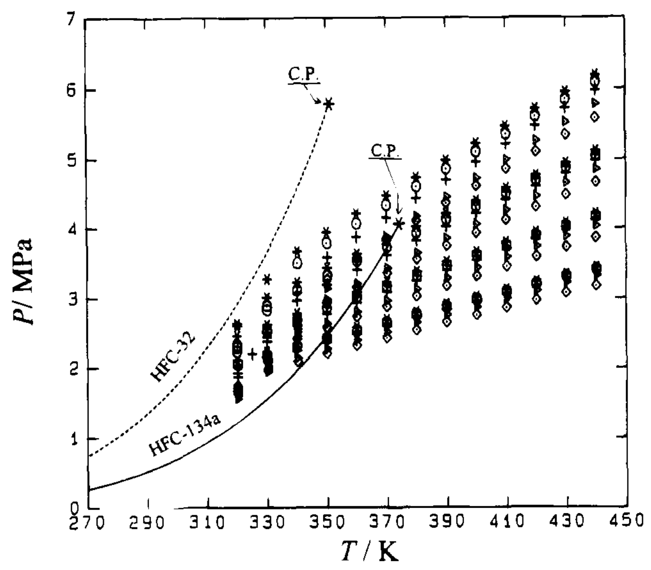

Figure 2. Distribution of the *PVTx* measurements on a pressure–temperature plane: (⊳) $w_1 = 0.20$, (◇) $w_1 = 0.25$, (+) $w_1 = 0.40$, (⊙) $w_1 = 0.60$, (*) $w_1 = 0.80$, (- - -) HFC-32 (*11*), (—) HFC-134a (*12*).

Table 2. Second Virial Coefficients *B* and Third Virial Coefficients *C* for HFC-32 (1) + HFC-134a (2)

T/K	*B*/(cm³·mol⁻¹)	*C*/(dm⁶·mol⁻²)	*T*/K	*B*/(cm³·mol⁻¹)	*C*/(dm⁶·mol⁻²)
$w_1 = 0.20$					
350.00	−279.9	0.027 92	400.00	−196.6	0.019 42
360.00	−258.8	0.025 20	410.00	−183.8	0.018 08
370.00	−241.3	0.023 80	420.00	−172.6	0.017 16
380.00	−224.8	0.022 07	430.00	−161.8	0.016 14
390.00	−210.1	0.020 72	440.00	−152.0	0.015 25
$w_1 = 0.25$					
340.00	−292.1	0.028 93	400.00	−190.5	0.018 75
350.00	−270.6	0.026 72	410.00	−178.3	0.017 56
360.00	−250.9	0.024 53	420.00	−167.2	0.016 56
370.00	−233.8	0.023 03	430.00	−157.3	0.015 85
380.00	−217.9	0.021 44	440.00	−147.3	0.014 79
390.00	−203.6	0.020 02			
$w_1 = 0.40$					
340.00	−269.0	0.026 85	400.00	−175.2	0.016 68
350.00	−248.1	0.023 69	410.00	−164.2	0.015 70
360.00	−230.5	0.021 98	420.00	−154.1	0.014 85
370.00	−215.0	0.020 66	430.00	−144.5	0.013 90
380.00	−200.8	0.019 34	440.00	−135.8	0.013 17
390.00	−187.5	0.018 01			
$w_1 = 0.60$					
330.00	−267.7	0.027 46	390.00	−172.5	0.016 33
340.00	−246.0	0.024 07	400.00	−161.7	0.015 36
350.00	−227.2	0.021 43	410.00	−151.6	0.014 44
360.00	−211.5	0.019 99	420.00	−142.1	0.013 48
370.00	−197.1	0.018 60	430.00	−134.0	0.012 94
380.00	−184.3	0.017 46	440.00	−126.0	0.012 26
$w_1 = 0.80$					
320.00	−270.3	0.028 35	390.00	−160.6	0.014 80
330.00	−246.4	0.023 54	400.00	−150.3	0.013 76
340.00	−226.8	0.020 70	410.00	−141.5	0.013 18
350.00	−210.5	0.019 12	420.00	−132.7	0.012 31
360.00	−196.8	0.018 23	430.00	−124.9	0.011 74
370.00	−183.5	0.016 89	440.00	−117.4	0.011 05

Fifty-seven second and third virial coefficients were also determined from the present measurements and are tabulated in Table 2, where the temperature is given according to the temperature scale ITS-90.

Discussion

The compressibility factors, Z, for HFC-32 (1) + HFC-134a (2) with compositions of $w_1 = 0.20$, 0.25, 0.40, 0.60, and 0.80 were derived in the superheated vapor region from the measurements by using the following relations:

$$Z = P/\varrho RT \qquad (1)$$

and

$$R = R_0/(x_1M_1 + x_2M_2) \qquad (2)$$

where P, ϱ, and T denote pressure, density, and temperature, respectively. R_0 is the universal gas constant, $R_0 = 8.31451$ J/(mol·K), and x_1, x_2 and M_1, M_2 are mole fraction and molar mass of each component, respectively. Figure 3 shows a typical example of the compressibility factors derived for $w_1 = 0.25$.

The *PVTx* results were represented within the estimated experimental uncertainty by the following truncated virial expression:

$$(Z - 1)/\varrho = B + C\varrho \qquad (3)$$

One of the typical examples of the results represented by eq 3 is shown in Figure 4 for the $w_1 = 0.25$ 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 Table 2. We have estimated

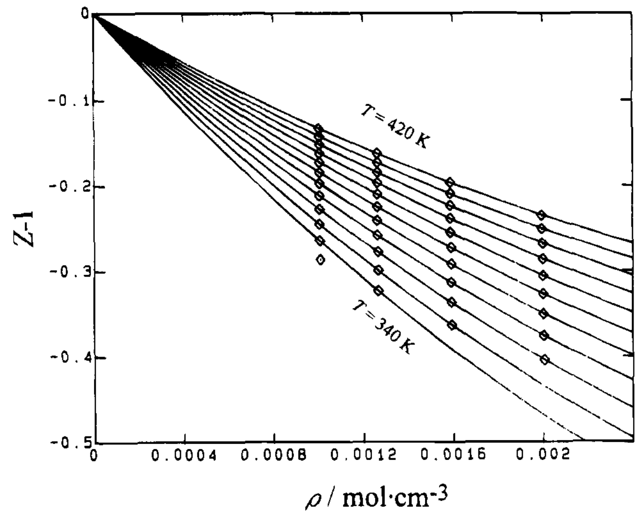

Figure 3. $Z - 1$ at different temperatures for mixtures with $w_1 = 0.25$ for HFC-32 (1) + HFC-134a (2).

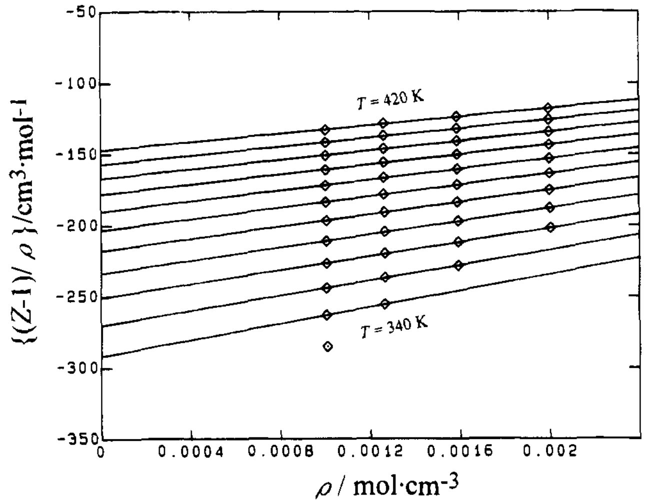

Figure 4. Relation of $(Z - 1)/\varrho$ vs ϱ for mixtures with $w_1 = 0.25$ at different temperatures.

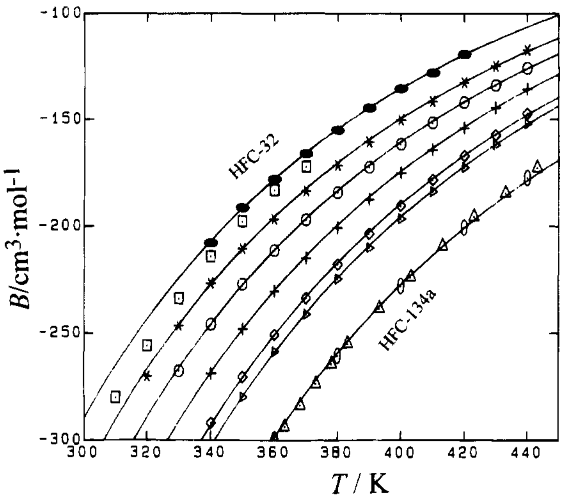

Figure 5. Temperature dependence of the second virial coefficients for HFC-32 (1) + HFC-134a (2): (▷) w_1 = 0.20, (·) w_1 = 0.25, (+) w_1 = 0.40, (⊙) w_1 = 0.60, (*) w_1 = 0.80, (●) w_1 = 1.00 (*11*), (⊙) Goodwin and Moldover (HFC-134a) (*14*), (△) Tillner-Roth and Baehr (HFC-134a) (*15*), (⊡) Qian et al. (HFC-32) (*13*), (—) Sato et al. (*16*).

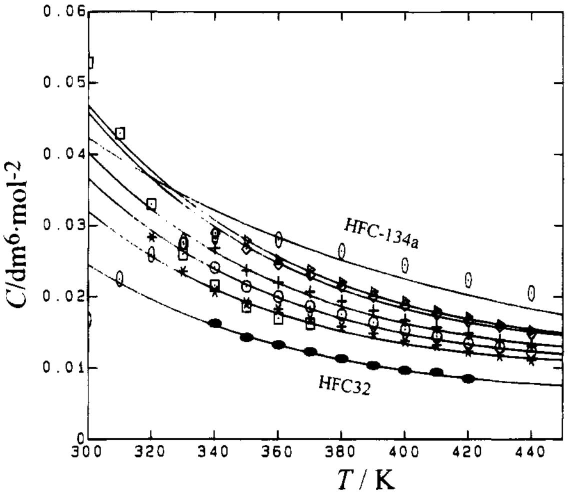

Figure 6. Temperature dependence of determined third virial coefficients for HFC-32 (1) + HFC-134a (2): (▷) w_1 = 0.20, (·) w_1 = 0.25, (+) w_1 = 0.40, (⊙) w_1 = 0.60, (*) w_1 = 0.80,(●) w_1 = 1.00 (*11*), (⊙) Goodwin and Moldover (HFC-134a) (*14*), (⊡) Qian et al. (HFC-32), (*15*) (—) Sato et al. (*16*).

that the uncertainty for the determined B and C values to be not greater than ±3% and ±6% for the present mixtures, respectively, although we have claimed them to be ±1.5% and ±3% for the pure components (*11*).

Figures 5 and 6 show the temperature dependence of B and C at different compositions, respectively. The values of B and C are the first set of values for this important binary mixture in a wide range of temperatures. For HFC-32, the B and C values of Qian et al. (*13*) are included in Figures 5 and 6. A comparison with the values for HFC-134a by Goodwin and Moldover (*14*) and Tillner-Roth and Baehr (*15*) is also made in Figures 5 and 6. Our second virial coefficient values (*11*) agree well with the available data except the values by Qian et al. (*13*) for pure HFC-32 which have some systematic difference from the present values. Our third virial coefficient values (*11*) disagree with the values by Qian et al. (*13*) and Goodwin and Moldover (*14*) by more than the estimated uncertainties for HFC-32 and HFC-134a. Note that the solid curves appearing in Figures 5 and 6 are the calculated results by our own equations of state (*16*) developed for each mixture.

Conclusion

The present study provides *PVTx* results for the binary refrigerant HFC-32 + HFC-134a. Two hundred sixty densities were measured along 20 isochores, and second and third virial coefficients were derived.

Acknowledgment

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