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An Experimental Study of the Thermodynamic Properties of 1, 1-Difluoroethane

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Experimental vapor pressures and $P-\rho-T$ data of an important alternative refrigerant, 1, 1-difluoroethane (HFC-152a), have been measured by means of a constant-volume method coupled with expansion procedures. Sixty $P-\rho-T$ data were measured along eight isochores in a range of temperatures T from 330 to 440 K, at pressures P from 1.6 to 9.3 MPa, and at densities ρ from 51 to 811 $kg \cdot m^{-3}$. Forty-six vapor pressures were also measured at temperatures from 320 K to the critical temperature. The uncertainties of the temperature and pressure measurements are within ±7 mK and ±2 kPa, respectively, while the uncertainty of the density values is within ±0.1%. The purity of the sample used is 99.9 wt%. On the basis of the measurements along each isochore, five saturation points were determined and the critical pressure was determined by correlating the vapor-pressure measurements. The second and third virial coefficients for temperatures from 360 to 440 K have also been determined.

KEY WORDS: critical parameters; equation-of-state data; HFC-152a; vapor–liquid equilibrium; vapor pressure; virial coefficient.

1. INTRODUCTION

The hydrofluorocarbon, 1, 1-difluoroethane (HFC-152a), has zero ozone-depletion potential because it contains no chlorine atoms. It has not been applied to engineering practice due to its flammability, but the expected improvement in performance of a refrigeration system by applying this refrigerant is making it an attractive replacement for dichlorodifluoromethane (CFC-12).

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Information on the thermodynamic properties of HFC-152a is essential for its application as a working fluid in refrigeration systems. Therefore $P-\rho-T$ data, vapor pressures, critical pressure, and second and third virial coefficients are presented here.

2. EXPERIMENTS

Since the experimental apparatus and procedure have been reported by Takaishi et al. [1, 2], only a brief explanation is given here. The isochoric method coupled with expansion procedures was used for measuring vapor pressures and *PVT* properties. The experimental apparatus shown in Fig. 1 is composed of a sample cell (A), an expansion cell (B), a differential pressure detector (C), a platinum resistance thermometer calibrated on ITS-90 (G), a thermostated bath (H), temperature control measuring devices, and pressure measuring instruments.

The inner volumes of the sample cell and expansion cell have been carefully calibrated by using pure water; they are about 283 and 55 cm^3,

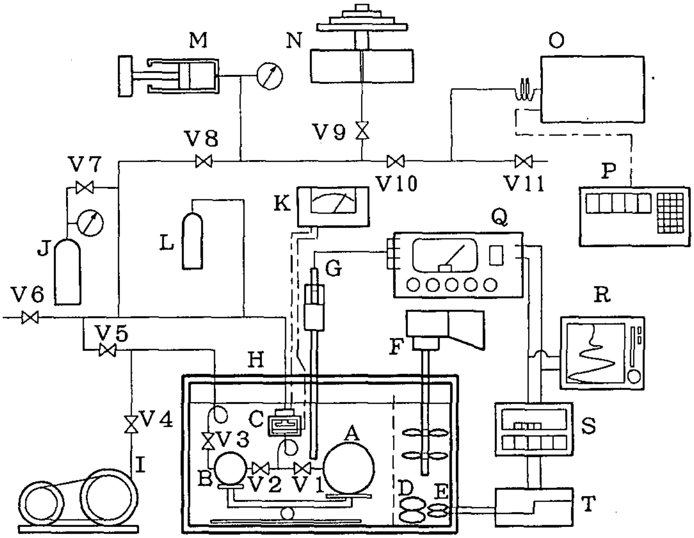

Fig. 1. Experimental apparatus. (A) Sample cell; (B) expansion cell; (C) differential pressure detector; (D) main heater; (E) auxiliary heater; (F) stirrer (G) platinum resistance thermometer; (H) thermostated bath; (I) vacuum pump; (J) nitrogen cylinder; (K) electric resistance detector; (L) nitrogen gas damper; (M) precise pressure controller; (N) air piston-type dead-weight pressure gauge; (O) digital quartz pressure transducer; (P) digital quartz pressure computer; (Q) thermometer bridge; (R) pen recorder (S) PID controller; (T) dc power supply; (V1–V11) valves.

respectively. The temperature in the thermostated bath filled with silicone oil was controlled within ±2 mK. After establishing thermal equilibrium between the sample and the heat transfer oil in the bath and the pressure remaining constant, the temperature and the pressure of the sample fluid were measured along the prescribed isochore. To obtain another isochore, we expanded the sample fluid to the expansion cell with the fluid in the single phase, after a series of measurements along the isochore.

3. RESULTS

Sixty $P - \rho - T$ data along eight isochores at temperatures from 330 to 440 K, pressures from 1.6 to 9.3 MPa, and densities from 51 to 811 $\mathrm{kg \cdot m^{-3}}$ were measured. Figure 2 shows the distribution of the data in a pressure–temperature plane. Forty-six vapor pressures from 320 K to the critical temperature were also measured, as well as five saturated liquid/vapor densities. All measured data are tabulated in Tables I–III with temperatures on ITS-90.

The experimental errors of the present $P - \rho - T$ and vapor-pressure measurements are estimated to be within ±7 mK in temperature T, ±2 kPa in pressure P, and ±0.1% in density ρ. Saturated liquid/vapor densities are expected to be accurate within ±0.5% including the uncertainty due to extrapolation procedure. The purity of the sample we used was 99.9 wt%.

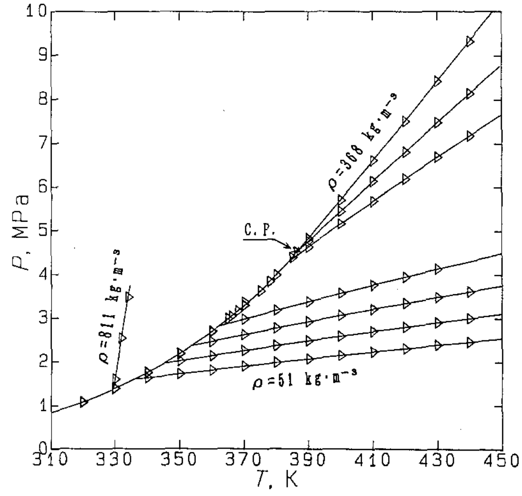

Fig. 2. Distribution of the present measurements in the $P - T$ plane.

Table I. $P-\rho-T$ Data for HFC-152a

No.	ρ ($kg \cdot m^{-3}$)	T (K)[a]	P (MPa)
1	811.30	330.000	1.5931
2	811.19	332.000	2.5352
3	811.08	334.000	3.4820
4	643.29	370.000	3.3712
5	368.06	386.430	4.5180
6	368.00	390.000	4.8285
7	367.80	400.000	5.7153
8	367.61	410.000	6.6141
9	367.41	420.000	7.5118
10	367.21	430.000	8.4191
11	367.01	440.000	9.3289
12	292.37	390.000	4.7646
13	292.22	400.000	5.4587
14	292.06	410.000	6.1410
15	291.91	420.000	6.8110
16	291.76	430.000	7.4818
17	291.60	440.000	8.1477
18	232.28	390.000	4.6336
19	232.16	400.000	5.1675
20	232.04	410.000	5.6870
21	231.92	420.000	6.1971
22	231.80	430.000	6.6939
23	231.68	440.000	7.1900
24	103.83	370.000	2.9776
25	103.78	380.000	3.1831
26	103.73	390.000	3.3825
27	103.68	400.000	3.5793
28	103.63	410.000	3.7683
29	103.58	420.000	3.9549
30	103.52	430.000	4.1393
31	82.53	360.000	2.4645
32	82.49	370.000	2.6223
33	82.45	380.000	2.7744
34	82.41	390.000	2.9231
35	82.37	400.000	3.0685
36	82.33	410.000	3.2112
37	82.29	420.000	3.3521
38	82.25	430.000	3.4903
39	82.21	440.000	3.6269
40	65.60	350.000	2.0200
41	65.57	360.000	2.1404
42	65.54	370.000	2.2576
43	65.51	380.000	2.3709

[a] Temperatures on ITS-90.

Table I. *(Continued)*

No.	ρ (kg·m^{-3})	T (K)[a]	P (MPa)
44	65.47	390.000	2.4821
45	65.44	399.994	2.5911
46	65.41	410.000	2.6989
47	65.38	420.000	2.8046
48	65.34	430.000	2.9092
49	65.31	440.000	3.0124
50	51.65	340.000	1.6342
51	51.63	350.000	1.7251
52	51.61	360.000	1.8139
53	51.58	370.000	1.9004
54	51.56	380.000	1.9855
55	51.53	390.000	2.0680
56	51.51	400.000	2.1495
57	51.48	410.000	2.2311
58	51.45	420.000	2.3102
59	51.43	430.000	2.3899
60	51.40	440.000	2.4677

[a] Temperatures on ITS-90.

4. DISCUSSION

4.1. The Critical-Pressure and Vapor-Pressure Measurements

Table IV shows the critical parameters of HFC-152a reported in the literature [3–5]. We used the critical temperature and density values determined by Higashi et al. [5] since they are the most reliable directly measured values. We measured the vapor pressures along the isochore at the critical density, and then the critical pressure was determined as the vapor-pressure value at the critical temperature. The value of the critical pressure is

$$P_c = (4.5157 \pm 0.0025)\ \text{MPa} \tag{1}$$

We developed a vapor-pressure correlation based exclusively on the present vapor-pressure measurements using a functional form proposed by Wagner [6]:

$$\ln P_r = \frac{1}{T_r}\{A(1-T_r) + B(1-T_r)^{1.5} + C(1-T_r)^3 + D(1-T_r)^4 + E(1-T_r)^5\} \tag{2}$$

Table II. Vapor Pressures of HFC-152a

No.	T (K)	P (MPa)
1	320.000	1.0866
2	330.000	1.3908
3	340.000	1.7565
4	350.000	2.1881
5	360.000	2.6989
6	370.000	3.2970
7	380.000	3.9960
8	320.000	1.0876
9	320.000	1.0879
10	330.000	1.3920
11	340.000	1.7564
12	350.000	2.1896
13	360.000	2.6990
14	366.000	3.0454
15	368.000	3.1696
16	320.000	1.0870
17	330.000	1.3921
18	340.000	1.7571
19	350.000	2.1914
20	360.000	2.6984
21	370.000	3.2950
22	320.000	1.0867
23	330.000	1.3917
24	340.000	1.7574
25	350.000	2.1902
26	360.000	2.6998
27	370.000	3.2959
28	378.000	3.8463
29	380.000	3.9947
30	320.000	1.0840
31	330.000	1.3908
32	340.000	1.7572
33	350.000	2.1903
34	360.000	2.6979
35	320.000	1.0879
36	330.000	1.3929
37	340.000	1.7586
38	350.000	2.1915
39	360.000	2.7014
40	365.000	2.9881
41	370.000	3.2981
42	375.000	3.6348
43	380.000	3.9985
44	385.000	4.3959
45	386.390	4.5142
46	386.410	4.5157

Table III. Densities of the Saturated Vapor (ρ'') and Liquid (ρ') of HFC-152a

No.	ρ'' ($\mathrm{kg \cdot m^{-3}}$)	T (K)
1	51.66	335.82
2	65.62	344.87
3	82.56	353.60
4	103.88	361.96
No.	ρ' ($\mathrm{kg \cdot m^{-3}}$)	T (K)
5	811.3	329.55

with

$$P_r = P/P_c, \qquad T_r = T/T_c$$

$$P_c = 4.5157\ \mathrm{MPa}, \qquad T_c = 386.41\ \mathrm{K}$$

$$A = -7.40803, \qquad B = 1.62715, \qquad C = -5.63186,$$

$$D = 10.1497, \qquad E = -11.6949.$$

Figure 3 shows the pressure deviations from Eq. (2), which reproduces the present measurements and the data of Higashi et al. [5], Baehr and Tillner-Roth [7], Yada et al. [8], and Iso and Uematsu [9] within ±0.15% except at temperatures below 330 K. The data of Takahashi et al. [10] and Zhao et al. [11] show systematic deviations from the present correlation. The curve for the correlation reported by Baehr and Tillner-Roth [7] is similar to that of the correlation reported by Higashi et al. [5], while the correlation of McLinden [12] seems to have a small wavy deviation from Eq. (2).

Table IV. Critical Parameters of HFC-152a

Reference	T_c (K)	P_c (MPa)	ρ_c ($\mathrm{kg \cdot m^{-3}}$)
Soll [3]	380	—	—
Mears et al. [4]	386.6	4.50	365
Higashi et al. [5]	386.41	4.5198	368
This work	386.41	4.5157	368

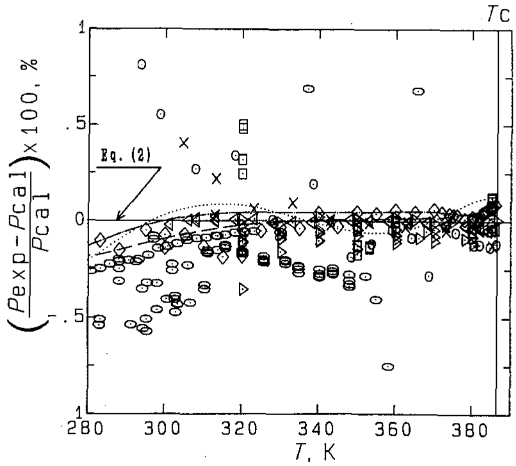

Fig. 3. Deviation of vapor-pressure measurements from Eq. (2). (▷) This work; (◇) Higashi et al. [5]; (×) Yada et al. [8]; (⊙) Takahashi et al. [10]; (⊡) Iso and Uematsu [9]; (◁) Baehr and Tillner-Roth [7]; (⊖) Zhao et al. [11]; (—) Higashi et al. [5]; (–·–) Baehr and Tillner-Roth [7]; (···) McLinden [12].

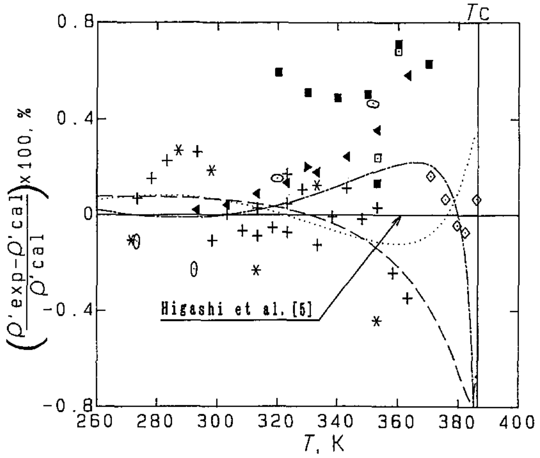

Fig. 4. Saturated liquid densities. (▶) This work; (◇) Higashi et al. [5]; (+) Sato et al. [13]; (∗) Mears et al. [4]; (⊙) Soll [3]; (⊖) Zhao et al. [11]; (⊡) Iso and Uematsu [9]; (■) Iso and Uematsu (extrapolated); (◀) Baehr and Tillner-Roth [7, 15] (extrapolated); (—) Sato et al. [13]; (–·–) Tillner-Roth et al. [14]; (···) McLinden [12].

4.2. Saturated Liquid and Vapor Densities

Figure 4 shows the deviations of the densities of the saturated liquid from the correlation reported by Higashi et al. [5]. The present saturated-liquid density exceeds the correlation by +0.2% at 330 K. The saturated-liquid densities reported by Sato et al. [13], Mears et al. [4], and Soll [3] are within +0.2 and −0.4%. We also determined densities of the saturated liquid from the $P-\rho-T$ data reported by Iso and Uematsu [9] and Baehr and Tillner-Roth [7, 15] by extrapolation. The extrapolated values from the data of Iso and Uematsu are systematically higher than the correlation by about 0.6%. The deviations of those of Baehr and Tillner-Roth increase with increasing temperature toward the critical temperature.

Figure 5 shows the deviations of the saturated-vapor densities from the correlation of Kabata [16]. The present saturated-vapor densities tend to deviate from the correlation up to about 2%. We also determined saturated-vapor densities from $P-\rho-T$ data reported by Majima et al. [17, 18] and Takahashi et al. [19] by extrapolation. These densities also deviate from the correlation of Kabata [16] because the latter was based only on densities reported by Higashi et al. [5].

4.3. $P-\rho-T$ Data

Figure 6 shows the pressure deviations of the $P-\rho-T$ data from an equation of state developed by Tamatsu et al. [20]. In the vapor phase, the

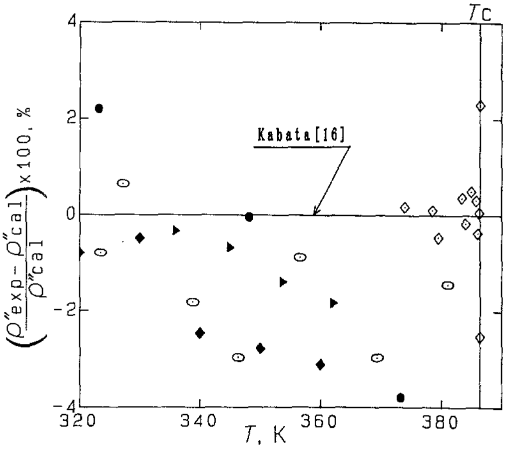

Fig. 5. Saturated vapor densities. (▶) This work; (◇) Higashi et al. [5]; (○) Zhao et al. [11]; (◆) Majima et al. [17, 18] (extrapolated); (●) Takahashi et al. [19] (extrapolated).

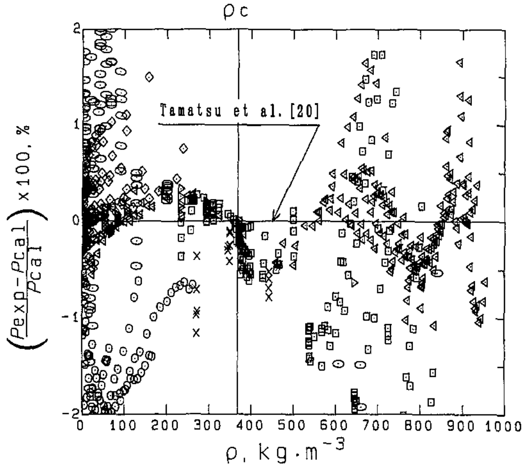

Fig. 6. Pressure deviations from the equation of state reported by Tamatsu et al. [20]. (▷) This work; (◇) Majima et al. [17, 18]; (×) Yada et al. [8]; (○) Takahashi et al. [19]; (□) Iso and Uematsu [9]; (◁) Tillner-Roth and Baehr [15]; (⬭) Zhao et al. [11].

equation of state reproduces the present measurements and the data of Majima et al. [17, 18] within ±1%, while the deviations of the pressures of Takahashi et al. [19] are always larger and those of Zhao et al. [11] are always smaller than the equation. In the critical region, the data of Baehr and Tillner-Roth [7] and of Iso and Uematsu [9] are in agreement with

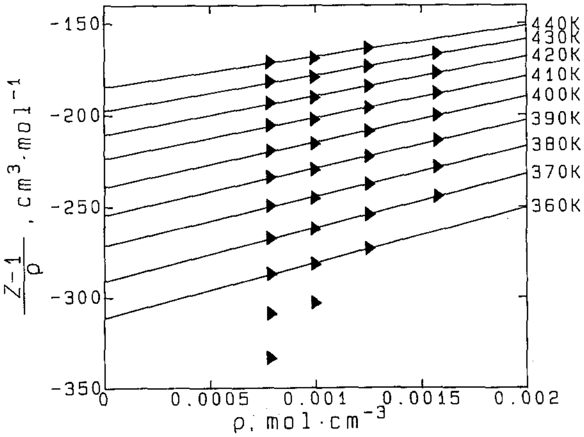

Fig. 7. $(Z-1)/\rho$ values from the $P-\rho-T$ measurements in the gaseous phase. (▶) This work.

Table V. Second and Third Virial Coefficients of HFC-152a

T (K)	$B(T)$ ($\mathrm{cm^3 \cdot mol^{-1}}$)	$C(T)$ ($\mathrm{dm^6 \cdot mol^{-2}}$)
360.00	−311.3	0.03048
370.00	−291.1	0.02956
380.00	−271.7	0.02744
390.00	−254.8	0.02595
400.00	−239.4	0.02476
410.00	−223.8	0.02245
420.00	−210.8	0.02129
430.00	−197.7	0.01957
440.00	−184.8	0.01681

the equation, while the data of Yada et al. [8] are always smaller than the values predicted from the equation.

4.4. Virial Coefficients

The compressibility factors of HFC-152a in the superheated vapor region have been deduced from the measurements as

$$Z = P/\rho RT \tag{3}$$

where R is the gas constant.

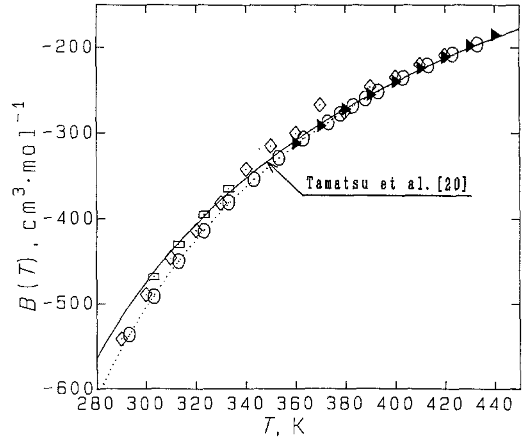

Fig. 8. The second virial coefficient of HFC-152a as a function of temperature. (▶) This work; (◇) Majima et al. [17, 18]; (□) Fuijwara et al. [21]; (○) Tillner-Roth and Baehr [15]; (···) Tillner-Roth and Baehr [15].

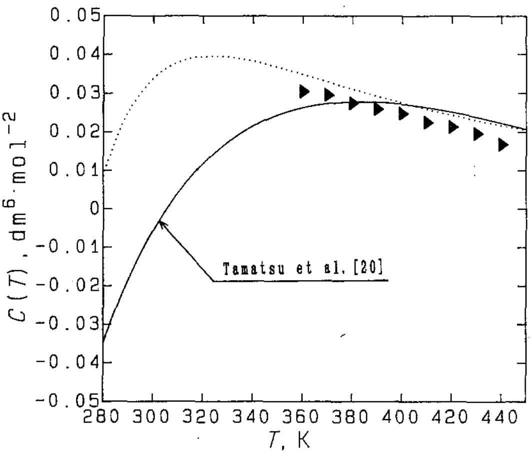

Fig. 9. The third virial coefficient of HFC-152a as a function of temperature. (▶) This work; (···) Tillner-Roth and Baehr [15].

In Fig. 7, $(Z-1)/\rho$ values calculated from the present $P-\rho-T$ data are plotted. Each isotherm can be correlated as a straight line.

The second and third virial coefficients for temperatures from 360 to 440 K were determined by fitting the following truncated virial expression to the data along each isotherm:

$$(Z-1)/\rho = B + C\rho \tag{4}$$

The second and third virial coefficients are shown in Figs. 8 and 9, respectively. The second virial coefficients obtainded in the present study, by Tillner-Roth and Baehr [15], by Majima et al. [17, 18], and by Fujiwara et al. [21] show a reasonable temperature dependence from a physical point of view and agree with the equation of state of Tamatsu et al. [20] and a correlation of Tillner-Roth and Baehr [15]. The third virial coefficients are also in reasonable agreement with the equation of state and the third term of the virial equation of state developed by Tillner-Roth and Baehr [15].

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