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

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The experimental pressure–volume–temperature–composition (*PVTx*) properties of the binary refrigerant 1,1-difluoroethane (HFC-152a) + 1,1,2,2-tetrafluoroethane (HFC-134) have been measured by means of a constant-volume method coupled with expansion procedures in an extensive range of temperatures, pressures, and densities. A total of 202 *PVTx* property data were measured in a range of temperatures from 320 to 440 K, pressures from 1.0 to 4.3 MPa, and densities from 54 to 155 kg/m^3. A Clausius–Clapeyron-type correlation for the dew-point pressures was developed which can reproduce the measurements within ±5 kPa.

Introduction

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

The binary refrigerant 1,1-difluoroethane (HFC-152a) + 1,1,2,2-tetrafluoroethane (HFC-134) has zero ODP (ozone depletion potential), and both pure components have similar vapor pressures. Because of its flammable characteristics, HFC-152a is not considered as a suitable working fluid for domestic refrigeration systems. The mixture of HFC-152a with a nonflammable refrigerant, HFC-134, however, may overcome such a drawback in practical application. This mixture with around 20 wt % HFC-152a showed azeotropic behavior for $T > 330$ K due to our previous study system (*8*). The present work is to reconfirm this observation and to provide precise *PVTx* measurements for the binary refrigerant of present interest.

Samples and Sample Purification

The purities of the samples used are 99.9 wt % for HFC-152a and 99.94 wt % for HFC-134 according to the analysis of the supplier. We did not purify and analyze the samples ourselves.

Experimental Section

The apparatus and procedure have been reported by Takaishi et al. (*9*, *10*). The isochoric method coupled with expansion procedures was applied for measuring dew-point pressures and *PVTx* properties, i.e., *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 calibrated on ITS-90 (G), a thermostated bath (H), temperature control/measuring devices, and pressure-measuring instruments.

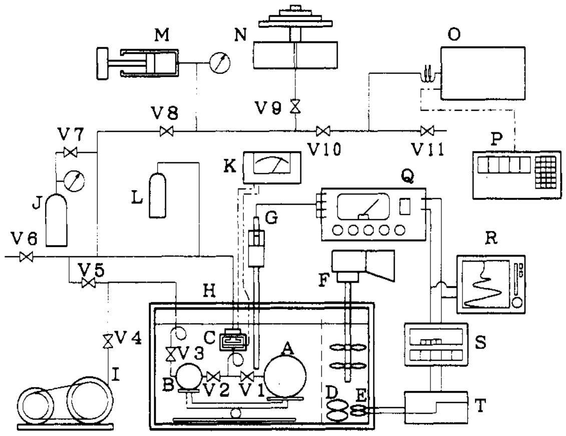

Figure 1. Experimental apparatus: (A) sample cell; (B) expansion cell; (C) differential pressure detector; (D) main heater; (E) auxiliary heater; (F) stirrer; (G) platinum resistance thermometer; (H) thermostated bath; (I) vacuum pump; (J) nitrogen cylinder; (K) electric resistance detector; (L) nitrogen 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; (R) pen recorder; (S) PID controller; (T) dc power supply; (V1)–(V11) valves.

The inner volumes of the sample cell and expansion cell were carefully calibrated with pure water; they were 238.368 ± 0.0027 and 55.583 ± 0.007 cm^3 at room temperature condition, respectively. The temperature in the thermostated bath filled with silicone oil was controlled within ±2 mK. After thermal equilibrium was confirmed and the pressure remained 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, we expanded part of the sample fluid into the expansion cell in the single phase to obtain another isochore, with the 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, ±0.10% in density, and ±0.20% in each composition.

Results

A total of 202 density values were measured along 16 isochores at temperatures from 320 to 440 K, pressures from 1.0 to 4.3 MPa, and mass fractions of 20 wt % (27.911 mol %),

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Table I. Density ρ for HFC-152a + HFC-134

$\rho/(\mathrm{kg \cdot m^{-3}})$	T/K	P/MPa	$\rho/(\mathrm{kg \cdot m^{-3}})$	T/K	P/MPa	$\rho/(\mathrm{kg \cdot m^{-3}})$	T/K	P/MPa
20.041 wt % (27.911 mol %) HFC-152a								
155.70^a	320.000	0.9755	123.34	380.000	2.8885	97.80	420.000	2.9605
155.63^a	330.000	1.2566	123.28	390.000	3.0521	97.75	430.000	3.0748
155.55^a	340.00	1.5953	123.22	400.000	3.2130	97.70	440.000	3.1881
155.48^a	350.000	1.9978	123.16	410.000	3.3704	78.07^a	320.000	0.9744
155.40^a	360.000	2.4709	123.09	420.000	3.5244	78.03^a	330.000	1.2541
155.32^a	370.000	3.0164	123.03	430.000	3.6758	78.00^a	340.000	1.5875
155.25	380.000	3.2774	122.97	440.000	3.8250	77.96	350.000	1.8152
155.18	388.988	3.4798	98.27^a	320.000	0.9756	77.92	360.000	1.9134
155.09	400.000	3.7209	98.23^a	330.000	1.2556	77.89	370.000	2.0086
155.02	410.000	3.9328	98.18^a	340.000	1.5930	77.85	380.000	2.1015
154.94	420.000	4.1410	98.13^a	350.000	1.9892	77.81	390.000	2.1926
123.70^a	320.000	0.9755	98.08	360.000	2.2319	77.77	400.000	2.2823
123.64^a	330.000	1.2563	98.04	370.000	2.3599	77.73	410.000	2.3713
123.58^a	340.000	1.5943	97.99	380.000	2.4850	77.70	420.000	2.4586
123.52^a	350.000	1.9961	97.94	390.000	2.6065	77.66	430.000	2.5457
123.46^a	360.000	2.4628	97.89	400.000	2.7270	77.62	440.000	2.6315
123.40	370.000	2.7187	97.84	410.000	2.8442			
39.983 wt % (50.717 mol %) HFC-152a								
131.11^a	320.000	0.9911	103.91	370.000	2.5985	82.35	420.000	2.7902
131.05^a	330.000	1.2761	103.86	380.000	2.7535	82.31	430.000	2.8948
130.99^a	340.000	1.6177	103.81	390.000	2.9023	82.27	440.000	2.9980
130.92^a	350.000	2.0249	103.76	400.000	3.0488	65.74^a	320.000	0.9907
130.86^a	360.000	2.5047	103.71	410.000	3.1917	65.71^a	330.000	1.2747
130.79	370.000	2.9405	103.66	420.000	3.3324	65.68^a	340.000	1.6160
130.73	380.000	3.1496	103.60	430.000	3.4717	65.65	350.000	1.7220
130.67	390.000	3.3510	103.55	440.000	3.6079	65.62	360.000	1.8108
130.60	400.000	3.5479	82.75^a	320.000	0.9909	65.59	370.000	1.8975
130.54	410.000	3.7400	82.71^a	330.000	1.2749	65.55	380.000	1.9823
130.47	420.000	3.9288	82.67^a	340.000	1.6171	65.52	390.000	2.0663
130.40	430.000	4.1141	82.63	350.000	2.0035	65.49	400.000	2.1488
130.34	440.000	4.2970	82.59	360.000	2.1250	65.46	410.000	2.2297
104.16^a	320.000	0.9915	82.55	370.000	2.2415	65.43	420.000	2.3110
104.11^a	330.000	1.2742	82.51	380.000	2.3561	65.39	430.000	2.3898
104.06^a	340.000	1.6171	82.47	390.000	2.4673	65.36	440.000	2.4681
104.01^a	350.000	2.0245	82.43	400.000	2.5761			
103.96	360.000	2.4395	82.39	410.000	2.6835			
59.999 wt % (69.852 mol %) HFC-152a								
120.50^a	320.000	1.0175	95.50	370.000	2.5994	75.72	410.000	2.6847
120.44^a	330.000	1.3068	95.45	380.000	2.7525	75.68	420.000	2.7904
120.38^a	340.000	1.6535	95.41	390.000	2.9016	75.65	430.000	2.8949
120.32^a	350.000	2.0668	95.36	400.000	3.0466	75.61	440.000	2.9982
120.26^a	360.000	2.5525	95.31	410.000	3.1904	60.42^a	320.000	1.0161
120.21	370.000	2.9431	95.26	420.000	3.3303	60.39^a	330.000	1.3054
120.15	380.000	3.1516	95.22	430.000	3.4692	60.36	340.000	1.6287
120.09	390.000	3.3529	95.17	440.000	3.6061	60.33	350.000	1.7210
120.03	400.000	3.5507	76.05^a	320.000	1.0160	60.31	360.000	1.8107
119.97	410.000	3.7422	76.02^a	330.000	1.3069	60.28	370.000	1.8979
119.91	420.000	3.9290	75.98^a	340.000	1.6537	60.25	380.000	1.9827
119.85	430.000	4.1142	75.94	350.000	2.0047	60.22	390.000	2.0669
95.73^a	320.000	1.0163	75.91	360.000	2.1256	60.19	400.000	2.1490
95.68^a	330.000	1.3008	75.87	370.000	2.2423	60.16	410.000	2.2300
95.64^a	340.000	1.6533	75.83	380.000	2.3560	60.13	420.000	2.3111
95.59^a	350.000	2.0639	75.80	390.000	2.4678	60.10	430.000	2.3900
95.55	360.000	2.4392	75.76	400.000	2.5772	60.07	440.000	2.4685
79.909 wt % (86.002 mol %) HFC-152a								
109.68^a	320.000	1.0531	86.93	370.000	2.5771	68.89	420.000	2.7558
109.63^a	330.000	1.3484	86.89	380.000	2.7271	68.86	430.000	2.8581
109.58^a	340.000	1.7012	86.85	390.000	2.8727	68.82	440.000	2.9586
109.53^a	350.000	2.1237	86.80	400.000	3.0144	54.97^a	330.000	1.3431
109.47^a	360.000	2.6193	86.76	410.000	3.1548	54.95	340.000	1.6144
109.42	370.000	2.9296	86.72	420.000	3.2920	54.92	350.000	1.7043
109.37	380.000	3.1314	86.67	430.000	3.4278	54.89	360.000	1.7919
109.31	390.000	3.3271	86.63	440.000	3.5595	54.87	370.000	1.8771
109.26	400.000	3.5174	69.19^a	330.000	1.3399	54.84	380.000	1.9603
109.20	410.000	3.7037	69.16^a	340.000	1.6979	54.81	390.000	2.0430
109.15	420.000	3.8863	69.13	350.000	1.9871	54.79	400.000	2.1236
109.09	430.000	4.0670	69.10	360.000	2.1046	54.76	410.000	2.2035
87.14^a	320.000	1.0486	69.06	370.000	2.2196	54.73	420.000	2.2821
87.10^a	330.000	1.3399	69.03	380.000	2.3307	54.71	430.000	2.3591
87.06^a	340.000	1.6989	69.00	390.000	2.4391	54.68	440.000	2.4348
87.01^a	350.000	2.1198	68.96	400.000	2.5472			
86.97	360.000	2.4227	68.93	410.000	2.6519			

[a] Under the vapor–liquid equilibrium.

Table II. Saturated-Vapor Densities ρ'' and Dew-Point Pressures P_d

T/K	P_d/MPa	ρ''/(kg·m^{-3})	T/K	P_d/MPa	ρ''/(kg·m^{-3})
		20 wt % (27.911 mol %) HFC-152a			
370.9	3.069	155.3	353.5	2.149	98.1
362.4	2.590	123.4	344.6	1.764	78.0
		40 wt % (50.717 mol %) HFC-152a			
366.7	2.873	130.8	349.4	1.998	82.6
358.2	2.413	104.0	340.6	1.639	65.7
		60 wt % (69.852 mol %) HFC-152a			
365.3	2.845	120.2	348.2	1.985	76.0
356.9	2.393	95.6	339.3	1.624	60.4
		80 wt % (86.002 mol %) HFC-152a			
363.1	2.790	109.4	345.9	1.940	69.1
354.6	2.341	87.0	337.2	1.590	55.0

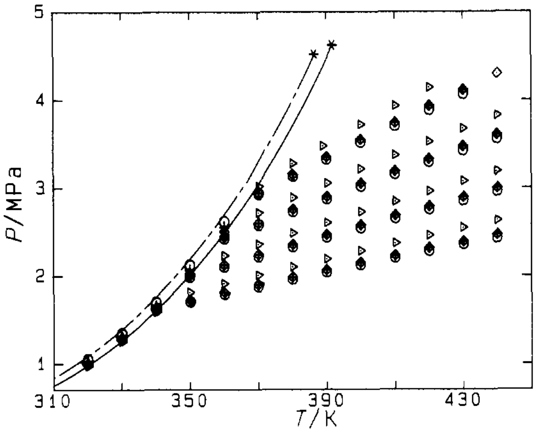

Figure 2. Distribution of the *PVTx* measurements on a pressure–temperature plane: (▶) 20 wt % HFC-152a; (+) 60 wt % HFC-152a; (◇) 40 wt % HFC-152a; (⊙) 80 wt % HFC-152a, HFC-134, — (*11*); HFC-152a, - - - (*12*).

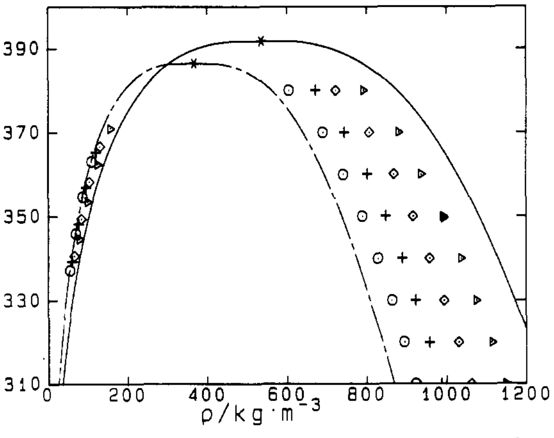

Figure 3. Available saturated vapor and liquid density data: (▶) 20 wt % HFC-152a; (+) 60 wt % HFC-152a; (◇) 40 wt % HFC-152a; (⊙) 80 wt % HFC-152a; HFC-134, — (*15, 16*); HFC-152a, - - - (*13, 14*).

Table III. Parameters in Equation 1 for Each Composition

	C	D
20 wt % (27.911 mol %) HFC-152a	8.327	2672.7
40 wt % (50.717 mol %) HFC-152a	8.329	2668.2
60 wt % (69.852 mol %) HFC-152a	8.296	2649.7
80 wt % (79.909 mol %) HFC-152a	8.271	2631.5

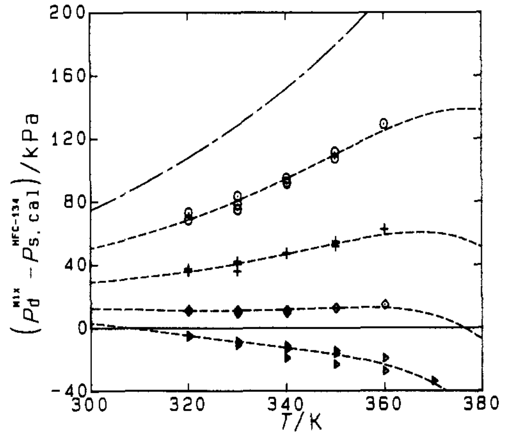

Figure 4. Deviation of dew-point pressure measurements from the vapor pressure of HFC-134 (*11*): (▶) 20 wt % HFC-152a; (+) 60 wt % HFC-152a; (◇) 40 wt % HFC-152a; (⊙) 80 wt % HFC-152a; HFC-134, — (*11*); HFC-152a, - - - (*12*), eq 1, - - -.

40 wt % (50.717 mol %), 60 wt % (69.852 mol %), and 80 wt % (86.002 mol %) HFC-152a, as tabulated in Table I. Figure 2 shows the distribution of the *PVTx* data on a pressure–temperature plane, while the vapor-pressure curves are calculated from the correlations of both pure components (*11, 12*).

We have also determined 16 saturated-vapor densities and dew-point pressures within the uncertainty of ±0.5% and ±7 kPa by finding the breaking point of each isochore graphically on a pressure–temperature plane. The values are given in Table II, and Figure 3 shows the available saturated-vapor and -liquid densities on the temperature–density plane. The data for saturated-vapor densities are those by the present study, while those for saturated-liquid densities were reported by Maezawa et al. (*8*). The saturated-liquid and -vapor curves for HFC-152a were drawn from the correlations by Higashi et al. (*13*) and by Kabata (*14*), whereas those for HFC-134 were by Maezawa et al. (*15*) and by Tamatsu (*16*), respectively.

Discussion

The dew-point pressures were correlated by a simple Clausius–Clapeyron correlation as follows:

$$\ln (P_d/\mathrm{MPa}) = C - D/(T/\mathrm{K}) \qquad (1)$$

Because of the limited number of available data along each isopleth, the simplest functional form of eq 1 was applied. P_d denotes the dew-point pressure and T the temperature, and C and D are the parameters determined by a least-squares fit. Those are listed in Table III.

Figure 4 shows the pressure deviations of the dew-point-pressure data from the vapor-pressure correlation of HFC-134 (*11*). The data of each composition, i.e., 20, 40, 60, and 80 wt % HFC-152a, are correlated by eq 1 within ±5 kPa. Furthermore, it should be noted that dew-point pressures of 20 wt % HFC-152a are always lower than vapor pressures of HFC-134, with the maximum difference of about 35 kPa at 370 K. Azeotropic behavior was evident at temperatures above 310 K for the blend with a composition of about 20 wt % HFC-152a. Since the composition dependence of measured pressures is less significant, this binary refrigerant system would be applied in practice as a near-azeotropic refrigerant.

Conclusion

The present study provides the first set of *PVTx* property data for the binary HFC-152a + HFC-134 system. A total of 202 densities for HFC-152a + HFC-134 were measured along 16 isochores. A dew-point pressure correlation being effective in the temperature range from T = 320 to T = 370 K was developed for each composition. The existence of azeotropic behavior was reconfirmed at the blend of 20 wt %

HFC-152a for $T > 310$ K as reported by our previous study of the present binary system (*8*).

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