Liquid Densities and Vapor Pressures of 1,1,2,2-Tetrafluoroethane (HFC 134) and 1,1-Dichloro-1-fluoroethane (HCFC 141b)

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Saturated liquid densities and vapor pressures of HFC 134 and HCFC 141b were measured at temperatures from 200 to 400 K by a magnetic densimeter coupled with a variable volume cell. For HFC 134, 38 saturated liquid densities associated with the vapor pressures and 5 compressed liquid *PVT* properties at temperatures 280–400 K and pressures up to 2 MPa were measured. For HCFC 141b, 37 saturated liquid densities associated with the vapor pressures and 24 compressed liquid *PVT* properties were measured at the same ranges. The experimental uncertainties in temperature, pressure, and density measurements were estimated to be not greater than ±15 mK, ±10 kPa, and ±0.2%, respectively. The purities of the sample used were 99.4 and 99.8 wt % for HFC 134 and 98.8 wt % for HCFC 141b. The simple correlations for saturated liquid densities and vapor pressures were developed for both substances on the basis of the present measurements. Compressed liquid *PVT* properties were compared with the Kumagai's Tait-equation.

Introduction

HFC 134 (1,1,2,2-tetrafluoroethane) is one of the environmentally acceptable refrigerants. It does not contain the chlorine atom so that its ODP (ozone depletion potential) value is zero. On the other hand, HCFC 141b (1,1-dichloro-1-fluoroethane) is expected to become a substitute for CFC 11 (trichlorofluoromethane), especially as a blowing agent. These substances became available only in the past 2 years, so that their thermodynamic properties have not been sufficiently elucidated up to the present time. This paper reports saturated liquid densities, vapor pressures, and compressed liquid pressure–volume–temperature (*PVT*) properties of these new substances.

Experimental Section

A magnetic densimeter coupled with a variable volume cell accompanying a metallic bellows was applied for all measurements in the present study. The apparatus and procedure used here were reported in detail in our previous publication (*1*). And, by means of the present apparatus, the liquid densities and vapor pressures were measured for several refrigerants: HCFC 123 (1,1-dichloro-2,2,2-trifluoroethane) (*1*), HFC 134a (1,1,1,2-tetrafluoroethane) (*1*), and HCFC 142b (1-chloro-1,1-difluoroethane) (*2*); binary refrigerant mixtures, HFC 152a (1,1-difluoroethane) + CFC 114 (1,2-dichloro-1,1,2,2-tetrafluoroethane) (*3*) and HCFC 22 (chlorodifluoromethane) + HFC 152a (*4*).

The sample temperature was measured by a 25-Ω standard platinum resistance thermometer. The sample pressure was measured by a precision digital pressure gauge (Heise Model 901B) and a differential pressure gauge. The Validyne Model DP15-42 was used as the differential pressure gauge in our previous work (*1*), but in the present study, a small metallic bellows cell and linear variable differential transformer were used. The sample density was measured by the magnetic densimeter.

The experimental uncertainty in temperature was estimated to be within ±15 mK as the sum of 2 mK, the precision of the thermometer, 1 mK, the precision of the thermometer bridge, and 12 mK, the possible temperature fluctuation of the thermostated liquid in the bath. The uncertainty in pressure was estimated to be within ±10 kPa as the sum of 5 kPa, the precision of the pressure gauge, and 5 kPa, the reproducibility of the differential pressure gauge. The uncertainty in density was estimated to be within ±0.2% as the reproducibility of the magnetic densimeter.

The purities of the samples used were 99.4 and 99.8 wt % for HFC 134, while that for HCFC 141b was 98.8 wt %.

Results

Saturated liquid densities and vapor pressures were measured at temperatures from 200 to 400 K for both substances. For HFC 134 and HCFC 141b, 38 and 37 data points were obtained, respectively. Compressed liquid *PVT* properties were measured in the ranges of temperatures from 280 to 400 K and of pressures from 0.5 to 2.0 MPa. With regard to the compressed liquid *PVT* properties, 5 and 24 data points were obtained for HFC 134 and HCFC 141b, respectively. All results are listed in Tables I–IV. A difference of 0.4 wt % in sample purities for HFC 134 did not provide any significant difference in the present results, as shown in Table I. In the experiments of HCFC 141b, the two measured points with negative pressures in Table II are considered due to the difficulty of pressure measurements at lower pressures.

Figure 1 shows temperature dependences of the saturated liquid densities of HFC 134, HFC 134a, and CFC 12 (dichlorodifluoromethane). The saturated liquid densities of HFC 134 are larger than those of HFC 134a, being an isomer of HFC 134, by about 100 kg/m^3, but close to those of CFC 12. The solid curves in Figure 1 were calculated from the saturated liquid density correlations developed in this work for HFC 134, developed in our previous work (*1*) for HFC 134a, and developed by Okada et al. (*5*) for CFC 12, respectively.

Figure 2 shows temperature dependences of the saturated liquid densities of HCFC 141b, HCFC 123, and CFC 11. The saturated liquid densities of HCFC 141b are smaller than those of HCFC 123 and CFC 11. The solid curves in Figure 2 were calculated from the saturated liquid density correlations developed in this work for HCFC 141b, developed in our previous work (*1*) for HCFC 123, and developed by Okada et al. (*5*) for CFC 11, respectively.

Figure 3 shows temperature dependences of the vapor pressures of HFC 134, HFC 134a, and CFC 12. The vapor pressures of HFC 134 are always smaller than those of HFC 134a and CFC 12, but close to those of CFC 12 at high temperatures. The solid curves in Figure 3 were calculated from saturated vapor pressure correlations developed in this work for HFC 134, developed by Piao et al. (*6*) for HFC 134a, and cited in JAR Tables (*7*) for CFC 12, respectively.

Figure 4 shows temperature dependences of the vapor pressures of HCFC 141b, HCFC 123, and CFC 11. The vapor pressures of HCFC 141b are always smaller than those of

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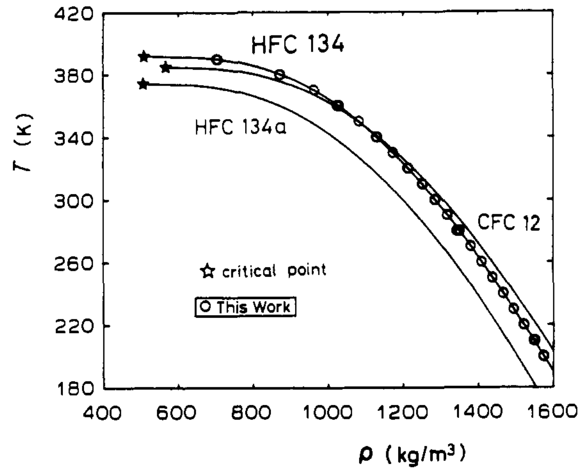

Figure 1. Saturated liquid densities of HFC 134, HFC 134a, and CFC 12.

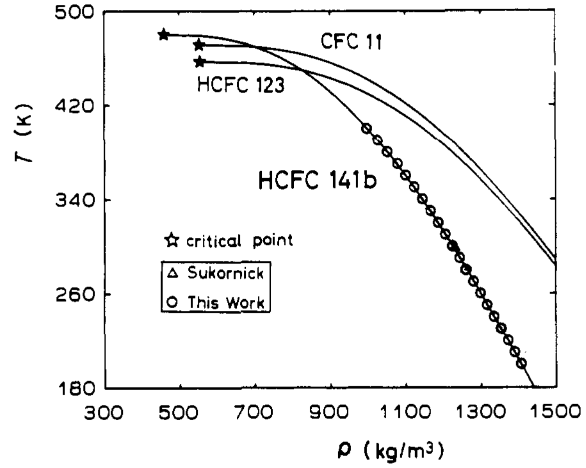

Figure 2. Saturated liquid densities of HCFC 141b, HCFC 123, and CFC 11.

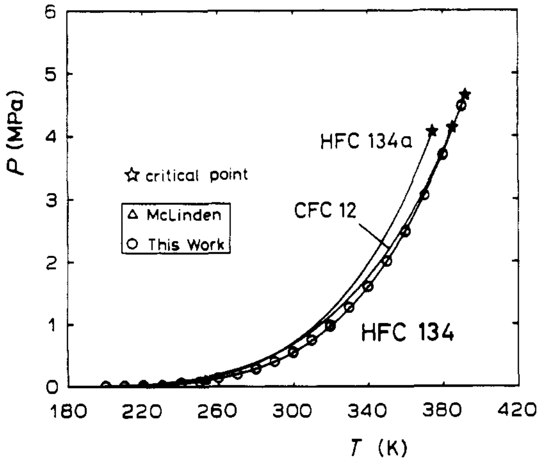

Figure 3. Vapor pressures of HFC 134, HFC 134a, and CFC 12.

HCFC 123 and CFC 11. The solid curves in Figure 4 were calculated from the saturated vapor pressure correlations developed in this work for HCFC 141b, developed by Piao et al. (*8*) for HFC 123, and cited in the compilation in ref 9 for CFC 11, respectively.

Figure 5 shows the saturated and compressed liquid densities of HFC 134 on a pressure-density diagram. The solid curves in Figure 5 were calculated from the above-mentioned correlations for the saturated liquid curve and from the Kumagai's Tait equation (*10*) for the compressed liquid isotherms.

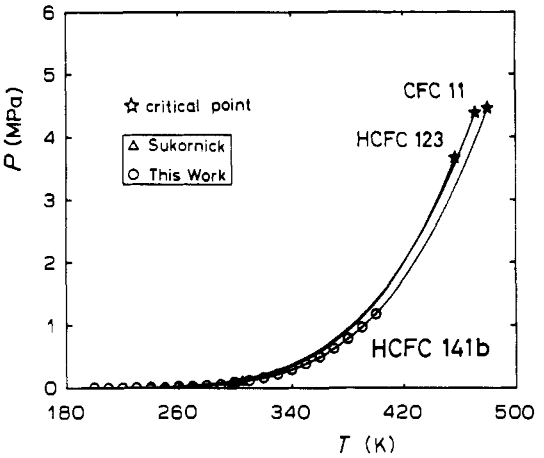

Figure 4. Vapor pressures of HCFC 141b, HCFC 123, and CFC 11.

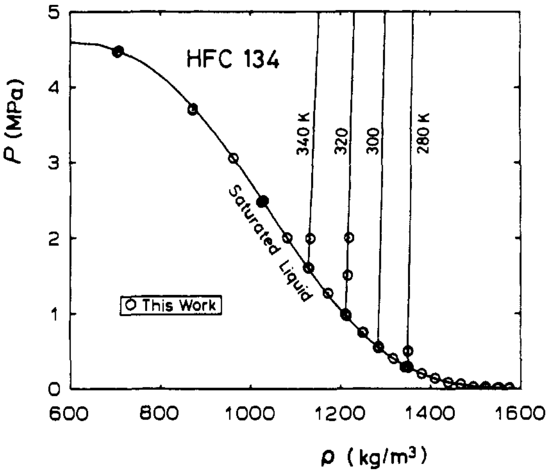

Figure 5. Compressed liquid *PVT* properties of HFC 134.

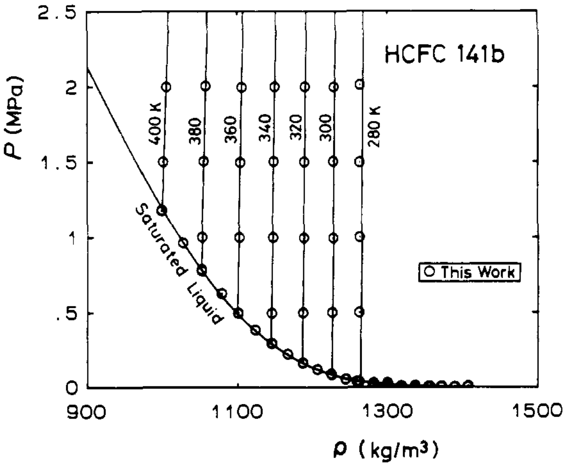

Figure 6. Compressed liquid *PVT* properties of HCFC 141b.

Figure 6 shows the saturated and compressed liquid densities of HCFC 141b on a pressure-density diagram. The solid curves in Figure 6 were calculated from the above-mentioned correlations for the saturated liquid curve and from the Kumagai's Tait equation (*10*) for the compressed liquid isotherms.

Discussion

The present saturated liquid densities were correlated as a simple function of temperature as follows:

$$\rho'_r = 1 + A(1 - T_r)^a + B(1 - T_r)^b \qquad (1)$$

$$\rho'_r = \rho'/\rho_c, \quad T_r = T/T_c$$

where ρ' and T denote the saturated liquid density and temperature, respectively, and ρ_c and T_c are the critical density and

Table I. Experimental Saturated Liquid Densities and Vapor Pressures of HFC 134[a]

no.	T/K	P/MPa	ρ/(kg/m^3)
1	199.999	0.015	1574.3
2	200.001	0.003	1573.4
3	210.003	0.017	1550.6
4	210.012	0.006	1547.8
5	220.000	0.010	1521.9
6	220.000	0.027	1521.5
7	229.997	0.025	1495.1
8	240.007	0.062	1467.1
9	250.004	0.082	1439.3
10	260.002	0.138	1410.3
11	270.006	0.199	1380.3
12*	279.944	0.284	1348.6
13*	279.990	0.281	1350.0
14*	279.996	0.284	1341.9
15	279.994	0.291	1347.9
16	279.990	0.292	1349.4
17*	289.918	0.401	1317.1
18*	299.994	0.546	1284.0
19*	299.997	0.541	1284.9
20	300.001	0.555	1285.4
21*	310.001	0.739	1249.9
22*	310.004	0.746	1251.0
23*	320.020	0.980	1213.0
24*	320.008	0.966	1213.0
25	320.001	0.973	1212.5
26	319.989	0.987	1211.7
27*	330.001	1.268	1172.8
28*	339.990	1.601	1130.7
29*	340.016	1.599	1130.2
30	340.001	1.605	1129.0
31*	349.998	2.005	1082.3
32*	360.001	2.495	1029.2
33	359.930	2.475	1024.2
34*	370.000	3.056	963.1
35*	380.007	3.711	873.1
36	379.980	3.691	872.4
37*	390.001	4.484	707.3
38	390.018	4.465	704.0

[a] For the numbers marked with an asterisk, the sample with 99.4 wt % purity was used, while for the others that with 99.8 wt % purity was used.

Table II. Experimental Saturated Liquid Densities and Vapor Pressures of HCFC 141b

no.	T/K	P/MPa	ρ/(kg/m^3)
1	199.996	0.004	1406.4
2	200.001	0.008	1407.6
3	210.003	0.002	1390.2
4	210.012	0.001	1389.1
5	220.000	0.003	1371.7
6	220.000	0.004	1372.7
7	230.002	0.002	1354.0
8	230.002	0.004	1356.7
9	239.997	0.011	1336.6
10	240.002	−0.010	1336.6
11	250.004	−0.009	1318.1
12	250.009	0.008	1318.4
13	259.992	0.029	1300.0
14	260.002	0.011	1300.3
15	270.001	0.013	1281.0
16	270.006	0.028	1281.3
17	279.874	0.039	1258.5
18	279.964	0.038	1261.6
19	289.969	0.056	1243.8
20	299.968	0.086	1224.9
21	299.989	0.090	1224.4
22	310.001	0.119	1205.9
23	319.998	0.163	1186.1
24	320.006	0.166	1186.3
25	330.005	0.223	1166.1
26	339.996	0.293	1144.6
27	340.004	0.295	1145.4
28	350.001	0.385	1123.3
29	359.982	0.498	1100.5
30	359.998	0.497	1100.7
31	370.008	0.627	1078.9
32	380.002	0.779	1052.2
33	380.003	0.787	1052.2
34	390.001	0.963	1027.1
35	400.004	1.180	999.7
36	400.005	1.174	999.3
37	400.009	1.177	998.5

Table III. Experimental Compressed Liquid *PVT* Properties of HFC 134[a]

no.	T/K	P/MPa	ρ/(kg/m^3)
1*	279.929	0.498	1351.7
2	279.990	0.495	1350.3
3*	319.998	1.499	1216.2
4*	320.003	2.000	1218.9
5*	340.011	1.994	1133.8

[a] For the numbers marked with an asterisk, the sample with 99.4 wt % purity was used, while for the others that with 99.8 wt % purity was used.

the critical temperature, respectively. A, a, B, and b are adjustable parameters. A set of the two exponents, a and b, was determined by trial and error, while the two coefficients, A and B, were determined by least-squares fitting. The critical parameters are not available for either refrigerant so that the estimated values were used. The critical density of HFC 134 was assumed to be equal to that of HFC 134a, and the critical temperature of HFC 134 was determined so as to reproduce the temperature dependence of the present saturated liquid densities at high temperatures. For HCFC 141b, the abovementioned procedure could not be applied because the present data are restricted to lower temperatures far from the critical point. Therefore Joback's group-contribution method (*11*) was used for estimating the critical temperature and the critical density of HCFC 141b. The normal boiling temperature used for Joback's method was calculated from the present vapor pressure correlation, eq 2. Input data to develop eq 1 were 38 and 37 points of the present results for HFC 134 and HCFC 141b, respectively. Standard deviations of parameters A and B are ±0.003 and ±0.0073 for HFC 134 and ±0.002 and ±0.0060 for HCFC 141b, respectively. Parameters used in eq 1 are listed in Table V.

Figure 7 shows saturated liquid density deviations of HFC 134 from eq 1. Equation 1 reproduces the present saturated liquid density measurements with the standard and maximum deviations of 0.10% and 0.32%, respectively, except a single data point at 280 K.

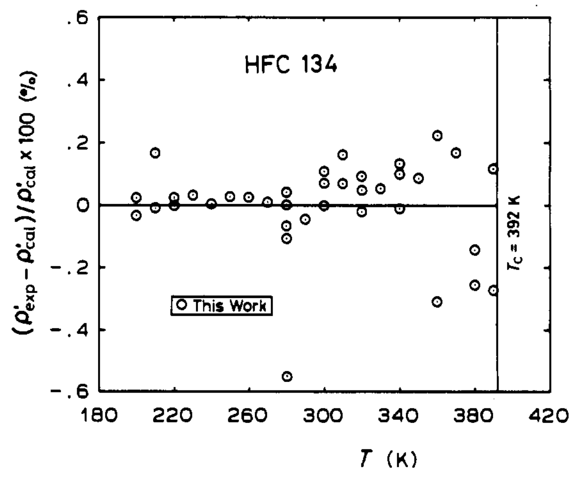

Figure 7. Saturated liquid density deviations from eq 1 for HFC 134.

Figure 8 shows saturated liquid density deviations of HCFC 141b from eq 1. Equation 1 reproduces the present saturated liquid density measurements with standard and maximum deviations of 0.08% and 0.22%, respectively, except a single data point at 280 K. Only a single datum for the saturated liquid

Table IV. Experimental Compressed Liquid PVT Properties of HCFC 141b

no.	T/K	P/MPa	ρ/(kg/m^3)
1	280.015	0.501	1261.7
2	280.046	1.002	1262.1
3	279.954	1.498	1262.6
4	280.051	2.013	1262.8
5	299.994	0.501	1225.7
6	299.999	0.996	1226.6
7	299.999	1.503	1227.3
8	299.999	1.999	1228.0
9	320.003	0.500	1186.7
10	320.003	0.996	1187.5
11	319.992	1.499	1188.6
12	320.003	2.000	1189.5
13	340.001	0.496	1145.0
14	340.001	1.000	1146.4
15	340.006	1.502	1147.7
16	340.006	2.000	1148.9
17	359.992	1.000	1102.0
18	360.003	1.496	1103.7
19	360.003	1.997	1105.5
20	380.007	1.002	1053.0
21	380.007	1.503	1055.4
22	380.002	2.006	1057.9
23	400.009	1.498	1001.0
24	400.009	1.998	1005.1

Table V. Parameters and Constants Used in Equations 1 and 2 and Kumagai's Tait Equations

	HFC 134	HCFC 141b
critical temperature/K	392	480
critical density/(kg/m^3)	510	460
critical pressure/MPa	4.64	4.46
normal boiling temperature/K	253.23	305.26
latent heat at NBP/(kJ/kg)[a]	226.468	220.798
dipole moment/D	0	2.14
A, coefficient in eq 1	2.314	2.262
a, exponent in eq 1	0.34	0.38
B, coefficient in eq 1	0.6849	0.5078
b, exponent in eq 1	1.3	1.6
C, parameter in eq 2	8.515	8.105
D, parameter in eq 2	2736	3173

[a] NBP = normal boiling point.

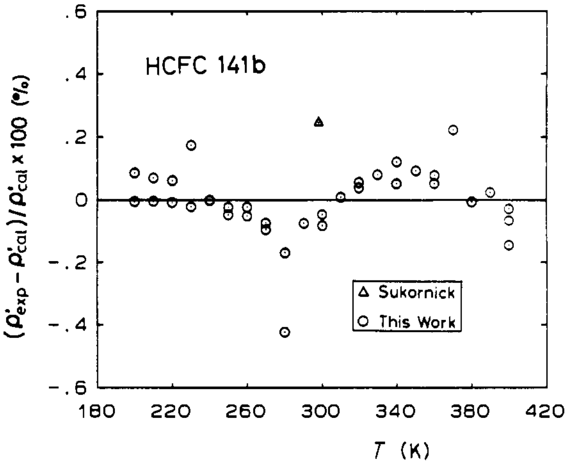

Figure 8. Saturated liquid density deviations from eq 1 for HCFC 141b.

density by Sukornick (*12*) is available as far as the present authors have surveyed. This datum is larger than the present results by about 0.3%, as shown in Figure 8.

The present vapor pressures were correlated as a simple function of temperature as follows:

$$P_s = \exp(C - D/T) \tag{2}$$

where P_s (MPa) denotes the vapor pressure, T (K) is temperature, and C and D are adjustable parameters determined by least-squares fitting on the basis of the present results. It should be noted that the data at very low temperatures have a bad effect on least-squares fitting, since the uncertainty of pressure measurements is 10 kPa. Hence, we have selected 27 points for higher temperatures above 270 K as our input data to develop eq 2 for HFC 134, whereas 21 points were similarly chosen for HCFC 141b. Determined parameters are listed in Table V.

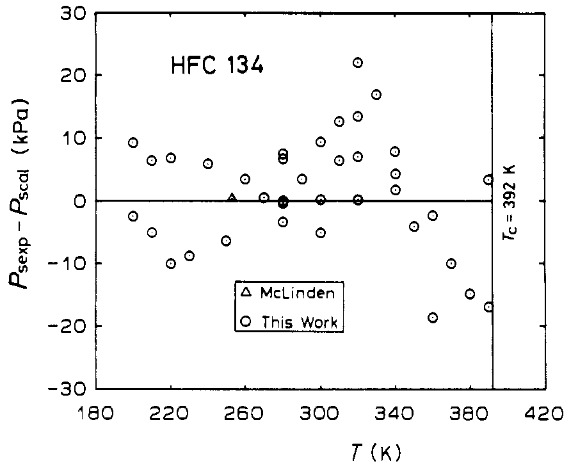

Figure 9. Vapor pressure deviations from eq 2 for HFC 134.

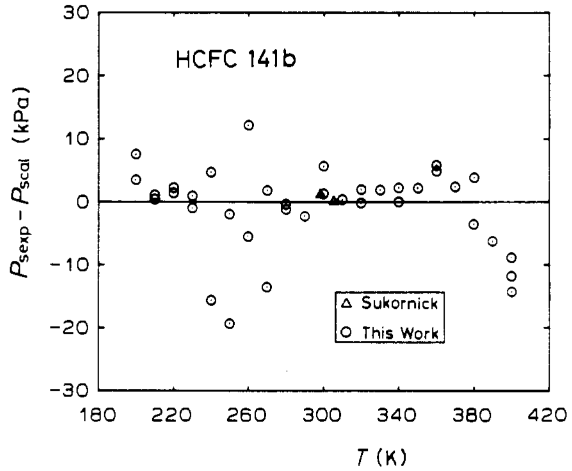

Figure 10. Vapor pressure deviations from eq 2 for HCFC 141b.

Figure 9 shows the vapor pressure deviations of HFC 134 from eq 2. Equation 2 reproduces the present vapor pressure measurements with the standard and maximum deviations of 10 kPa and 22 kPa, respectively. McLinden et al. (*13*) reported the normal boiling temperature. This datum shows very good agreement with the present results, as shown in Figure 9.

Figure 10 shows the vapor pressure deviations of HCFC 141b from eq 2. Equation 2 reproduces the present vapor pressure measurements with the standard and maximum deviations of 7 kPa and 19 kPa, respectively. Sukornick (*12*) reported two vapor pressures, including the normal boiling temperature. These data show excellent agreement with the present results, as shown in Figure 10.

The present compressed liquid *PVT* properties were compared with the Kumagai's Tait equation (*10*). The Kumagai's Tait equation requires many parameters or numerical constants, i.e., the critical temperature, pressure, and density, the normal boiling temperature, the saturated liquid density at the normal boiling temperature, the heat of vaporization at the normal boiling temperature, the saturated liquid densities and vapor pressures at the specified temperature, and the dipole moment. Unfortunately, however, most of these parameters are not available. So, the above-mentioned critical temperatures and critical densities, which are used in eq 1, were also used here.

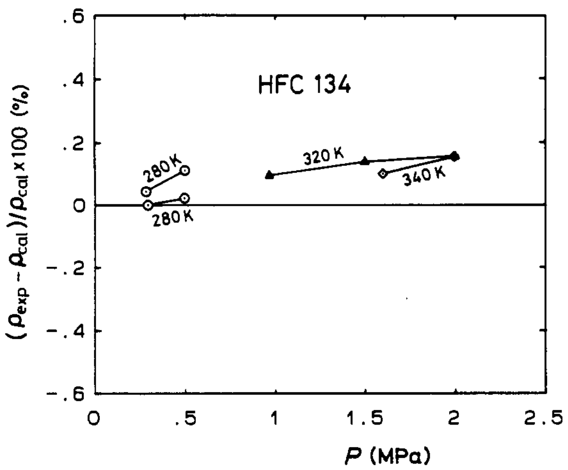

Figure 11. Density deviations from Kumagai's Tait equation for HFC 134.

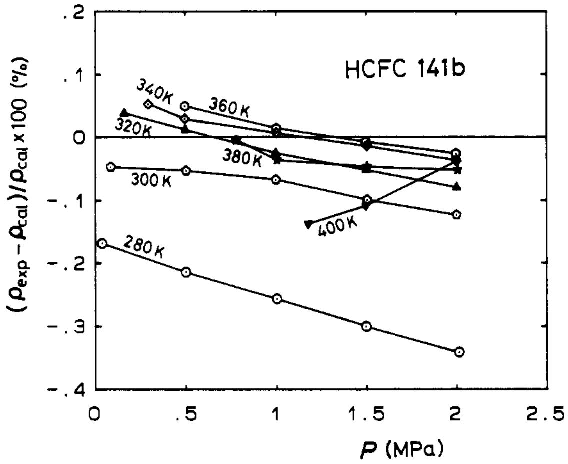

Figure 12. Density deviations from Kumagai's Tait equation for HCFC 141b.

The critical pressures were calculated from eq 2 at the critical temperature, whereas the normal boiling temperature was also calculated from eq 2. The saturated liquid densities and vapor pressures were calculated from eqs 1 and 2 at each temperature. The heat of vaporization was calculated by using the Clausius–Clapeyron relation, where the saturated vapor density was calculated from the Soave–Redlich–Kwong equation of state (*14*), the parameters of which were fitted to the present saturated vapor pressures. The dipole moment, on the other hand, was estimated by using the group-contribution method (*15*). The determined values are listed in Table V.

Figure 11 shows the density deviations of HFC 134 from the combination of eqs 1 and 2 for the saturated liquid data and from Kumagai's Tait equation (*10*) for the compressed liquid isothermal data. The isothermal compressibility of compressed liquid HFC 134 is represented very well by Kumagai's Tait equation because every isotherm is independent of the pressure increment, as shown in Figure 11. The lowest pressure data of every isotherm are saturation points measured as a part of the runs for the *PVT* isotherm measurements, listed with numbers 13, 16, 24, and 29 in Table I.

Figure 12 shows the density deviations of HCFC 141b from the combination of eqs 1 and 2 for the saturated liquid data and from Kumagai's Tait equation (*10*) for the compressed liquid isothermal data. The isothermal compressibility of compressed liquid HCFC 141b is represented very well by Kumagai's Tait equation, but slight systematic deviations depending both on pressure and temperature are observed. These can be considered due to the possible error in estimating the parameters, especially in predicting the dipole moment and/or the critical parameters. All of these deviations, however, are less than the experimental uncertainty. The lowest pressure data of every isotherm are saturation points measured as a part of the runs for the *PVT* isotherm measurements, listed with numbers 18, 20, 23, 26, 29, 32, and 37 in Table II.

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