252 *J. Chem. Eng. Data* **2007,** *52,* 252−255

Specific Volumes of Chlorodifluoromethane in the Temperature Range from (298 to 573) K and Pressures up to 500 MPa

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The specific volumes of chlorodifluoromethane have been measured up to 500 MPa at eight isotherms ranging from (298.2 to 573.2) K. Experiments were performed with a thin-walled sample holder with equal pressure inside and outside. The volume change of the sample was determined with a separation system at 298.2 K by making use of a magnetic float on mercury and a linear variable differential transformer. The specific volume of chlorodifluoromethane varies in this region from (0.579 to 4.957) $cm^3 \cdot g^{-1}$. The experimental uncertainty in specific volumes was estimated to be no greater than ± 0.4 %. The Tait equation was used to correlate the data.

Introduction

Chlorodifluoromethane ($CHClF_2$) is one of the important chemical compounds because of its conveniently low values of critical points ($T_c = 369.29$ K, $p_c = 4.989$ MPa, $V_c = 1.923$ $cm^3 \cdot g^{-1}$), its high dipole moment ($\mu = 4.74 \cdot 10^{-30}$ C·m), and its lack of reactivity. From a scientific viewpoint, the molecule chlorodifluoromethane is not far from spherical but has a very high dipole moment. Such a fluid is of great interest for the study of intermolecular interaction in dense phases because of the obviously strong interaction. All models of intermolecular forces such as the pair intermolecular potential energy functions, rough hard-sphere require knowledge of density as a function of pressure and temperature. Binary and multi-component fluid mixture properties can be calculated from the expressions that describe the pure component data when mixing rules are prescribed. Chlorodifluoromethane is also commonly known as R-22 or freon-22. It is a single-component refrigerant with low ozone depletion potential. It has long been used in a variety of air conditioning and refrigeration applications in a variety of markets. Production of R-22 will cease in 2010 per the Montreal Protocol. Consequently, its technical importance will diminish and fade out in time.

The *pVT* properties of chlorodifluoromethane have been intensively studied at low and moderate pressures by various authors detailed in Table 1, which gives a summary of the previous studies conducted above 10 MPa. The purpose of this study is to provide *pVT* data of chlorodifluoromethane on an extended pressure range up to 500 MPa for the consideration of model fluids.

Experimental Section

The apparatus and experimental procedures used here were described in detail in a previous publication.[11] The sample of known mass was filled in a thin-walled sample holder with equal pressure inside and outside. The volume change of the sample for different applied pressure was determined with a separation system at 298.2 K by making use of a magnetic float on mercury and a linear variable differential transformer. Pressures of the inside and outside of the sample holder were measured by three precision Bourdon gauges. Reproducibility of gauges is given 0.1 % of the full scale. The temperatures were measured with an accuracy of ± 0.1 K via three chromel−alumel thermocouples placed at different height between the sample holder and the inside wall of the autoclave. Temperature difference within the autoclave was not greater than 0.2 K. The position of the magnetic float was located with an accuracy of $\pm 1 \cdot 10^{-5}$ m by a linear variable differential transformer. Chlorodifluoromethane was obtained from the Matheson Company and specified as 99.7 % pure by the manufacturer. It was solidified in liquid nitrogen before its use, while non-condensable gases were pumped off. The combined absolute uncertainty in specific volume increases as pressure is reduced and as temperature increases. It is 0.4 % at the lowest pressure and highest temperature point.

Table 1. Previous Measurements of Density of Chlorodifluoromethane Performed at Pressures above 10 MPa and at Various Temperatures

ref	year	(P_{min} to P_{max})/MPa	(T_{min} to T_{max})/K
1	1994	1.2 to 15.4	304 to 372
2	1991	1.5 to 10	310 to 400
3	1988	1.1 to 30	120 to 325
4	1987	0.1 to 16.8	338 to 438
5	1985	2.1 to 60.6	252 to 523
6	1979	0.2 to 11	252 to 363
7	1979	1.5 to 50	133 to 313
8	1978	9.5 to 157.4	253 to 313
9	1968	0.3 to 35	287 to 473
10	1957	0.6 to 13.0	292 to 423

Results and Discussion

The specific volumes of chlorodifluoromethane were measured along eight isotherms in the range of temperatures from (298 to 573) K and pressures from (10 to 500) MPa. The results listed in Table 2 are used to calculate the compressibility factor ($Z = pV/RT$), which is plotted in Figure 1 as a function of pressure. The compressibility factor over low-pressure and high-temperature ranges are shown in Figure 2. Most of the previous *pVT* measurements were conducted below 60 MPa and performed with smaller uncertainty limits (0.05 to 0.2) % than present studies. A direct comparison is not possible with the measurement points of the previous studies because of the selected temperatures or units of pressure. To make a compari-

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Table 2. Experimental Specific Volumes of Chlorodifluoromethane, V at T = (298 to 573) K and at p = (10 to 500) MPa

	V/cm^3·g^{-1}							
p/MPa	T/K = 298.2	T/K = 323.2	T/K = 348.2	T/K = 373.2	T/K = 423.2	T/K = 473.2	T/K = 523.2	T/K = 573.2
10.0	0.815	0.870	0.955	1.091	2.006	3.216	4.117	4.957
20.0	0.787	0.831	0.887	0.967	1.169	1.531	1.932	2.440
30.0	0.771	0.810	0.852	0.907	1.037	1.210	1.431	1.751
40.0	0.755	0.790	0.828	0.875	0.973	1.089	1.241	1.393
50.0	0.743	0.773	0.807	0.842	0.923	1.015	1.126	1.258
75.0	0.717	0.743	0.768	0.797	0.856	0.922	0.987	1.050
100.0	0.698	0.715	0.742	0.765	0.814	0.867	0.920	0.968
125.0	0.682	0.699	0.719	0.741	0.784	0.830	0.872	0.911
150.0	0.670	0.683	0.701	0.722	0.759	0.797	0.835	0.870
175.0	0.657	0.670	0.686	0.705	0.738	0.772	0.808	0.840
200.0	0.646	0.660	0.674	0.689	0.721	0.754	0.785	0.814
225.0	0.638	0.651	0.663	0.677	0.707	0.735	0.764	0.790
250.0	0.630	0.643	0.655	0.667	0.695	0.720	0.744	0.767
275.0	0.624	0.635	0.646	0.658	0.682	0.705	0.728	0.749
300.0	0.617	0.628	0.639	0.650	0.673	0.694	0.714	0.732
325.0	0.611	0.621	0.632	0.642	0.661	0.683	0.698	0.717
350.0	0.606	0.616	0.625	0.636	0.655	0.671	0.687	0.704
375.0	0.600	0.610	0.619	0.629	0.645	0.661	0.676	0.692
400.0	0.596	0.605	0.614	0.623	0.638	0.652	0.666	0.680
425.0	0.591	0.600	0.608	0.617	0.631	0.644	0.658	0.671
450.0	0.587	0.595	0.603	0.612	0.625	0.637	0.649	0.663
475.0	0.582	0.590	0.598	0.606	0.619	0.629	0.640	0.651
500.0	0.579	0.586	0.594	0.602	0.614	0.623	0.633	0.643

son with the results of these authors, the specific volumes were calculated from their measurement of compressibility using 86.469 g·mol^{-1} molar mass of chlorodifluoromethane. Then, the corresponding specific volumes were calculated by the method of interpolation where comparisons are possible. Relative deviations of specific volumes between the previous and the present study are depicted in Figure 3 as a function of pressure along various isotherms over the range of (298 to 523) K. As can be seen in Figure 3, agreements are close and can be considered within 0.6 % overall uncertainties.

Various authors have developed a region-specific equation of state for chlorodifluoromethane that fit their data.[6,9] Kamei et al.,[12,13] Span and Wagner,[14] and Lemmon et al.[15] have all developed multi-parameter technical equations for chlorodifluoromethane in terms of dimensionless Helmholtz energy with various numbers of parameters. The equation from Lemmon et al.[15] was chosen to make comparisons, and the relative variances between experimental and calculated results are shown in Figure 3.

The Tait equation[16] for correlating high-pressure density data for dense gases, liquids, and liquid mixtures is a suitable empirical equation due to simplicity and accuracy.[17] In its integrated form, this equation is usually written for an isotherm in terms of volume:

$$V = V_0\left[1 - A \ln \frac{B + p/\text{MPa}}{B + p_0/\text{MPa}}\right] \qquad (1)$$

Here, A and B are temperature-dependent parameters. V_0 is the volume at a reference pressure p_0. The selection of p_0 is somewhat arbitrary. p_0 is usually taken as 0.1 MPa for liquids. For dense gases, p_0 should be greater than p_c, and the sum ($B + p_0$) should be positive. As the parameter B goes negative, p_0 has to be increased so that this sum remains positive. Consequently, the area of representation reduces due to exclusion of low-pressure and high-temperature regions where B is negative. Limits of validity of the Tait equation were discussed by Sauermann and Kohler.[18] They indicate the need of a sufficient pressure range for a reasonable correlation and recommend that $p - p_0$ should be between (10 and 100) MPa. When the range goes beyond the 100 MPa, the range density correlation still remains tolerable.

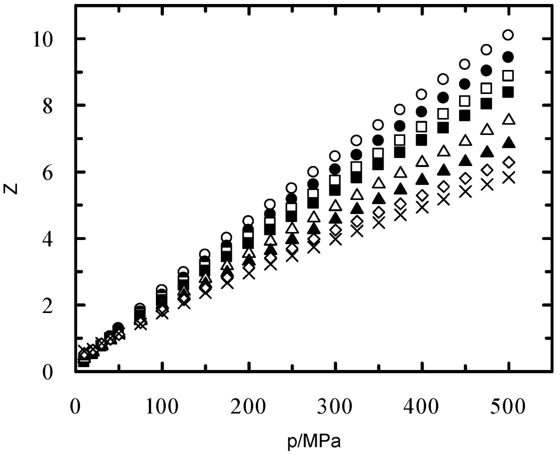

Figure 1. Compressibility factor, Z, for chlorodifluoromethane as a function of pressure: ○, T = 298 K; ●, T = 323 K; □, T = 348 K; ■, T = 373 K; △, T = 423 K; ▲, T = 473 K; ◇, T = 523 K; ×, T = 573 K.

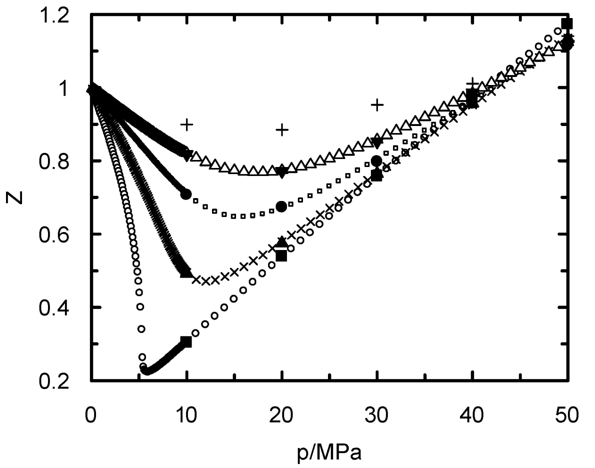

Figure 2. Compressibility factor, Z, for chlorodifluoromethane over low-pressure and high-temperature ranges: ○, ref 15, T = 373 K; ×, ref 15, T = 423 K; □, ref 15, T = 473 K; △, ref 15, T = 523 K; ■, this work, T = 373 K; ▲, this work, T = 423 K; ●, this work, T = 473 K; ▼, this work, T = 523 K; +, this work, T = 573 K.

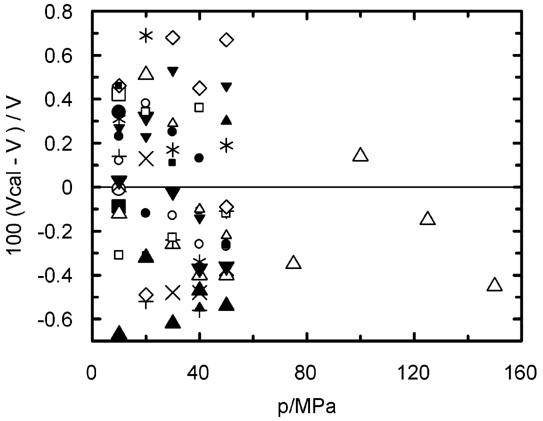

Figure 3. Comparison of the specific volume of chlorodifluoromethane between the literature (V_{lit}) and this work (V): ○, ref 1, T = 323 K; ●, ref 2, T = 298 K; □, ref 2, T = 323 K; ■, ref 2, T = 348 K; △, ref 8, T = 298 K; ▲, ref 15, T = 298 K;, ×, ref 15, T = 323 K; ▼, ref 15, T = 348 K; +, ref 15, T = 373 K; ∗, ref 15, T = 423 K; ◇, ref 15, T = 473 K; small solid triangle down, ref 15, T = 523 K, small open circle, ref 5, T = 298 K; small solid circle, ref 5, T = 323 K; small open box, ref 5, T = 348 K; small solid box, ref 5, T = 373 K; small open triangle up, ref 5, T = 423 K; small solid triangle up, ref 5, T = 473 K; small open diamond, ref 5, T = 523 K.

Table 3. Coefficient of the Tait Equation for Chlorodifluoromethane

p_0/MPa	V_0/cm^3	T/K	A	B/MPa	AAD %
10	0.815	298.2	0.0982	16.81	0.14
30	0.810	323.2	0.1023	3.72	0.18
30	0.828	348.2	0.1070	−1.09	0.24
40	0.875	373.2	0.1075	−13.64	0.20
40	0.973	423.2	0.1141	−21.39	0.15
40	1.089	473.2	0.1206	−26.51	0.14
50	1.126	523.2	0.1308	−33.80	0.16
50	1.258	573.2	0.1261	−40.49	0.22

The Tait equation is usually applied for liquids. Application of this equation to dense polar gases, such as methyl chloride[11] up to 400 MPa, hydrogen fluoride[19] up to 200 MPa, and ammonia[20] up to 950 MPa yielded a reproduction of experimental data within the reported experimental uncertainties. The parameters of the Tait equation were calculated for methylchlorodifluoromethane from the experimental pVT data for each of the eight isotherms by the method of generalized nonlinear least squares and are given in Table 3 together with the average absolute deviation (AAD %) in specific volumes. The accuracy of the isothermal fit is described here by AAD % given by

$$\mathrm{AAD}\ \% = \frac{100}{NP}\sum_{i=1}^{i=NP}\left|\frac{V_{\mathrm{exp},i} - V_{\mathrm{cal},i}}{V_{\mathrm{exp},i}}\right| \tag{2}$$

The relative variances of specific volumes between experimental measurements and calculated from the Tait equation are shown in Figure 4. As it can be seen in Table 3, the Tait A parameter is a weak function of T, whereas B is the strong function of T. As discussed by Malhotra and Woolf,[21] theTait B parameter decreases to a negative number, equal to the negative of the critical pressure at the critical temperature. The optimized B values lay on smooth curves when platted versus reduced temperature.

Conclusion

The specific volume or density of chlorodifluoromethane data have been reported in literature in the temperature range of (252 to 523) K up to 60.6 MPa and in the temperature range of (253 to 313) K up to 157 MPa. This work fills the gap in the temperature range from (298 to 573) K and extends the pressure range up to 500 MPa. A comparison of the specific volume values of this work with the previously reported values in the literature revealed an agreement with in the combined experimental uncertainty of 0.6 %. The Tait equation provides a reproduction of the chlorodifluoromethane data within the 0.4 % overall experimental uncertainty at high temperature and pressure.

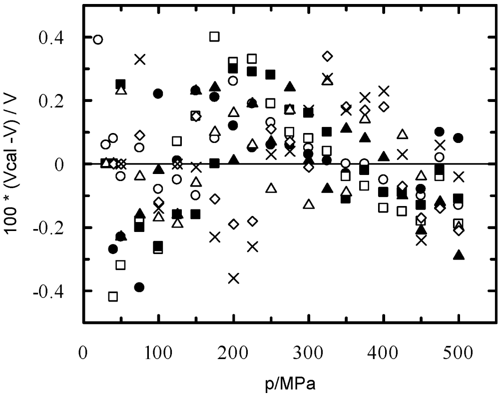

Figure 4. Relative deviations between experimental specific volumes V and calculated values by the Tait equation V_{calc}: ○, T = 298 K; ●, T = 323 K; □, T = 348 K; ■, T = 373 K; △, T = 423 K; ▲, T = 473 K; ◇, T = 523 K; ×, T = 573 K.

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