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# *PVT* and Vapor Pressure Measurements on 1,1-Dichloro-2,2,2-trifluoroethane (HCFC-123)

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**A complete set of *PVT* properties, vapor pressures, and critical parameters of 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) were measured by a constant-volume method. Values of 134 *PVT* property data were obtained along 19 isochores in a range of temperatures from 311 to 523 K, pressures from 0.5 to 12 MPa, and densities from 95 to 1440 kg·m$^{-3}$, respectively. Results for 68 vapor pressures were obtained at temperatures from 308 K to the critical temperature, while a vapor pressure correlation representing the experimental data within ±0.26% was developed. The critical pressure was determined as 3.6655 ± 0.0030 MPa in the course of developing the vapor pressure correlation. The uncertainties of measurements are less than ±10 mK in temperature, ±2 kPa in pressure, and ±0.01 to ±0.14% in density, respectively. The purity of samples used was 99.8 and 99.82 wt %.**

## Introduction

1,1-Dichloro-2,2,2-trifluoroethane (HCFC-123, $CHCl_2CF_3$) is one of the promising substitutes for the conventional refrigerant CFC-11 ($CCl_3F$), but studies of the thermodynamic properties of HCFC-123 are rather limited, not only in the quantity of the reported data but also in the range of the measurements up to the present.

In the present study, the vapor pressures and *PVT* properties are reported in extensive temperature, pressure, and density range covering the entire fluid phase. A vapor pressure correlation and the critical pressure have also been derived from the experimental data.

## Experimental Apparatus and Procedure

A constant-volume method was applied for measuring the vapor pressures and *PVT* properties of HCFC-123. Figure 1 shows the experimental apparatus, which is composed of a constant-volume cell immersed in a thermostated bath, a temperature-measurement device, a PID temperature controller, and a pressure-measurement device, etc. We have already measured *PVT* properties of 1,1,1,2-tetrafluoroethane (HFC-134a) (*1*), and perfluoro-2-methylpentane (*2*), with this apparatus.

The inner volume of the constant-volume cell was carefully calibrated by using the density of water and its volume change due to changes in temperature and pressure was calculated by using the thermal expansivity and Young's modulus of stainless steel. The volume was about 139 cm$^3$ at room temperature. The density of the sample was determined from the inner volume of the cell and the mass of the sample confined in the cell, which was measured by a precision balance. The uncertainty of the cell volume was about ±0.02 to ±0.12%, depending on temperature and pressure, while the uncertainty of the sample mass was ±3 mg.

Table I. Uncertainties of Data and Purities of Samples of HCFC-123

| | series | $\Delta T$/ mK | purity/ wt % | $\Delta\rho$/ (kg·m$^{-3}$) | purity/ wt % |
|---|---|---|---|---|---|
| vapor pressures | | ±10 | ±2 | | 99.8/99.82 |
| *PVT* properties | a | ±10 | ±2 | ±0.1 | 99.82 |
| | b | | | ±0.1 | 99.8 |
| | c | | | ±0.2 | 99.82 |
| | d | | | ±0.3 | 99.82 |
| | e | | | ±0.4 | 99.82 |
| | f | | | ±0.5 | 99.8 |
| | g | | | ±0.5 | 99.8 |
| | h | | | ±0.7 | 99.82 |
| | i | | | ±0.7 | 99.82 |
| | j | | | ±0.8 | 99.82 |
| | k | | | ±0.8 | 99.82 |
| | l | | | ±0.9 | 99.82 |
| | m | | | ±0.9 | 99.82 |
| | n | | | ±0.9 | 99.82 |
| | o | | | ±0.9 | 99.82 |
| | p | | | ±0.8 | 99.82 |
| | q | | | ±0.8 | 99.82 |
| | r | | | ±0.7 | 99.82 |
| | s | | | ±0.4 | 99.82 |

The temperature of silicon oil filled in a thermostated bath was controlled within ±3 mK by the PID temperature controller. At thermal equilibrium, which was confirmed by the pressure of the sample fluid in the cell being stable, the pressure and the temperature of the sample were measured.

The pressure of the sample was measured by the pressure gauges O1, O2, and O3 in Figure 1. The sample cell is connected with a differential pressure detector (B), which transfers the pressure of the sample to pressure-transfer medium, nitrogen gas. The mechanical behavior of the differential pressure detector (B) was calibrated before and after each series of measurements.

The temperature was measured with a standard platinum resistance thermometer (D in Figure 1), which was located near the sample cell. The platinum resistance thermometer was calibrated according to IPTS-68 at the National Laboratory of Metrology, Ibaraki, Japan.

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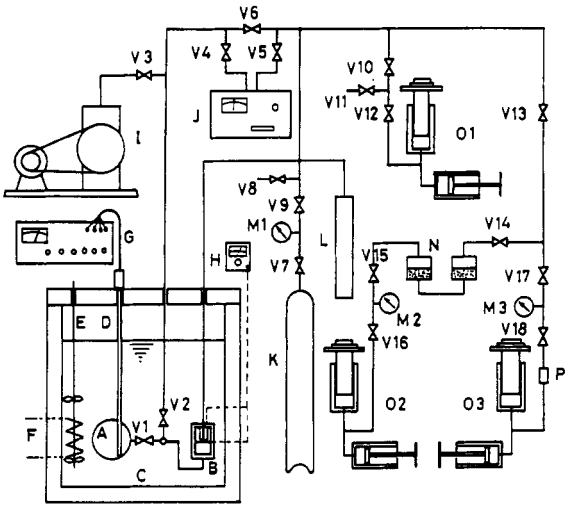


**Figure 1.** Experimental apparatus: (a) sample vessel, (B) differential pressure indicator, (C) thermostated bath, (D) platinum resistance thermometer, (E) stirrer, (F) heater, (G) bridge, (H) resistance meter, (I) vacuum pump, (J) precision Bourdon tube pressure gauge, (K) nitrogen bottle, (L) pressure damper, (M1–M3) pressure gauges, (N) oil–gas separator, (O1) air piston type pressure gauge (up to 0.4 MPa), (O2) oil piston type pressure gauge (up to 15.1 MPa), (O3) air piston type pressure gauge (1.1–15.1 MPa), (P) dust filter, (V1–V18) valves.

The experimental uncertainty in the temperature was estimated to be within ±10 mK and ±2.0 kPa in pressure. By considering the uncertainties of the volume of the sample cell and sample mass confined, the uncertainty of the density was estimated to be between ±0.1 and 0.9 kg·m$^{-3}$. The purity of the sample analyzed by the supplier was 99.8 and 99.82 wt %. The uncertainties and sample purities for each series of measurements are summarized in Table I.

## Results

***Vapor Pressures.*** Vapor pressures measured at temperatures from 308 K to the critical temperature are given in Table II. On the basis of these measurements, a vapor pressure equation that represents the experimental data within ±0.26% at temperatures above 308 K was established as follows:

$$\ln (P/P_c) = (a_1\tau + a_2\tau^{1.2} + a_3\tau^2 + a_4\tau^3)/(1 - \tau) \quad (1)$$

$$\tau = 1 - T_{68}/T_{c(68)}$$

$$a_1 = -7.875\,76 \qquad a_2 = 1.457\,51 \qquad a_3 = 0.520\,220$$

$$a_4 = -3.479\,70$$

$$P_c = 3.6655 \pm 0.0030 \text{ MPa} \qquad T_{c(68)} = 456.86 \pm 0.02 \text{ K}$$

Table II gives the calculated values from eq 1 as $P_{cal}$, the deviations of the present data from $P_{cal}$, and the temperatures in ITS-90 as $T_{90}$, which were calculated from the temperatures of IPTS-68 as $T_{68}$.

Figure 2 shows the comparison of the measurements and correlating equations reported by Weber (*3*), Yamashita et al. (*4*), Fukushima et al. (*5*), Yamagishi and Oguchi (*6*), McLinden et al. (*7*), and the measurements of Morrison and Ward (*8*) with eq 1.

Equation 1 agrees with the previous measurements within ±0.3% except for those reported by Yamagishi and Oguchi (*6*), which show a large deviation from the others at temperatures below 320 K. It should be noted that the absolute pressure deviation of the data by Yamagishi and Oguchi (*6*) is less than 1.5 kPa. Equation 1 represents the present results with the standard deviation of 0.07% and the maximum deviation of 0.26%, the measurements of Weber (*3*) with 0.13 and 0.17%, the measurements of Yamashita et al. (*4*) with 0.10 and

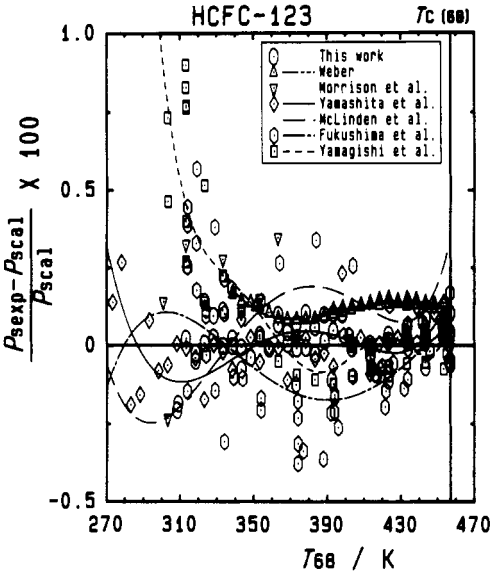


**Figure 2.** Percent vapor pressure deviations from eq 1.

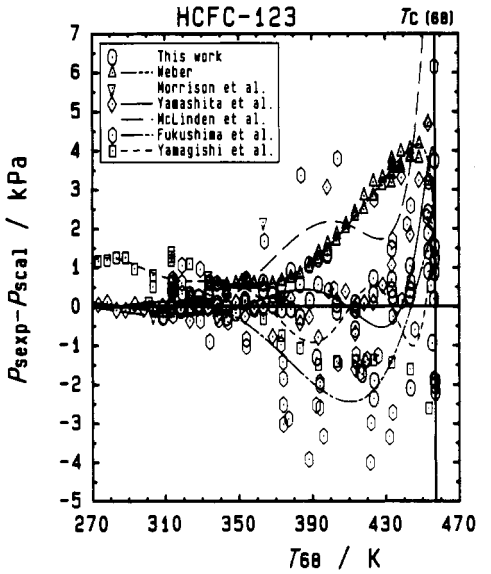


**Figure 3.** Absolute vapor pressure deviations from eq 1.

0.27%, the measurements of Fukushima et al. (*5*) with 0.21 and 0.57%, the measurements of Yamagishi and Oguchi (*6*) with 1.1 and 3.5%, and the measurements of Morrison and Ward (*8*) with 0.23 and 0.34%, respectively. Figure 3 shows the absolute pressure deviations of the above measurements from eq 1. Below the temperature of 350 K, eq 1 reproduces all of the measurements within ±1.5 kPa, but for the region where the temperature is above 350 K, systematic deviations were found for each measurement.

***The Critical Pressure.*** In the course of developing the vapor pressure correlation, the critical pressure was determined so as to coincide with the measured critical temperature and critical density reported by Tanikawa et al. (*9*). Along five isochores at densities of 530.1 ± 0.5, 532.1 ± 0.5, 554.7 ± 0.6, 557.9 ± 0.7, and 598.8 ± 0.7 kg·m$^{-3}$ which encompass the critical density and two of them are within the critical density accompanied with the uncertainty observed by Tanikawa et al. (*9*), 556 ± 3 kg·m$^{-3}$. The vapor pressures were measured at very small temperature intervals in the critical region, as shown in Figure 4 and Table II. On the basis of these experimental results, the vapor pressure correlation, eq 1, was developed, which fits the vapor pressures near the critical point very well. The critical pressure corresponding to the critical temperature $T_{c(68)}$ = 456.86 ± 0.02 K, measured by Tanikawa et al. (*9*),

**Table II. Measured Vapor Pressures for HCFC-123 and Comparison with Values Calculated from Equation 1[a]**

| no. | $T_{68}$/K | $T_{90}$/K | $P_{exp}$/MPa | $P_{cal}$/MPa | dev/% | no. | $T_{68}$/K | $T_{90}$/K | $P_{exp}$/MPa | $P_{cal}$/MPa | dev/% |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 308.27 | 308.26 | 0.131 | 0.131 | −0.208 | 35 | 393.14 | 393.11 | 1.201 | 1.200 | 0.047 |
| 2 | 308.75 | 308.74 | 0.133 | 0.133 | −0.187 | 36 | 398.12 | 398.09 | 1.326 | 1.324 | 0.099 |
| 3 | 312.98 | 312.97 | 0.154 | 0.154 | 0.022 | 37 | 398.13 | 398.10 | 1.326 | 1.325 | 0.102 |
| 4 | 313.53 | 313.52 | 0.157 | 0.156 | 0.255 | 38 | 403.15 | 403.11 | 1.459 | 1.459 | 0.003 |
| 5 | 318.14 | 318.13 | 0.182 | 0.182 | −0.051 | 39 | 403.15 | 403.12 | 1.459 | 1.459 | −0.010 |
| 6 | 318.14 | 318.13 | 0.182 | 0.182 | −0.025 | 40 | 413.18 | 413.14 | 1.758 | 1.759 | −0.033 |
| 7 | 323.13 | 323.11 | 0.212 | 0.212 | 0.006 | 41 | 413.19 | 413.16 | 1.759 | 1.759 | 0.005 |
| 8 | 323.13 | 323.12 | 0.213 | 0.212 | 0.140 | 42 | 416.76 | 416.73 | 1.874 | 1.876 | −0.093 |
| 9 | 327.98 | 327.96 | 0.246 | 0.246 | 0.095 | 43 | 423.11 | 423.07 | 2.096 | 2.099 | −0.113 |
| 10 | 328.13 | 328.12 | 0.247 | 0.247 | 0.025 | 44 | 423.14 | 423.11 | 2.100 | 2.100 | 0.015 |
| 11 | 333.14 | 333.12 | 0.286 | 0.286 | 0.112 | 45 | 423.16 | 423.12 | 2.101 | 2.100 | 0.035 |
| 12 | 333.14 | 333.12 | 0.286 | 0.286 | −0.002 | 46 | 423.38 | 423.34 | 2.107 | 2.109 | −0.090 |
| 13 | 338.13 | 338.11 | 0.329 | 0.329 | −0.003 | 47 | 433.14 | 433.10 | 2.492 | 2.491 | 0.017 |
| 14 | 338.13 | 338.12 | 0.329 | 0.329 | 0.023 | 48 | 433.17 | 433.13 | 2.493 | 2.492 | 0.059 |
| 15 | 343.13 | 343.11 | 0.377 | 0.377 | −0.006 | 49 | 433.18 | 433.15 | 2.494 | 2.493 | 0.028 |
| 16 | 343.14 | 343.12 | 0.377 | 0.378 | −0.077 | 50 | 443.13 | 443.09 | 2.938 | 2.938 | 0.009 |
| 17 | 348.14 | 348.12 | 0.431 | 0.431 | −0.040 | 51 | 443.14 | 443.10 | 2.939 | 2.939 | 0.014 |
| 18 | 353.13 | 353.11 | 0.490 | 0.490 | 0.034 | 52 | 443.16 | 443.12 | 2.940 | 2.939 | 0.035 |
| 19 | 353.13 | 353.11 | 0.490 | 0.490 | 0.022 | 53 | 443.18 | 443.14 | 2.938 | 2.941 | −0.071 |
| 20 | 358.14 | 358.12 | 0.554 | 0.554 | −0.011 | 54 | 453.12 | 453.08 | 3.452 | 3.451 | 0.041 |
| 21 | 363.13 | 363.10 | 0.626 | 0.625 | 0.100 | 55 | 453.12 | 453.08 | 3.452 | 3.451 | 0.026 |
| 22 | 363.14 | 363.12 | 0.626 | 0.625 | 0.066 | 56 | 453.15 | 453.11 | 3.454 | 3.452 | 0.054 |
| 23 | 368.16 | 368.13 | 0.703 | 0.703 | 0.042 | 57 | 453.17 | 453.13 | 3.456 | 3.454 | 0.070 |
| 24 | 368.19 | 368.17 | 0.703 | 0.703 | 0.003 | 58 | 455.17 | 455.13 | 3.565 | 3.566 | −0.026 |
| 25 | 373.13 | 373.11 | 0.786 | 0.786 | −0.011 | 59 | 456.14 | 456.10 | 3.623 | 3.623 | 0.005 |
| 26 | 373.14 | 373.11 | 0.787 | 0.787 | 0.070 | 60 | 456.17 | 456.13 | 3.623 | 3.624 | −0.052 |
| 27 | 378.12 | 378.09 | 0.878 | 0.878 | −0.009 | 61 | 456.52 | 456.48 | 3.646 | 3.645 | 0.024 |
| 28 | 378.18 | 378.15 | 0.880 | 0.880 | 0.105 | 62 | 456.55 | 456.51 | 3.648 | 3.647 | 0.032 |
| 29 | 383.14 | 383.11 | 0.978 | 0.977 | 0.058 | 63 | 456.57 | 456.53 | 3.646 | 3.648 | −0.056 |
| 30 | 383.15 | 383.12 | 0.977 | 0.978 | −0.028 | 64 | 456.62 | 456.58 | 3.652 | 3.651 | 0.033 |
| 31 | 388.13 | 388.10 | 1.085 | 1.084 | 0.098 | 65 | 456.65 | 456.61 | 3.654 | 3.653 | 0.042 |
| 32 | 388.41 | 388.38 | 1.091 | 1.091 | 0.014 | 66 | 456.68 | 456.64 | 3.658 | 3.655 | 0.102 |
| 33 | 392.15 | 392.12 | 1.175 | 1.177 | −0.112 | 67 | 456.77 | 456.74 | 3.658 | 3.660 | −0.052 |
| 34 | 393.13 | 393.10 | 1.201 | 1.200 | 0.101 | 68 | 456.77 | 456.74 | 3.658 | 3.660 | −0.060 |

[a] $T_{68}$ = IPTS-68; $T_{90}$ = ITS-90.

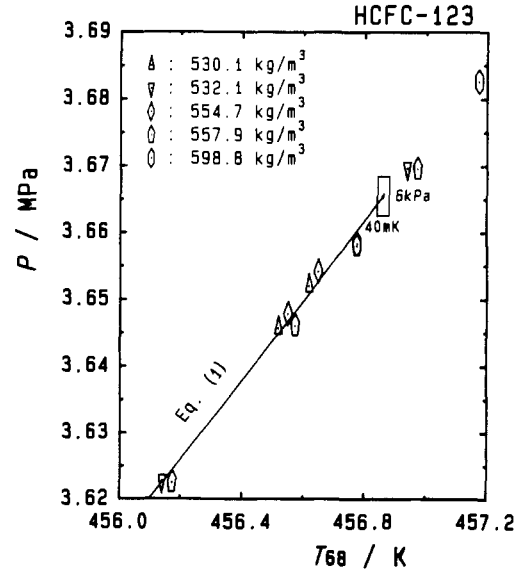


**Figure 4.** Vapor pressure measurements near the critical point of HCFC-123.

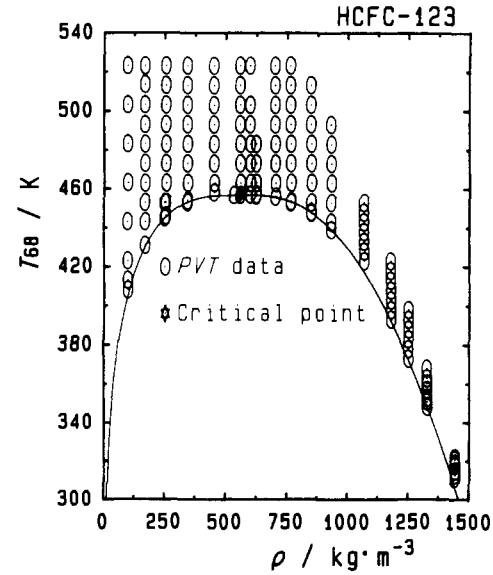


**Figure 5.** Distribution of the present *PVT* property data.

was finally determined as $P_c$ = 3.6655 ± 0.0030 MPa.

***PVT Properties.*** The *PVT* properties of HCFC-123 were measured along 19 isochores in an extensive range of densities from 95 to 1440 kg·m$^{-3}$, temperatures from 311 to 523 K, and pressures from 0.5 to 12 MPa, respectively. The 134 *PVT* measurements are listed in Table III, in both temperature scales of IPTS-68 and ITS-90 as $T_{68}$ and $T_{90}$, respectively. The distribution of the present measurements in a temperature–density plane is illustrated in Figure 5.

So far, six experimental studies are available regarding the *PVT* properties of HCFC-123, i.e., those of Weber (*3*), Fukushima et al. (*5*), Yamagishi and Oguchi (*6*), Morrison and Ward (*8*), Maezawa et al. (*10*), and Matsuo (*11*). Figure 6 shows these measurements on a pressure–temperature plane with the present results. Matsuo (*11*) reported a set of *PVT* values up to 39 MPa in the liquid phase. Morrison and Ward (*8*) and Maezawa et al. (*10*) also reported the *PVT* measurements in the liquid region, while Weber (*3*) published a set of measurements in the gaseous phase. Fukushima et al. (*5*) and Yamagishi and Oguchi (*6*) reported the *PVT* measurements in the limited range of gaseous and liquid phase, whereas the present

**Table III. *PVT* Measurements for HCFC-123[a]**

| no. | $T_{68}$/K | $T_{90}$/K | $P$/MPa | $\rho$/(kg·m$^{-3}$) | no. | $T_{68}$/K | $T_{90}$/K | $P$/MPa | $\rho$/(kg·m$^{-3}$) | no. | $T_{68}$/K | $T_{90}$/K | $P$/MPa | $\rho$/(kg·m$^{-3}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | a Series | | | | | h Series | | | | | n Series | | |
| 1 | 408.16 | 408.12 | 1.540 | 95.98 | 48 | 456.97 | 456.93 | 3.670 | 557.9 | 94 | 439.17 | 439.13 | 2.781 | 931.0 |
| 2 | 413.16 | 413.13 | 1.577 | 95.96 | 49 | 463.17 | 463.14 | 4.046 | 557.7 | 95 | 443.17 | 443.13 | 3.408 | 930.8 |
| 3 | 423.16 | 423.13 | 1.650 | 95.91 | 50 | 473.18 | 473.14 | 4.662 | 557.5 | 96 | 453.17 | 453.13 | 5.051 | 930.3 |
| 4 | 443.17 | 443.13 | 1.791 | 95.83 | 51 | 483.18 | 483.14 | 5.287 | 557.2 | 97 | 463.18 | 463.14 | 6.737 | 929.9 |
| 5 | 463.18 | 463.14 | 1.930 | 95.73 | 52 | 493.18 | 493.14 | 5.917 | 556.9 | 98 | 473.17 | 473.13 | 8.448 | 929.4 |
| 6 | 483.18 | 483.14 | 2.062 | 95.64 | 53 | 503.19 | 503.14 | 6.548 | 556.6 | 99 | 483.18 | 483.14 | 10.178 | 928.9 |
| 7 | 503.18 | 503.14 | 2.192 | 95.55 | 54 | 513.19 | 513.15 | 7.180 | 556.3 | 100 | 493.18 | 493.14 | 11.929 | 928.4 |
| 8 | 523.19 | 523.15 | 2.320 | 95.45 | 55 | 523.19 | 523.15 | 7.813 | 556.0 | | | | | |
| | | b Series | | | | | i Series | | | | | o Series | | |
| 9 | 431.11 | 431.08 | 2.376 | 167.8 | 56 | 457.17 | 457.13 | 3.683 | 598.8 | 101 | 423.17 | 423.13 | 3.333 | 1066.7 |
| 10 | 443.13 | 443.09 | 2.555 | 167.7 | 57 | 463.18 | 463.14 | 4.075 | 598.6 | 102 | 428.16 | 428.13 | 4.570 | 1066.4 |
| 11 | 453.14 | 453.10 | 2.698 | 167.6 | 58 | 473.18 | 473.14 | 4.752 | 598.3 | 103 | 433.17 | 433.13 | 5.824 | 1066.1 |
| 12 | 463.15 | 463.11 | 2.837 | 167.5 | 69 | 483.18 | 483.14 | 5.443 | 598.0 | 104 | 438.17 | 438.13 | 7.108 | 1065.9 |
| 13 | 473.14 | 473.10 | 2.972 | 167.4 | 60 | 493.18 | 493.14 | 6.141 | 597.7 | 105 | 443.17 | 443.13 | 8.342 | 1065.6 |
| 14 | 483.15 | 483.11 | 3.106 | 167.3 | 61 | 503.18 | 503.14 | 6.845 | 597.4 | 106 | 448.17 | 448.13 | 9.607 | 1065.3 |
| 15 | 493.16 | 493.12 | 3.231 | 167.3 | 62 | 523.19 | 523.15 | 8.260 | 596.8 | 107 | 453.17 | 453.13 | 10.878 | 1065.0 |
| 16 | 503.18 | 503.14 | 3.367 | 167.2 | | | | | | | | | | |
| 17 | 513.61 | 513.57 | 3.501 | 167.1 | | | j Series | | | | | p Series | | |
| 18 | 523.14 | 523.10 | 3.621 | 167.0 | 63 | 456.68 | 456.64 | 3.658 | 623.2 | 108 | 393.27 | 393.24 | 1.414 | 1175.6 |
| | | | | | 64 | 457.18 | 457.14 | 3.691 | 623.1 | 109 | 398.16 | 398.12 | 3.087 | 1175.3 |
| | | c Series | | | 65 | 463.18 | 463.14 | 4.102 | 623.0 | 110 | 403.16 | 403.13 | 4.809 | 1175.0 |
| 19 | 445.22 | 445.18 | 3.024 | 249.1 | 66 | 473.18 | 473.14 | 4.815 | 622.6 | 111 | 408.16 | 408.12 | 6.536 | 1175.0 |
| 20 | 453.17 | 453.13 | 3.222 | 249.0 | 67 | 483.18 | 483.14 | 5.547 | 622.3 | 112 | 413.16 | 413.13 | 8.266 | 1174.3 |
| | | | | | | | | | | 113 | 418.16 | 418.13 | 10.002 | 1174.0 |
| | | d Series | | | | | k Series | | | 114 | 423.16 | 423.13 | 11.737 | 1173.7 |
| 21 | 446.26 | 446.22 | 3.066 | 254.4 | 68 | 456.17 | 456.13 | 3.639 | 701.5 | | | | | |
| 22 | 453.16 | 453.12 | 3.241 | 254.3 | 69 | 463.17 | 463.13 | 4.216 | 701.2 | | | q Series | | |
| 23 | 463.18 | 463.14 | 3.497 | 254.2 | 70 | 473.18 | 473.14 | 5.085 | 700.9 | 115 | 373.15 | 373.12 | 1.195 | 1248.9 |
| 24 | 473.18 | 473.14 | 3.721 | 254.0 | 71 | 483.18 | 483.14 | 5.980 | 700.5 | 116 | 378.15 | 378.12 | 3.339 | 1248.5 |
| 25 | 483.18 | 483.14 | 3.945 | 253.9 | 72 | 493.18 | 493.14 | 6.890 | 700.2 | 117 | 383.15 | 383.12 | 5.485 | 1248.2 |
| 26 | 493.18 | 493.14 | 4.169 | 253.8 | 73 | 503.18 | 503.14 | 7.815 | 699.8 | 118 | 388.15 | 388.12 | 7.655 | 1247.8 |
| 27 | 503.18 | 503.14 | 4.387 | 253.7 | 74 | 513.19 | 513.15 | 8.744 | 699.4 | 119 | 393.15 | 393.12 | 9.778 | 1247.5 |
| 28 | 513.19 | 513.15 | 4.597 | 253.5 | 75 | 523.19 | 523.15 | 9.680 | 699.1 | 120 | 398.15 | 398.12 | 11.933 | 1247.2 |
| 29 | 523.19 | 523.15 | 4.803 | 253.4 | | | | | | | | | | |
| | | | | | | | l Series | | | | | r Series | | |
| | | e Series | | | 76 | 453.17 | 453.13 | 3.456 | 764.6 | 121 | 348.34 | 348.32 | 0.524 | 1324.7 |
| 30 | 453.18 | 453.14 | 3.443 | 342.3 | 77 | 453.67 | 453.64 | 3.502 | 764.5 | 122 | 351.14 | 351.12 | 2.032 | 1324.5 |
| 31 | 454.06 | 454.02 | 3.476 | 342.3 | 78 | 463.18 | 463.14 | 4.438 | 764.2 | 123 | 353.14 | 353.12 | 3.109 | 1324.3 |
| 32 | 463.17 | 463.13 | 3.805 | 342.1 | 79 | 473.18 | 473.14 | 5.474 | 763.8 | 124 | 357.14 | 357.12 | 5.260 | 1324.0 |
| 33 | 473.19 | 473.15 | 4.152 | 342.0 | 80 | 483.18 | 483.14 | 6.539 | 763.4 | 125 | 360.43 | 360.41 | 7.030 | 1323.8 |
| 34 | 483.19 | 483.15 | 4.489 | 341.8 | 81 | 493.18 | 493.14 | 7.622 | 763.0 | 126 | 363.14 | 363.12 | 8.486 | 1323.6 |
| 35 | 493.19 | 493.15 | 4.819 | 341.6 | 82 | 503.18 | 503.14 | 8.718 | 762.6 | 127 | 368.15 | 368.12 | 11.173 | 1323.2 |
| 36 | 503.19 | 503.15 | 5.146 | 341.4 | 83 | 513.19 | 513.15 | 9.824 | 762.2 | | | | | |
| 37 | 513.19 | 513.15 | 5.468 | 341.3 | 84 | 523.19 | 523.15 | 10.938 | 761.8 | | | s Series | | |
| 38 | 523.19 | 523.15 | 5.787 | 341.1 | | | | | | 128 | 311.28 | 311.28 | 3.429 | 1439.5 |
| | | | | | | | m Series | | | 129 | 313.14 | 313.13 | 4.834 | 1439.3 |
| | | f Series | | | 85 | 447.77 | 447.73 | 3.176 | 848.4 | 130 | 315.14 | 315.13 | 6.340 | 1439.2 |
| 39 | 458.24 | 458.20 | 3.727 | 451.2 | 86 | 448.17 | 448.13 | 3.223 | 848.4 | 131 | 318.14 | 318.12 | 8.614 | 1438.9 |
| 40 | 463.12 | 463.08 | 3.969 | 451.1 | 87 | 453.17 | 453.13 | 3.844 | 848.2 | 132 | 319.14 | 319.13 | 9.366 | 1438.8 |
| 41 | 473.17 | 473.13 | 4.455 | 450.9 | 88 | 463.18 | 463.14 | 5.132 | 847.8 | 133 | 321.14 | 321.13 | 10.870 | 1438.7 |
| 42 | 483.14 | 483.10 | 4.931 | 450.6 | 89 | 473.18 | 473.14 | 6.462 | 847.3 | 134 | 322.14 | 322.12 | 11.624 | 1438.6 |
| 43 | 493.15 | 493.11 | 5.406 | 450.4 | 90 | 483.20 | 483.16 | 7.817 | 846.9 | | | | | |
| 44 | 503.13 | 503.09 | 5.875 | 450.2 | 91 | 493.18 | 493.14 | 9.190 | 846.4 | | | | | |
| 45 | 513.13 | 513.09 | 6.343 | 449.9 | 92 | 503.18 | 503.14 | 10.576 | 846.0 | | | | | |
| 46 | 523.15 | 523.11 | 6.810 | 449.7 | 93 | 513.19 | 513.15 | 11.968 | 845.5 | | | | | |
| | | g Series | | | | | | | | | | | | |
| 47 | 456.94 | 456.90 | 3.670 | 532.1 | | | | | | | | | | |

[a] $T_{68}$ = IPTS-68; $T_{90}$ = ITS-90.

measurements cover a wide range of the conditions in the entire fluid phase, as shown in Figure 6.

## Discussion

Since the first thermodynamic property studies of HCFC-123 started only 3 years ago, only a single equation of state reported by McLinden et al. (*7*) is available for HCFC-123 at present. This equation of state was developed mainly on the basis of *PVT* measurements by Weber (*3*) in the gaseous phase. The comparison of the available *PVT* data with that equation of state is shown in Figures 7 and 8. Below a density of 200 kg·m$^{-3}$, the equation represents the present data, the measurements of Weber (*3*), and those of Fukushima et al. (*5*) very well, but above 200 kg·m$^{-3}$ the equation does not reproduce the measurements.

Concerning the critical parameters, four reports are available beside the present study for HCFC-123, which are listed in Table IV. The reported values of the critical pressure and temperature together with the claimed uncertainties are summarized in Figure 9. A set of the critical temperature observed by Tanikawa et al. (*9*) and the critical pressure by the present authors agrees well with that of Weber (*3*). On the other hand, the critical parameters reported by Yamashita et al. (*4*) and Fukushima et al. (*5*) agree with each other, although their values differ from the present results by more than the mutual estimated uncertainties.

**Table IV. Critical Parameters of HCFC-123[a]**

| first author | year | $T_{c(68)}$/K | $T_{c(90)}$/K | $\Delta T_c$/K | $P_c$/MPa | $\Delta P_c$/MPa | $\rho_c$/(kg·m$^{-3}$) | $\Delta\rho_c$/(kg·m$^{-3}$) | purity/wt % | ref no. |
|---|---|---|---|---|---|---|---|---|---|---|
| Tanikawa | 1989 | 456.86 | 456.82 | ±0.02 | | | 556 | ±3 | 99.8/99.99 | 9 |
| Yamashita | 1989 | 456.96 | 456.92 | ±0.05 | 3.675 | ±0.005 | | | 99.5 | 4 |
| Fukushima | 1990 | 456.94 | 456.90 | ±0.04 | 3.672 | ±0.004 | 553 | ±5 | 99.8/99.9 | 5 |
| Weber | 1990 | 456.87 | 456.83 | ±0.03 | 3.668 | ±0.004 | 550 | ±4 | 99.95 | 3 |
| this work | 1990 | 456.86[b] | 456.82[b] | ±0.02[b] | 3.6655 | ±0.0030 | 556[b] | ±3[b] | 99.8/99.82 | |

[a] Scales used: $T_{c(68)}$, IPTS-68; $T_{c(90)}$, ITS-90. [b] Values reported by Tanikawa et al. (9).

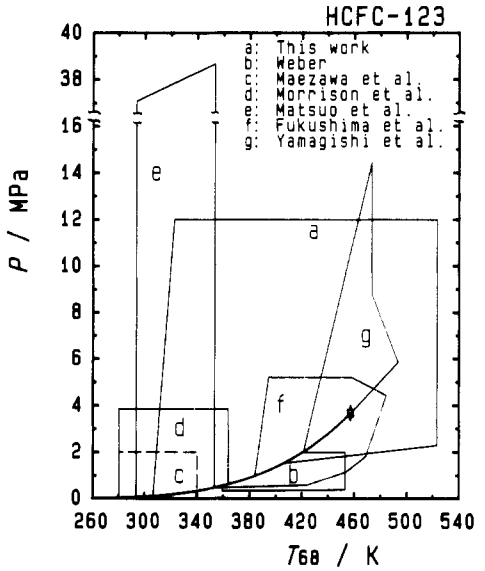


**Figure 6.** Measured ranges of the *PVT* property data for HCFC-123.

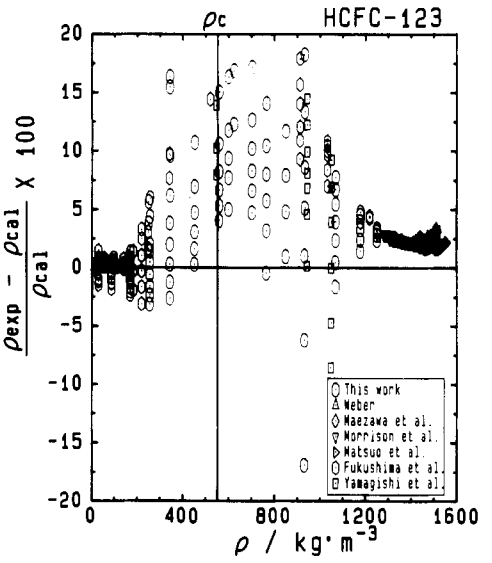


**Figure 8.** Density deviation from the equation of state developed by McLinden et al. (7).

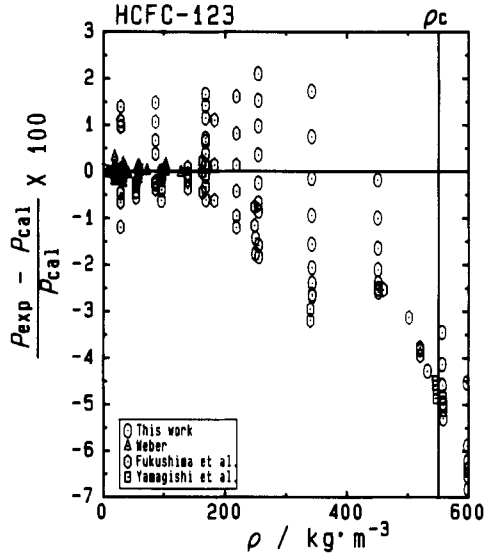


**Figure 7.** Pressure deviation from the equation of state developed by McLinden et al. (7).

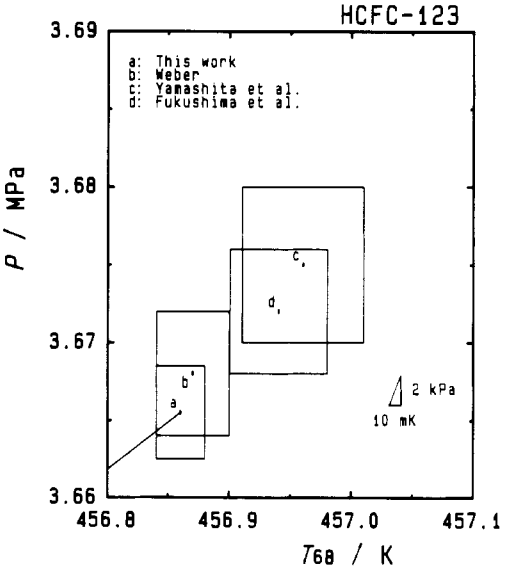


**Figure 9.** Comparison of the critical parameters associated with the claimed uncertainties.

## Conclusion

An extensive set of *PVT*, vapor pressure, and the critical parameters of HCFC-123 has been measured. The present experimental *PVT* measurements are the first set covering a wide range of the state parameters in the entire fluid phase. Vapor pressures and the critical pressure have also been reported with high reliability, i.e., ±2 and ±3 kPa, respectively. A vapor pressure correlation was developed which is considered effective in the temperature range from 300 K to the critical temperature, although it may be extrapolated to the lowest temperature of 270 K.

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**Registry No.** $CHCl_2CF_3$, 306-83-2.

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# Apparent and Partial Molal Volumes of Selected Symmetrical Tetraalkylammonium Bromides in 2-Methoxy-1-ethanol at 25 °C

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**The apparent and partial molal volumes of six symmetrical tetraalkylammonium bromides, $R_4NBr$ (R = $C_2H_5$ to $C_7H_{15}$) in 2-methoxy-1-ethanol (ME) have been determined at 25 °C. The limiting apparent molal volumes ($\phi^\circ_v$) and the experimental slopes ($S^*_v$) have been interpreted in terms of ion-solvent and ion-ion interactions, respectively. Use has been made of the nonthermodynamic, so-called extrapolation method to split the limiting apparent molal volumes into ionic contributions. The $\bar{V}^\circ_{R_4NX}$ values in 2-methoxy-1-ethanol are found to be almost similar to those in other organic solvents examined and differ greatly from the values in water and heavy water solutions. The ion-solvent interaction effect, as estimated by the combination of the viscosity $B_{ion}$ values with $\bar{V}^\circ_{ion}$ values, indicates that these ions may be classified as "structure breakers" in this solvent medium.**

## Introduction

The volumetric behavior of solutes has proved to be very useful in elucidating the various interactions occurring in aqueous and nonaqueous solutions (*1*). Studies on the apparent and partial molal volumes of electrolytes have been used to examine the ion-ion, ion-solvent, and solvent-solvent interactions (*2*). The apparent and partial molal volumes of tetraalkylammonium salts have been investigated rather extensively in aqueous (*3-5*) and nonaqueous solutions (*6*, *7*). Such measurements have also been reported for water-organic solvent binary systems (*8*). However, no work has been reported on the apparent and partial molal volumes of tetraalkylammonium bromides, $R_4NBr$ (R = $C_2H_5$ to $C_7H_{15}$) in 2-methoxy-1-ethanol at 25 °C. 2-Methoxy-1-ethanol is a "quasi-aprotic" solvent (*9*) of low dielectric constant ($\epsilon_{25\,°C}$ = 16.93). In recent years much attention has been given to this solvent, since it is of particular interest in the field of various industrial processes, synthesis, and electrochemical studies (*10*, *11*).

## Experimental Section

2-Methoxy-1-ethanol (G.R.E. Merck) was distilled twice in an all-glass distillation set immediately before use. The purified solvent had a density of 0.960 02 g $cm^{-3}$, a coefficient of viscosity of 1.5414 cP, and a specific conductance of ca. 1.01 × $10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ at 25 °C. These values are in good agreement with the literature values (*12*), 0.960 24 g $cm^{-3}$, 1.60 cP, and 1.09 × $10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ (at 20 °C), respectively.

Tetraalkylammonium bromides were of Fluka purum or puriss grade; these were purified as described in the literature (*13*) and also described earlier by us (*14*). The salts were purified by recrystallization, and the higher homologues were recrystallized twice to ensure highest purity. The recrystallized salts were dried under vacuum at elevated temperatures for 12 h. The salts were stored in a vacuum desiccator and dried for 3-4 h at 100 °C prior to use.

A stock solution for each salt was prepared by weight, and working solutions in the concentration range $0.01 < c/(\text{mol dm}^{-3}) < 0.12$ were obtained by weight dilution. The conversion of the molality into molarity was done by using the density values. The densities were measured with an Ostwald-Sprengal type pycnometer having a bulb volume of about 25 $cm^3$ and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 25 °C with doubly distilled water. Measurements were made in an oil bath maintained at 25 ± 0.005 °C by means of a mercury-in-glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The precision of the density measurements was greater than ±3 × $10^{-5}$ g $cm^{-3}$.

## Results and Discussion

The apparent molal volumes, $\phi_v$, of the solutes were calculated from the densities of the solutions by using the equation

$$\phi_v = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \quad (1)$$

where $M$ is the molecular weight of the solute, $\rho_0$ and $\rho$ are the densities of the solvent and the solution, respectively, and $c$ is the concentration in molarity.

The partial molal volumes, $\bar{V}_2$, were computed from $\phi_v$ with the equation

$$\bar{V}_2 = \phi_v + \frac{1000 - c\phi_v}{2000 + c^{3/2}(\partial\phi_v/\partial c^{1/2})} c^{1/2}(\partial\phi_v/\partial c^{1/2}) \quad (2)$$

The molar concentrations, densities, and apparent and partial molal volumes of the solutions of various tetraalkylammonium bromides in 2-methoxy-1-ethanol at 25 °C are reported in Table I. The limiting apparent molal volumes, $\phi^\circ_v$ (equal to the partial molal volumes at infinite dilution, $\bar{V}^\circ_2$), were obtained by least-squares fitting of $\phi_v$ values to the equation

$$\phi_v = \phi^\circ_v + S^*_v c^{1/2} \quad (3)$$

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