PVT Property Measurements for Liquid 1,2-Dichloro-1,2,2-trifluoroethane from 278 to 338 K

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The effect of pressure on the volume of liquid 1,2-dichloro-1,2,2-trifluoroethane (R123a) has been measured relative to the volume at 0.1 MPa with a bellows volumometer for pressures up to 380 MPa over the temperature range (278.15 to 298.14) K and up to about 275 MPa for (313.14 to 338.13) K. The experimental volume ratios have been represented by equations to enable interpolation and extrapolation of volumetric properties. Isothermal compressibilities, isobaric expansivities, internal pressures, and the change in isobaric heat capacity from its value at 0.1 MPa have been calculated. Although there are similarities between these properties and those of 2,2-dichloro-1,1,1-trifluoroethane (R123), there are differences, indicating the effects of the greater asymmetry of the molecular structure of R123a.

Introduction

This work is part of an experimental program to determine the contributions of the various substituents to the volumetric properties of substituted ethanes. The overall aim is to explore the limitations of a simple scheme for predicting the volumetric properties of a series of related compounds (Malhotra and Woolf, 1995). The present results complement the earlier data (Malhotra and Woolf, 1993a) for 2,2-dichloro-1,1,1-trifluoroethane (R123), for which the normal boiling point of 300.7 K is 2 K lower than that of R123a (Kubota et al., 1989). Previous volumetric data for liquid R123a have been measured for pressures below 100 MPa (McLinden et al., 1991). Kumagai and Takahashi (1991) reported densities and shear viscosities for R123 and R123a along the coexistence curve from 273.1 to 353.15 K which showed significant differences between the values for the two compounds at the lower temperatures. The present work extends to pressures of about 380 MPa for temperatures up to 298 K, but for the higher temperatures which extend to 338 K, above the normal boiling point of 302.7 K (Kubota et al., 1989), the nature of the apparatus limits the maximum pressure to about 280 MPa.

Experimental Section

R123a was from PCR Inc., Gainesville, FL, with a stated purity of 98.5% and was fractionally distilled to obtain a middle fraction boiling over a 1 K temperature range from molecular sieves type 4A before use to decrease the higher boiling point impurities that are usually present in these commercial chemicals. The purity was not determined; it is general experience that the volume ratios used here to measure the effect of pressure on the liquid are affected only within the experimental error by small amounts of impurities. Densities at atmospheric pressure, ρ(0.1 MPa), were measured with an Anton Paar Model DMA60 digital densimeter with a DMA602HT external cell; this was frequently and carefully calibrated (Malhotra and Woolf, 1994). Temperatures were measured with a platinum resistance thermometer and adjusted to ITS-90. They were held constant to ±0.005 K and have an accuracy of ±0.01 K; the procedure for measuring the densities employs a short-term temperature stability corresponding to a density equivalent to $\pm 2 \times 10^{-3}$ kg·m^{-3} or better (Malhotra and Woolf, 1991a).

An automated bellows volumometer (Easteal and Woolf, 1985; Malhotra and Woolf, 1993a) was used for the high-pressure volumetric measurements which are reported in Table 1. This determines the effect of pressure on the volume of a fixed mass of liquid at constant temperature as the ratio of its volume at an experimental pressure, p, to the volume at a lower reference pressure usually chosen as 0.1 MPa. Because the measurements were made at several temperatures above the normal boiling point of R123a, a special technique had to be used. This requires decreasing the volume of the bellows at atmospheric pressure by means of a spacer and duplicating the measurements at the temperature closest to, but below, the boiling point; for higher temperatures the volumometer cell is maintained at a pressure above the saturated vapor pressure of the liquid (Malhotra and Woolf, 1993a). Pressures above 25 MPa were measured with a pressure transducer; the lower pressures were read from a Heise-Bourdon analogue gauge. Both the pressure transducer and Heise-Bourdon gauge had been calibrated with a dead weight gauge with an accuracy of ±0.05%. The volume ratios are estimated to have an accuracy of ±0.05% at and above 50 MPa and ±0.1% below that pressure for the sets of measurements extending above 300 MPa; for the measurements where the highest pressure was below 300 MPa the accuracy is estimated to be ±(0.1 to 0.2)% (Malhotra and Woolf, 1993a).

Results and Discussion

The ρ(0.1 MPa) values were 1514.04 kg·m^{-3} at 278.15 K, 1501.89 kg·m^{-3} at 283.15 K, 1489.80 kg·m^{-3} at 288.15 K, 1477.56 kg·m^{-3} at 293.15 K, and 1465.23 kg·m^{-3} at 298.14 K; they were reproducible to ±0.003 kg·m^{-3} and have an estimated accuracy of 0.03%. These densities are smaller by about 2 kg·m^{-3} than the apparently unpublished data of Yokoyama at the equilibrium vapor pressure tabled by Kumagai and Takahashi (1991). (Slightly smaller differences of about 1.4 kg·m^{-3} were found with the data of the same author for R123.) For the purpose of extrapolation to higher temperatures the present data were represented with a standard deviation of 0.11 kg·m^{-3} by

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Table 1. Experimental Pressures and Volume Ratios $k = V_P/V$ (0.1 MPa) for R123a at Temperatures from 278.15 to 338.13 K

P/MPa	k	P/MPa	k	P/MPa	k	P/MPa	k
T = 278.15 K							
2.550	0.9963	28.36	0.9654	151.09	0.8875	301.81	0.8382
5.163	0.9927	39.52	0.9548	176.57	0.8771	325.10	0.8325
10.215	0.9860	60.10	0.9381	201.75	0.8680	343.47	0.8282
14.549	0.9807	80.06	0.9244	226.80	0.8597	373.37	0.8216
18.323	0.9762	100.61	0.9122	251.34	0.8521	377.02	0.8208
24.480	0.9695	126.09	0.8989	276.39	0.8450		
T = 288.15 K							
2.175	0.9964	28.10	0.9617	149.99	0.8807	300.29	0.8299
4.899	0.9921	40.92	0.9486	175.88	0.8697	325.75	0.8234
10.938	0.9831	50.52	0.9400	200.56	0.8603	343.67	0.8192
14.924	0.9777	58.02	0.9338	225.77	0.8517	374.06	0.8123
18.703	0.9728	100.66	0.9055	250.54	0.8439	387.16	0.8095
24.473	0.9658	126.11	0.8920	276.50	0.8364		
T = 298.14 K							
2.465	0.9956	26.86	0.9599	150.32	0.8731	301.23	0.8212
4.974	0.9912	39.97	0.9455	175.68	0.8620	325.00	0.8151
9.799	0.9834	58.69	0.9284	200.06	0.8526	344.00	0.8105
14.949	0.9756	79.18	0.9130	225.27	0.8438	375.35	0.8036
20.024	0.9686	99.88	0.8997	251.03	0.8357	390.80	0.8001
23.619	0.9639	125.75	0.8852	276.50	0.8281		
T = 298.14 K[a]							
2.522	0.9954	28.53	0.9576	89.81	0.9051	181.18	0.8588
5.148	0.9908	39.03	0.9460	101.06	0.8980	200.70	0.8513
10.098	0.9827	48.93	0.9364	120.89	0.8867	219.57	0.8444
16.111	0.9737	58.94	0.9277	139.80	0.8770	239.22	0.8378
20.899	0.9671	69.16	0.9196	160.76	0.8673	252.04	0.8338
24.221	0.9628	79.26	0.9122				
T = 313.14 K[a]							
2.417	0.9947	39.96	0.9381	100.63	0.8873	200.59	0.8383
5.123	0.9892	49.73	0.9279	120.94	0.8750	217.78	0.8318
9.774	0.9803	60.41	0.9179	140.65	0.8645	240.59	0.8240
14.799	0.9717	70.33	0.9094	160.34	0.8552	259.57	0.8181
19.874	0.9637	80.05	0.9018	180.16	0.8466	276.38	0.8129
23.769	0.9581	90.29	0.8943				
T = 323.14 K[a]							
2.714	0.9935	29.12	0.9458	89.72	0.8866	201.21	0.8288
5.135	0.9880	39.17	0.9328	99.96	0.8795	220.39	0.8216
9.848	0.9781	48.98	0.9218	120.05	0.8669	239.43	0.8150
14.759	0.9687	59.51	0.9113	140.55	0.8557	259.46	0.8086
19.774	0.9600	69.55	0.9024	160.90	0.8459	275.94	0.8034
24.110	0.9532	79.54	0.8943	180.79	0.8371		
T = 338.13 K[a]							
5.098	0.9859	39.08	0.9232	100.54	0.8657	200.46	0.8138
10.520	0.9726	49.18	0.9108	120.04	0.8529	220.44	0.8061
14.769	0.9633	58.86	0.9005	140.60	0.8412	239.76	0.7992
20.099	0.9528	69.16	0.8906	159.55	0.8316	259.20	0.7929
24.171	0.9455	79.36	0.8818	179.82	0.8224	284.40	0.7850
28.630	0.9382	89.62	0.8736				

[a] Volumometer cell bellows compressed at atmospheric pressure at 298.14 K to enable the cell to be used at temperatures above the normal boiling point.

$$\varrho(0.1\ \text{MPa})/(\text{kg}\cdot\text{m}^{-3}) = 2060.187 - 1.5191(T/\text{K}) - 0.00160(T/\text{K})^2 \quad (1)$$

The volume ratios, $k = V_p/V(0.1\ \text{MPa})$, given in Table 1 were represented by either of two empirical equations with the coefficients, given in Table 2, obtained by a least squares fit

$$K = P/(1 - k) = a_0 + a_1P + a_2P^2 + a_3P^3 \quad (2)$$

$$1 - k = C \log[(B + P)/(B + 0.1)] \quad (3)$$

K is the secant bulk modulus, and eq 2 provides the most accurate representation of the experimental k. Equation 3, the modified Tait equation, is particularly useful for extrapolation outside the experimental temperature and pressure range for liquids (Malhotra and Woolf, 1991b). To enable interpolation or extrapolation of volume ratios, including the liquid−vapor coexistence region (Malhotra and Woolf, 1993a), it is convenient to choose a common value of C and to express the corresponding B in terms of either the absolute temperature, T, or reduced temperature, $T_r = T/T_c$ where T_c is the critical temperature, 461.6 K (Chae et al., 1990). The C values of Table 2 indicate a common C of 0.210; the B *values* for this value are represented by

$$B = 434.981 - 2.0169T + 0.00242T^2 \quad (4)$$

$$B = -117.448 + 107.45/T_r \quad (5)$$

with a standard deviation of 0.31 and 0.40, respectively. Equation 4 is preferred for interpolation and extrapolation of volume ratios while eq 5 is more suitable for comparisons with other substituted ethanes. Figure 1 shows that the

Table 2. Coefficients of Equations 1 and 2 and Standard Deviation of Their Fit to the Volume Ratio $k = V_P/V$ (0.1 MPa) for R123a

T/K	a_0/MPa	a_1	$-a_2$/GPa^{-1}	a_3/GPa^{-2}	$10^2\langle\Delta k/k\rangle$	B/MPa	C	$10^2\langle\Delta k/k\rangle$
278.15	679.88	5.1166	5.5594	5.344	0.011	62.34	0.2112	0.024
288.15	592.43	5.2312	6.2791	6.165	0.017	54.28	0.2088	0.053
298.14	540.20	5.0659	6.0206	5.983	0.023	49.37	0.2101	0.041
298.14	530.03	5.2617	8.0384	10.691	0.008	48.22	0.2090	0.033
313.14	448.01	5.2085	8.8586	12.748	0.024	41.44	0.2113	0.032
323.14	401.65	4.8951	7.0192	8.892	0.013	35.72	0.2088	0.026
338.13	335.26	4.6806	6.5611	8.151	0.019	29.34	0.2089	0.026

Table 3. Isothermal Compressibility, κ, Isobaric Expansivity, α, and Change in Molar Heat Capacity, ΔC_P, for R123a

	P/MPa = 0.1	P/MPa = 10	P/MPa = 20	P/MPa = 40	P/MPa = 60	P/MPa = 80	P/MPa = 100	P/MPa = 150	P/MPa = 200	P/MPa = 250
					T = 278.15 K					
κ_T/(10^{-4} MPa^{-1})	14.69	12.93	11.50	9.40	7.94	6.88	6.10	4.82	4.05	3.51
α/(10^{-3} K^{-1})	1.58	1.44	1.33	1.18	1.08	1.00	0.93	0.79	0.68	0.62
ΔC_P/(J·K·mol^{-1})	0	−2	−3	−4	−4	−4	−4	−2	−2	−1
					T = 288.15 K					
κ_T/(10^{-4} MPa^{-1})	16.85	14.52	12.69	10.10	8.39	7.19	6.33	4.98	4.19	3.65
α/(10^{-3} K^{-1})	1.64	1.47	1.35	1.18	1.07	0.98	0.91	0.78	0.67	0.61
ΔC_P/(J·K·mol^{-1})	0	−2	−3	−4	−4	−4	−4	−2	−2	−1
					T = 298.14 K					
κ_T/(10^{-4} MPa^{-1})	18.48	15.79	13.71	10.79	8.89	7.58	6.64	5.18	4.34	3.76
α/(10^{-3} K^{-1})	1.69	1.50	1.36	1.18	1.05	0.97	0.90	0.76	0.66	0.60
ΔC_P/(J·K·mol^{-1})	0	−2	−3	−4	−5	−4	−4	−2	−2	−1
					T = 298.14 K[a]					
κ_T/(10^{-4} MPa^{-1})	18.83	15.95	13.78	10.80	8.92	7.64	6.74	5.31	4.41	3.67
α/(10^{-3} K^{-1})	1.69	1.50	1.36	1.18	1.05	0.97	0.90	0.76	0.69	0.60
ΔC_P/(J·K·mol^{-1})	0	−2	−3	−4	−5	−4	−4	−2	−2	−1
					T = 313.14 K					
κ_T/(10^{-4} MPa^{-1})	22.27	18.38	15.56	11.88	9.66	8.22	7.22	5.67	4.66	3.77
α/(10^{-3} K^{-1})	1.77	1.55	1.39	1.17	1.04	0.94	0.87	0.74	0.65	0.59
ΔC_P/(J·K·mol^{-1})	0	−2	−4	−5	−5	−5	−4	−2	−2	−1
					T = 323.14 K					
κ_T/(10^{-4} MPa^{-1})	24.84	20.33	17.07	12.83	10.29	8.64	7.50	5.78	4.75	3.94
α/(10^{-3} K^{-1})	1.82	1.58	1.40	1.17	1.03	0.93	0.85	0.73	0.64	0.58
ΔC_P/(J·K·mol^{-1})	0	−3	−4	−5	−5	−5	−4	−3	−2	−1
					T = 338.13 K					
κ_T/(10^{-4} MPa^{-1})	29.75	23.71	19.50	14.23	11.19	9.28	7.98	6.08	4.98	4.13
α/(10^{-3} K^{-1})	1.90	1.62	1.43	1.17	1.01	0.90	0.83	0.70	0.63	0.57
ΔC_P/(J·K·mol^{-1})	0	−3	−4	−6	−6	−5	−5	−3	−2	−1

[a] See footnote *a* in Table 1.

Table 4. Internal Pressure for R123a

	π/MPa						
V_m/(cm^3·mol^{-1})	T/K = 278.15	T/K = 288.15	T/K = 298.14	T/K = 298.14	T/K = 313.14	T/K = 323.14	T/K = 338.13
89.5	297	286	271	274	253	239	219
91.5	304	294	282	284	265	253	234
93.5	307	298	286	288	271	259	242
95.5	307	298	287	289	272	261	244
97.5	305	296	286	287	270	260	243
99.5	302	293	283	283	267	256	240
101.0	299	290	280	280	264	253	236

slope of eq 5 is close to that obtained for R123, 92.224. The intercept is larger by 25 MPa for R123, and this may be attributed to the effect of the different symmetry of R123a on its volumetric properties. Malhotra and Woolf (1993b) used volumetric data for other fluoroethanes to estimate the contribution to each compound's overall B from adding individual −F and −Cl groups of −7 and −14 MPa, respectively. Those estimates were derived from compounds where adding the −Cl or −F did not result in the presence of both a −Cl and a −F on the same carbon. The principal difference between the carbon groups in R123a and those in R123 is that in the former each is bonded to a −Cl and a −F. These results may indicate that an allowance of −12.5 MPa should be made for the contribution of this asymmetry to the overall B.

The isothermal compressibilities, κ_T, given in Table 3 have been calculated from eq 2 using the relation

$$\kappa_T = -\{1/(P - K)\}\{1 - (P/K)(\partial K/\partial P)_T\} \qquad (6)$$

with the differentiation performed analytically. The κ_T values at 0.1 MPa for R123a are smaller than those of R123 from 278 to 313 K, but above that temperature they are larger. The differences decrease with increasing in pressure.

The isobaric thermal expansivity, α, is defined by

$$\alpha = (1/V_m)(\partial V_m/\partial T)_P \qquad (7)$$

V_m being the molar volume. The V_m values at pressures

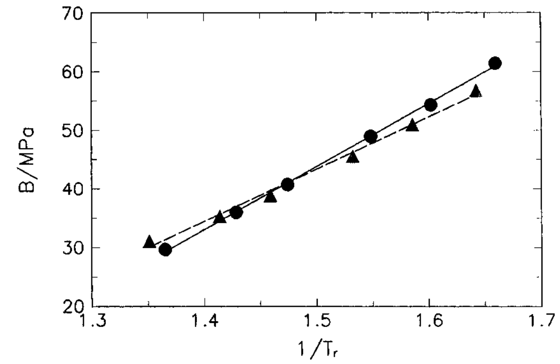

Figure 1. Variation of B of eq 3 with $C = 0.210$ for (●) R123a and (△) R123. A line has been fitted to each set.

above 0.1 MPa were determined by multiplying V_m at 0.1 MPa by k obtained from eq 2 using the coefficients of Table 2. The α values given in Table 3 were obtained by analytical differentiation of k expressed as a quadratic in T. The estimated fractional uncertainties in α are ±(0.02 to 0.03) for $P \geq 50$ MPa and possibly greater below that pressure. The comparison of α for R123a and R123 shows variations with temperature and pressure similar to those for κ_T. The α values enable calculation of the change in the isobaric molar heat capacity

$$\Delta C_P = C_P - C_P(0.1\ \text{MPa}) = -(TM/\varrho)\int_{0.1}^{P}\{(\partial a/\partial T)_P + a^2\}\,\mathrm{d}P \quad (8)$$

where M is the molar mass and ρ the density at P. The α values were represented by a quadratic in T to enable analytic differentiation. The ΔC_P values given in Table 3 are estimated to have an error of ±(1 to 2) J·K^{-1}·mol^{-1}; their change with pressure at each temperature is less than was found for R123.

The internal pressure, π, given in Table 4 was obtained using the relation

$$\pi = T(\partial P/\partial T)_V - P \quad (9)$$

with the derivatives determined analytically from a quadratic fit. The estimated error is ±4 MPa. The variation of π with molar volume, V_m, at constant T is less than was found for R123 although each isotherm shows a shallow maximum; the range of π at the highest V_m is greater than for R123. The π values decrease with an increase in temperature at constant V_m, which is opposite to the dependence observed for R123.

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