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PVT Property Measurements for Liquid Chlorobenzene and 1,2-Dichlorobenzene from (278 to 338) K and (0.1 to 300) MPa

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The effect of pressure on the volume in the liquid phase for chlorobenzene and 1,2-dichlorobenzene has been measured relative to their volumes at 0.1 MPa with a bellows volumometer for pressures up to 300 MPa over the temperature range (278.15 to 338.13) K. The experimental volume ratios have been represented by two sets of equations to enable interpolation and extrapolation of volumetric properties. The results of one of these representations suggests a means of extrapolating the volumetric properties of these chloro-substituted benzene derivatives. Isothermal compressibilities, thermal expansivities, normalized volume fluctuations, and the change in the isobaric heat capacity from its value at 0.1 MPa have been calculated from the results.

Introduction

This work on 1,2-dichlorobenzene was initiated to provide isothermal compressibilities for a continuing study by Rodriguez (see Shang et al., 1996) on rotational motions of fullerenes in various liquids. The present results complement some earlier volumetric measurements (Isdale and Spence, 1975) by providing data at both lower (278.15 and 288.14 K) and intermediate temperatures (313.14 and 338.13 K). The work on chlorobenzene was done much earlier (1986/87) but not published. Gibson and Loeffler (1939) made *pVT* measurements for chlorobenzene at 25, 45, 65, and 85 °C but at a maximum pressure of only 1000 atm (101.3 MPa).

Experimental Section

The chlorobenzene was Mallinckrodt Analytical Reagent of stated purity 99.5%, and the 1,2-dichlorobenzene was Aldrich HPLC grade with a stated minimum purity of 99%. Both were used without further purification. 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 of $\pm 2 \times 10^{-3}$ kg·m^{-3} or better (Malhotra and Woolf, 1991a, 1994). Densities of 1,2-dichlorobenzene at atmospheric pressure, ρ (0.1 MPa), were measured using an Anton Paar Model DMA60 digital densimeter with a DMA602HT external cell; this was frequently and carefully calibrated (Malhotra and Woolf, 1994). The overall reproducibility of the density is estimated to be ± 0.005 kg·m^{-3}. The density was measured at 293.14 and 298.14 K obtaining 1305.89 and 1300.31 kg·m^{-3}, respectively. The corresponding literature values (Riddick et al., 1986) are 1305.89 and 1300.33 kg·m^{-3} and 1300.2 kg·m^{-3} (Isdale and Spence, 1975). 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.

An automated bellows volumometer (Easteal and Woolf, 1985; Malhotra and Woolf, 1993) was used for the high-pressure volumetric measurements of 1,2-dichlorobenzene. This instrument determines the effect of pressure on the volume of a fixed mass of liquid at constant temperature as the ratio of its volume at the experimental pressure, *P*, to the volume at a lower reference pressure usually chosen as 0.1 MPa. Pressures above 25 MPa were measured with a pressure transducer; the lower pressures were read from a Heise-Bourdon analogue gauge except for those below 5 MPa, which were generated with a dead weight gauge. Both the pressure transducer and Heise-Bourdon gauge had been calibrated with a dead weight gauge with an accuracy of ±0.05%. Because 1,2-dichlorobenzene would be expected to freeze at pressures less than 300 MPa at 278.15 and 288.14 K, the maximum pressure used at those temperatures was less than that at the higher temperatures. The volumetric measurements for chlorobenzene were made with an earlier version of the volumometer that was not automated and used calibrated Heise-Bourdon analogue gauges for all of the pressure measurements (Easteal and Woolf, 1985). The volume ratios are estimated to have an accuracy of ±0.05% at and above 50 MPa and ±0.1% below that pressure.

Results and Discussion

The volume ratios, $k = V_P/V(0.1\ \text{MPa})$, are given in Tables 1 and 2. A direct comparison with the corresponding results of Isdale and Spence (1975) for 1,2-dichlorobenzene or Gibson and Loeffler (1939) for chlorobenzene is not possible since they did not publish their values of *k*. Data provided by Dymond (1996) for unpublished *k* values of Isdale and Spence (1975) indicates differences of 0.1% between their *k* and those of Table 1 at 298.14 and 323.14 K; these are within the expected experimental error. The *k* value can be used with the ρ(0.1 MPa) given in the table to obtain densities of the compressed liquid. For 1,2-dichlorobenzene the ρ(0.1 MPa) for the temperatures at which those densities were not measured were obtained by combining the present values at 293.14 and 298.14 K with those of Isdale and Spence (1975) at 323.14 and 348.13

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Table 1. Experimental Pressures, Volume Ratios $k = V_P/V(0.1\ \mathrm{MPa})$, and Densities at 0.1 MPa for 1,2-Dichlorobenzene 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; $\rho(0.1) = 1322.34$ kg·m^{-3}							
2.547	0.9986	18.939	0.9901	38.47	0.9807	68.14	0.9684
4.996	0.9973	24.085	0.9875	47.23	0.9769	82.38	0.9630
9.339	0.9950	28.52	0.9853	58.12	0.9723	90.03	0.9603
14.651	0.9923						
$T = 288.15$ K; $\rho(0.1) = 1311.37$ kg·m^{-3}							
2.547	0.9986	24.237	0.9868	57.38	0.9714	97.30	0.9559
4.996	0.9972	28.34	0.9848	67.24	0.9673	116.86	0.9491
9.797	0.9945	38.02	0.9801	77.50	0.9633	141.78	0.9412
14.505	0.9919	48.22	0.9754	88.31	0.9591	147.71	0.9394
19.255	0.9894						
$T = 298.14$ K; $\rho(0.1) = 1300.33$ kg·m^{-3}							
2.547	0.9984	23.555	0.9865	67.59	0.9656	136.83	0.9402
4.996	0.9970	27.96	0.9842	77.75	0.9614	158.65	0.9335
9.993	0.9940	37.39	0.9794	88.29	0.9573	181.74	0.9268
14.427	0.9915	47.19	0.9747	97.31	0.9539	196.54	0.9228
19.525	0.9887	57.74	0.9699	118.45	0.9463		
$T = 313.14$ K; $\rho(0.1) = 1283.95$ kg·m^{-3}							
2.547	0.9983	27.48	0.9832	86.32	0.9553	197.07	0.9183
4.996	0.9967	37.72	0.9777	98.44	0.9505	216.09	0.9132
9.333	0.9940	47.27	0.9728	116.87	0.9435	235.74	0.9081
14.453	0.9908	57.28	0.9680	138.38	0.9361	256.63	0.9030
19.581	0.9877	66.62	0.9637	156.99	0.9301	280.28	0.8976
24.297	0.9850	76.40	0.9594	176.62	0.9241	285.31	0.8965
$T = 323.14$ K; $\rho(0.1) = 1272.98$ kg·m^{-3}							
2.547	0.9982	28.21	0.9819	118.34	0.9406	222.70	0.9082
4.996	0.9965	38.28	0.9763	137.93	0.9336	247.96	0.9018
8.774	0.9940	57.23	0.9965	156.52	0.9274	272.35	0.8959
14.902	0.9900	77.67	0.9570	178.24	0.9207	289.11	0.8921
19.324	0.9873	98.22	0.9483	198.67	0.9148	308.19	0.8878
23.892	0.9845						
$T = 338.13$ K; $\rho(0.1) = 1256.63$ kg·m^{-3}							
2.547	0.9981	28.09	0.9805	117.86	0.9369	221.96	0.9033
4.996	0.9962	37.87	0.9746	136.77	0.9299	246.83	0.8968
8.979	0.9933	58.08	0.9635	156.91	0.9229	271.06	0.8907
14.953	0.9891	78.15	0.9537	178.13	0.9160	301.27	0.8838
18.850	0.9865	98.17	0.9448	198.30	0.9100	311.51	0.8815
23.702	0.9833						

Table 2. Experimental Pressures, Volume Ratios $k = V_P/V(0.1\ \mathrm{MPa})$, and Densities at 0.1 MPa for Chlorobenzene 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; $\rho(0.1) = 1122.5$ kg·m^{-3}							
2.201	0.9985	30.211	0.9815	90.35	0.9530	200.07	0.9160
4.707	0.9968	40.149	0.9761	100.33	0.9490	220.71	0.9104
10.178	0.9933	50.787	0.9707	120.92	0.9413	239.99	0.9054
15.206	0.9902	60.068	0.9662	141.30	0.9341	260.11	0.9005
19.891	0.9874	69.397	0.9619	160.46	0.9279	281.76	0.8955
24.740	0.9846	80.228	0.9572	180.62	0.9217		
$T = 288.15$ K; $\rho(0.1) = 1111.6$ kg·m^{-3}							
1.878	0.9987	29.91	0.9810	90.35	0.9512	200.67	0.9128
4.653	0.9968	40.20	0.9752	100.53	0.9469	220.61	0.9072
9.492	0.9935	50.34	0.9699	121.37	0.9388	240.34	0.9019
14.421	0.9903	60.12	0.9650	139.80	0.9321	259.91	0.8970
19.661	0.9870	70.45	0.9601	160.41	0.9251	281.46	0.8919
24.354	0.9842	80.48	0.9555	181.07	0.9186		
$T = 298.14$ K; $\rho(0.1) = 1100.8$ kg·m^{-3}							
2.448	0.9982	29.71	0.9799	90.30	0.9485	200.17	0.9092
5.092	0.9962	39.95	0.9738	100.38	0.9441	220.26	0.9035
10.097	0.9927	50.04	0.9682	120.27	0.9361	240.14	0.8981
15.260	0.9892	60.27	0.9628	140.40	0.9285	260.06	0.8930
19.983	0.9860	70.35	0.9578	160.82	0.9215	281.71	0.8879
25.23	0.9827	80.08	0.9531	180.52	0.9151		
$T = 313.14$ K; $\rho(0.1) = 1084.6$ kg·m^{-3}							
2.326	0.9981	29.91	0.9779	89.95	0.9447	200.02	0.9037
5.016	0.9959	39.90	0.9715	101.03	0.9397	220.21	0.8978
10.007	0.9921	50.19	0.9654	121.02	0.9312	241.04	0.8921
15.091	0.9883	60.37	0.9596	140.05	0.9238	259.91	0.8872
20.007	0.9847	70.20	0.9544	160.87	0.9163	282.06	0.8818
25.12	0.9811	79.73	0.9496	180.37	0.9098		
$T = 323.14$ K; $\rho(0.1) = 1074.2$ kg·m^{-3}							
2.405	0.9979	30.31	0.9765	90.41	0.9419	200.57	0.8995
4.653	0.9960	40.15	0.9699	101.08	0.9368	220.71	0.8934
9.872	0.9917	50.84	0.9632	120.92	0.9281	240.24	0.8879
15.044	0.9877	59.92	0.9579	140.55	0.9202	259.91	0.8825
19.902	0.9840	70.45	0.9521	160.87	0.9126	283.11	0.8767
25.75	0.9797	80.53	0.9468	180.57	0.9059		
$T = 338.13$ K; $\rho(0.1) = 1058.1$ kg·m^{-3}							
2.380	0.9977	30.06	0.9745	90.35	0.9382	200.07	0.8949
4.890	0.9953	40.50	0.9671	101.23	0.9329	220.46	0.8887
9.989	0.9907	50.29	0.9607	120.92	0.9240	239.89	0.8831
15.369	0.9861	60.42	0.9545	140.45	0.9159	260.71	0.8774
20.217	0.9821	70.30	0.9488	160.62	0.9083	282.66	0.8718
25.55	0.9779	79.93	0.9436	180.77	0.9012		

K and representing them by a linear equation

$$\rho(0.1\ \mathrm{MPa})/\mathrm{kg{\cdot}m}^{-3} = 1627.527 - 1.0972(T/\mathrm{K}) \quad (1)$$

with a standard deviation of 0.078 kg·m^{-3}, which enabled interpolation and extrapolation.

No densities were measured in this work for chlorobenzene; those given in Table 2 were obtained from a cubic spline fit of data along the liquid−vapor coexistence curve from 0 to 90 °C (Timmermans, 1950). Those data were used because of their extensive temperature range and the large scatter in the alternative data at atmospheric pressure. For both chlorobenzene and 1,2-dichlorobenzene the minimum error in the estimated density is ±0.1 kg·m^{-3}.

The k values were represented by either of eqs 2 or 3

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

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

with the coefficients, given in Table 3, obtained by a least-squares fit. K is the secant bulk modulus, and eq 2 provides the most accurate representation of the experimental k values.

Equation 3, the modified Tait equation, is particularly useful for interpolation or extrapolation outside the experimental temperature and pressure range for liquids (Malhotra and Woolf, 1991b), including the liquid−vapor coexistence region (Malhotra and Woolf, 1993). For that purpose a value of C is chosen, usually close to the average, to represent those determined independently for all the temperatures of the measurements and a corresponding set of B's calculated from the k. Those B values for $C = 0.21$ and the accuracy of the fit to k for that C are given in the second to the last and the last columns of Table 3. The B values are plotted against $1/T_r$, where T_r ($=T/T_c$) is the reduced temperature, in Figure 1. The T_c of 632.4 K (chlorobenzene) and 697.3 K (dichlorobenzene) were from Riddick et al. (1986). The two sets of B values are almost parallel with slopes of 104.2 (variance 0.6) for 1,2-dichlorobenzene and 101.5 (variance 0.7) for chlorobenzene suggesting that they can be combined. Also shown in the figure are B(chlorobenzene), which have been adjusted by adding 6.28 MPa, which is the difference between B(1,2-dichlorobenzene) and B(chlorobenzene) at an arbitrarily chosen $1/T_r$ of 2.2. The difference is, of course, a measure of the effect on B of substituting the second chlorine into the benzene ring. The combined data suggest that the chlorobenzene results can be extrapolated to higher values of $1/T_r$ while a corresponding extrapolation to lower values appears feasible for 1,2-dichlorobenzene. For those purposes the combined data shown in Figure 1 can be represented by

$$B/\mathrm{MPa} = -93.96 + 102.87/T_r \quad (4)$$

with a standard deviation in B of 0.6 MPa.

Table 3. Coefficients of Equations 2 and 3 and Standard Deviation of Their Fit to the Volume Ratio $k = V_P/V$(0.1 MPa) for 1,3-Dichlorobenzene and Chlorobenzene[a]

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	$10^2\langle\Delta k/k\rangle$	B/MPa	$10^2\langle\Delta k/k\rangle$
					1,2-Dichlorobenzene					
278.15	1824.32	4.0376	−16.2300	−72.961	0.002	154.40	0.1996	0.004	163.41	0.011
288.15	1739.05	4.0392	−14.3893	−66.887	0.004	152.25	0.2060	0.002	155.67	0.010
298.14	1620.62	5.3730	3.8722	2.605	0.001	146.14	0.2085	0.003	146.98	0.016
313.14	1492.17	5.4625	4.9121	4.531	0.001	138.78	0.2133	0.009	135.49	0.017
323.14	1416.30	5.3033	4.0992	2.949	0.001	132.14	0.2143	0.011	128.02	0.019
338.13	1290.68	5.4509	5.2973	5.128	0.001	120.47	0.2135	0.013	117.18	0.023
					Chlorobenzene					
278.15	1459.13	5.7971	8.2882	11.787	0.005	140.89	0.2190	0.010	132.53	0.030
288.15	1408.43	5.5438	7.9775	12.099	0.007	139.27	0.2253	0.007	126.34	0.059
298.14	1328.99	5.0779	4.6108	5.364	0.003	126.75	0.2208	0.003	118.35	0.051
313.14	1209.70	4.9393	3.6838	3.368	0.001	113.06	0.2178	0.003	107.49	0.043
323.14	1149.07	4.7501	3.1205	2.288	0.002	109.31	0.2224	0.004	101.08	0.076
338.13	1021.95	5.4050	6.6940	8.453	0.005	95.87	0.2150	0.010	92.34	0.026

[a] The values of B in the second to the last column are for $C = 0.2100$.

Table 4. Isothermal Compressibility, κ_T, Molar Volume, V_m, Isobaric Expansivity, α, Normalized Volume Fluctuaton, $\langle(\Delta V/V)^2\rangle$, and Change in Molar Heat Capacity, ΔC_P, for 1,2-Dichlorobenzene

	P/MPa						
	0.1	20	40	60	80	100	150
			T = 278.15 K				
$\kappa_T/10^{-4}$ MPa^{-1}	5.48	5.03	4.58	4.16	3.80		
V_m/cm^3·mol^{-1}	111.16	110.01	108.95	108.01	107.15		
$\alpha/10^{-3}$ K^{-1}	0.83	0.78	0.74	0.71	0.67		
$\langle(\Delta V/V)^2\rangle$	0.0114	0.0106	0.0097	0.0089	0.0082		
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.7	1.0	1.2	1.2		
			T = 288.15 K				
$\kappa_T/10^{-4}$ MPa^{-1}	5.75	5.26	4.78	4.34	3.97	3.67	3.33
V_m/cm^3·mol^{-1}	112.09	110.87	109.76	108.77	107.87	107.05	105.22
$\alpha/10^{-3}$ K^{-1}	0.84	0.78	0.74	0.70	0.67	0.64	0.59
$\langle(\Delta V/V)^2\rangle$	0.0123	0.0114	0.0104	0.0096	0.0088	0.0082	0.0076
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.7	1.1	1.2	1.2	1.2	1.1
			T = 298.14 K				
$\kappa_T/10^{-4}$ MPa^{-1}	6.17	5.51	4.97	4.53	4.16	3.86	3.27
V_m/cm^3·mol^{-1}	113.04	111.74	110.58	109.54	108.59	107.72	105.83
$\alpha/10^{-3}$ K^{-1}	0.84	0.78	0.74	0.70	0.67	0.63	0.58
$\langle(\Delta V/V)^2\rangle$	0.0135	0.0122	0.0111	0.0103	0.0095	0.0089	0.0077
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.8	14.2	1.3	1.3	1.2	1.2
			T = 313.14 K				
$\kappa_T/10^{-4}$ MPa^{-1}	6.70	5.91	5.29	4.80	4.39	4.06	3.43
V_m/cm^3·mol^{-1}	114.49	113.06	111.80	110.68	109.67	108.75	106.74
$\alpha/10^{-3}$ K^{-1}	0.85	0.79	0.74	0.69	0.66	0.63	0.57
$\langle(\Delta V/V)^2\rangle$	0.0152	0.0136	0.0123	0.0113	0.0104	0.0097	0.0084
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.8	1.2	1.4	1.3	1.3	1.2
			T = 323.14 K				
$\kappa_T/10^{-4}$ MPa^{-1}	7.06	6.21	5.54	5.01	4.57	4.20	3.53
V_m/cm^3·mol^{-1}	115.47	113.96	112.63	111.45	110.39	109.43	107.35
$\alpha/10^{-3}$ K^{-1}	0.86	0.79	0.73	0.69	0.65	0.62	0.56
$\langle(\Delta V/V)^2\rangle$	0.0164	0.0147	0.0132	0.0121	0.0111	0.0103	0.0088
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.9	1.3	1.4	1.4	1.4	1.2
			T = 338.13 K				
$\kappa_T/10^{-4}$ MPa^{-1}	7.74	6.71	5.92	5.31	4.82	4.42	3.69
V_m/cm^3·mol^{-1}	116.98	115.32	113.87	112.60	111.47	110.45	108.25
$\alpha/10^{-3}$ K^{-1}	0.87	0.79	0.73	0.68	0.65	0.62	0.55
$\langle(\Delta V/V)^2\rangle$	0.0186	0.0164	0.0146	0.0133	0.0122	0.0113	0.0096
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	1.0	1.4	1.5	1.5	1.4	1.3

The isothermal compressibilities, κ_T, given in Tables 4 and 5 have been calculated from eq 1 using the relation

$$\kappa_T = -\{1/(P - K)\}\{1 - (P/K)\,(\partial K/\partial P)_T\} \qquad (5)$$

with the differentiation performed analytically. The κ_T for chlorobenzene agree within 1% at 0.1 MPa with those available in the literature (Freyer et al., 1929; Gibson and Loeffler, 1939), but at 298.14 K and 100 MPa there is a difference of 2% between the present value and that of Gibson and Loeffler (1939). The κ_T were used to obtain the normalized volume fluctuations given in Tables 4 and 5 by using the relation (Koga, 1995)

$$\langle(\Delta V/V)^2\rangle = (RT\kappa_T/V_m) \qquad (6)$$

with V_m the molar volume. V_m at pressures above 0.1 MPa were determined by multiplying the V_m at 0.1 MPa, obtained from the densities in Tables 1 and 2, by the k obtained from eq 2 using the coefficients of Table 3. Both the κ_T and the $\langle(\Delta V/V)^2\rangle$ have an estimated error of ±1−2%. The variation of these two related quantities with pressure is free of anomalies for each substance as would

Table 5. Isothermal Compressibility, κ_T, Molar Volume, V_m, Isobaric Expansivity, α, Normalized Volume Fluctuation, $\langle(\Delta V/V)^2\rangle$, and Change in Molar Heat Capacity, ΔC_P, for Chlorobenzene

	P/MPa									
	0.1	20	40	60	80	100	150	200	250	275
$T = 278.15$ K										
$\kappa_T/10^{-4}$ MPa^{-1}	6.85	5.99	5.35	4.85	4.45	4.13	3.53	3.08	2.69	2.49
V_m/cm^3·mol^{-1}	100.27	99.00	97.89	96.90	96.00	95.18	93.38	91.85	90.54	89.95
$\alpha/10^{-3}$ K^{-1}	0.97	0.97	0.85	0.80	0.75	0.70	.062	0.58	0.54	0.52
$\langle(\Delta V/V)^2\rangle$	0.0158	0.0140	0.0126	0.0116	0.0107	0.0100	0.0088	0.0078	0.0069	0.0064
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.4	0.5	0.5	0.6	0.8	1.6	2.5	3.2	4.0
$T = 288.15$ K										
$\kappa_T/10^{-4}$ MPa^{-1}	7.10	6.22	5.56	5.05	4.64	4.30	3.67	3.19	2.75	2.53
V_m/cm^3·mol^{-1}	101.25	99.92	98.76	97.72	96.78	95.92	94.03	92.43	91.07	90.47
$\alpha/10^{-3}$ K^{-1}	0.97	0.91	0.85	0.79	0.74	0.70	0.63	0.58	0.55	0.52
$\langle(\Delta V/V)^2\rangle$	0.0168	0.0149	0.0135	0.0124	0.0115	0.0108	0.0094	0.0083	0.0072	0.0067
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.5	0.5	0.5	0.6	0.8	1.6	2.6	3.4	3.8
$T = 298.14$ K										
$\kappa_T/10^{-4}$ MPa^{-1}	7.52	6.61	5.90	5.33	4.86	4.48	3.75	3.24	2.82	2.64
V_m/cm^3·mol^{-1}	102.25	100.82	99.57	98.46	97.46	96.56	94.60	92.97	91.58	90.95
$\alpha/10^{-3}$ K^{-1}	0.98	0.90	0.84	0.78	0.74	0.70	0.63	0.58	0.55	0.53
$\langle(\Delta V/V)^2\rangle$	0.0182	0.0163	0.0147	0.0134	0.0124	0.0115	0.0098	0.0086	0.0076	0.0072
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.5	0.5	0.5	0.6	0.8	1.7	2.6	3.5	4.0
$T = 313.14$ K										
$\kappa_T/10^{-4}$ MPa^{-1}	8.26	7.20	6.37	5.71	5.17	4.73	3.91	3.34	2.92	2.74
V_m/cm^3·mol^{-1}	103.77	102.19	100.82	99.61	98.54	97.57	95.50	93.79	92.34	91.68
$\alpha/10^{-3}$ K^{-1}	0.99	0.90	0.83	0.78	0.73	0.70	0.64	0.59	0.55	0.54
$\langle(\Delta V/V)^2\rangle$	0.0207	0.0183	0.0164	0.0149	0.0137	0.0126	0.0107	0.0093	0.0082	0.0078
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.5	0.6	0.5	0.6	0.8	1.7	2.8	3.7	4.2
$T = 323.14$ K										
$\kappa_T/10^{-4}$ MPa^{-1}	8.70	7.57	6.68	5.97	5.40	4.93	4.06	3.46	3.03	2.86
V_m/cm^3·mol^{-1}	104.78	103.10	101.64	100.37	99.23	98.22	96.05	94.27	92.75	92.07
$\alpha/10^{-3}$ K^{-1}	0.99	0.89	0.82	0.77	0.73	0.70	0.64	0.59	0.56	0.54
$\langle(\Delta V/V)^2\rangle$	0.0223	0.0197	0.0177	0.0160	0.0146	0.0135	0.0114	0.0099	0.0088	0.0083
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.5	0.6	0.5	0.6	0.8	1.8	2.9	3.8	4.4
$T = 338.13$ K										
$\kappa_T/10^{-4}$ MPa^{-1}	9.78	8.21	7.07	6.23	5.58	5.08	4.18	3.56	3.07	2.84
V_m/cm^3·mol^{-1}	106.37	104.49	102.91	101.56	100.37	99.31	97.05	95.20	93.64	92.95
$\alpha/10^{-3}$ K^{-1}	1.00	0.88	0.81	0.76	0.73	0.70	0.64	0.60	0.56	0.55
$\langle(\Delta V/V)^2\rangle$	0.0258	0.0221	0.0193	0.0172	0.0156	0.0144	0.0121	0.0105	0.0092	0.0086
$-\Delta C_P$/J·mol^{-1}·K^{-1}	0.0	0.6	0.6	0.5	0.6	0.8	1.9	3.0	4.0	4.6

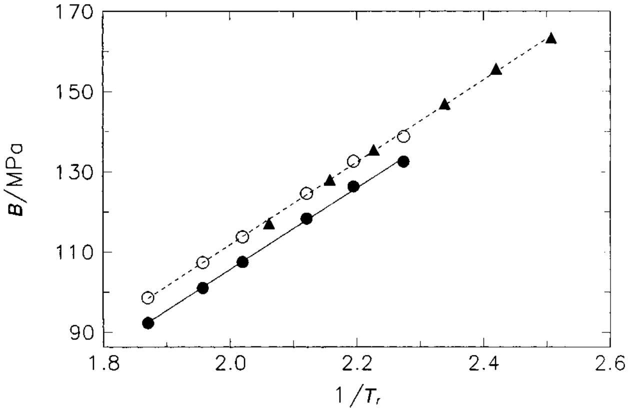

Figure 1. B values for eq 3 with $C = 0.21$ for chlorobenzene and 1,2-Dichlorobenzene. ●, chlorobenzene, ▲, 1,2-dichlorobenzene, ○, chlorobenzene. B value increased by 6.28 Mpa.

be expected for conditions that are well below the critical region.

The isobaric thermal expansivity, α, is defined by

$$\alpha = (\partial(\ln V_m)/\partial T)_P \quad (7)$$

The α given in Tables 4 and 5 were obtained by analytical differentiation of the ln V_m expressed as a quadratic in T. For 1,2-dichlorobenzene the volumetric data for all six temperatures were used to obtain the α at 278.15 K, but the data at that temperature were excluded to enable the calculations to be extended to 150 MPa at higher temperatures. The estimated fractional uncertainties in α are ±(0.02 to 0.03) for $P \geqslant 50$ MPa and possibly greater below that pressure. The values at 0.1 MPa and 298.14 K for 1,2-dichlorobenzene and chlorobenzene are in good agreement with 0.85×10^{-3} K^{-1} and 0.99×10^{-3} K^{-1}, respectively, given in the literature (Riddick et al., 1986).

The α values enable calculation of the change in the isobaric molar heat capacity

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

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 given in Tables 4 and 5 are estimated to have an error of ±1 J·mol^{-1}·K^{-1} on the basis of previous work for heptane (Malhotra and Woolf, 1991c). Their variation with pressure is negligibly small in comparison to C_P(0.1 MPa) at 298.14 K of 221.67 J·(mol·K)$^{-1}$ for 1,2-dichlorobenzene and 148.83 J·(mol·K)$^{-1}$ for chlorobenzene (Riddick et al., 1986).

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