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p, *V*, *T* and Derived Thermodynamic Data for Bromobenzene at Temperatures from 278 to 323 K and Pressures up to 280 MPa

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Experimentally determined *p*, *V*, *T* data are reported for bromobenzene at 278, 288, 298, 313, and 323 K, at pressures up to about 280 MPa or (at 278 and 288 K) a lower pressure slightly below the freezing pressure at the temperature of measurement. Values of the isobaric expansivity, isothermal compressibility, internal pressure, and equivalent hard-sphere diameter, derived from the *p*, *V*, *T* data, are presented.

KEY WORDS: bromobenzene; hard-sphere diameter; high pressure; internal pressure; isobaric expansivity; isothermal compressibility; *p*, *V*, *T* data.

1. INTRODUCTION

For most common organic liquids, including benzene and toluene, the isothermal compressibility (κ) is of the order 1 GPa^{-1} and above. Bromobenzene, chlorobenzene, and water were categorized by Bridgman [1] as being about 50% less compressible than is typical for common organic liquids. On the basis of κ at 298 K and 0.1 MPa, there are several other liquids such as aniline, formamide, *N*-methylformamide, *N*,*N*-dimethylformamide, and nitrobenzene, which can be similarly classified. For this group of liquids (and bromobenzene, chlorobenzene, and water) κ is in the approximate range 0.4 to 0.7 GPa^{-1}. Of these relatively incompressible liquids, nitrobenzene, bromobenzene, and chlorobenzene are

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unusual in that the other liquids in the group have strong intermolecular interactions and, in some cases, are highly associated, but such is not the case for nitrobenzene, bromobenzene, and chlorobenzene. The p, V, T properties of the these three liquids are, consequently, of intrinsic interest.

An additional motivation for the present study arose from a research program on the application of hard-sphere models of liquid-state transport properties to the density dependence of tracer diffusion coefficients. Work in progress in this laboratory utilizes bromobenzene as a tracer, and the method used for interpretation of the tracer diffusion data requires values for the equivalent hard-sphere diameter of the tracer molecule. These values can be derived independently of the diffusion coefficient measurements, from p, V, T data in conjunction with freezing pressures.

For these reasons, the purpose of the present work was to investigate the p, V, T behavior of bromobenzene over reasonably wide temperature and pressure ranges. This work extends to intermediate temperatures the measurements of Bridgman [2] (at 278, 323, and 368 K) and to lower temperatures and higher pressures those of Gibson and Loeffler [3] (at 298, 318, 338, and 358 K; maximum pressure, 101.3 MPa).

2. EXPERIMENTAL

The bromobenzene was British Drug Houses Laboratory reagent-grade material which was fractionally distilled, and the fraction with boiling point 462.2 ± 0.2 K at 95.1 kPa was used for the p, V, T measurements.

Volume ratios, V_p/V_0, where V_0 and V_p are volumes at 0.1 MPa and pressure p, were determined at 278, 288, 298, 313, and 323 K using the bellows volumometer whose construction, calibration, and use have been described previously [4, 5]. The pressure range at each temperature was from about 2.5 MPa to either a pressure just below the freezing pressure [6] or about 280 MPa, which is the highest pressure at which the volumometer is currently operated.

Temperatures were maintained constant to ±0.005 K and measured with a calibrated platinum resistance thermometer with an uncertainty of ±0.01 K. Pressures were measured using Heise–Bourdon tube gauges which had been calibrated against deadweight testers. For pressures up to 25 MPa a 0- to 25-MPa gauge was used with an uncertainty of ±0.01 MPa, and at higher pressures a 0- to 300-MPa gauge gave pressures to ±0.1 MPa. The overall uncertainty in V_p/V_0 corresponds to about ±0.02–0.04% in density at pressures above 50 MPa, increasing to about ±0.1% at pressures approaching 0.1 MPa.

3. RESULTS AND DISCUSSION

In Table I volume ratios from the present work are compared with values from Bridgman [2] and Gibson and Loeffler [3]. It is apparent that there is very good agreement (maximum difference, 0.04%) between the two sets of data at 298 K. At 323 K the two sets of data agree to within about 0.1–0.2%; the differences arise primarily from the uncertainty in the literature data [2] at this temperature.

From the measured volume ratios, values of the secant bulk modulus, K, defined by

$$K = p/(1 - V_p/V_0) \tag{1}$$

were calculated and fitted to cubic equations of the form

$$K = \sum_{i=0}^{2} A_i p^i \tag{2}$$

Table I. Comparison of Volume Ratios with Literature Data for Bromobenzene

T (K)	p (MPa)	$V_p/V_0{}^a$	$V_p/V_0{}^{b,c}$
298.15	2.631	0.99826	0.99824
	5.016	0.99671	0.99669
	9.854	0.99364	0.99360
	15.26	0.99033	0.99028
	19.85	0.98761	0.98755
	25.38	0.98442	0.98435
	30.46	0.98159	0.98152
	39.60	0.97671	0.97662
	49.88	0.97150	0.97139
	59.97	0.96666	0.96651
	70.55	0.96183	0.96164
	80.43	0.95754	0.95729
	90.35	0.95342	0.95311
	99.78	0.94967	0.94929
323.15	49.03	0.96812	0.9673
	98.07	0.94411	0.9450
	147.10	0.92486	0.9264
	196.13	0.90879	0.9102
	294.20	0.88289	0.8848

[a] This work.

[b] Data at 298 K from Ref. 3; calculated from the Tait equation parameters given therein.

[c] Data at 323 K from Ref. 2.

Table II. Coefficients of Eq. (2) for the Secant Bulk Modulus for Bromobenzene

T (K)	A_0 (MPa)	A_1	$-10^3 A_2$ (MPa^{-1})	$10^6 A_3$ (MPa^{-2})	p_{Max} (MPa)	$10^3 \delta$ (%)[a]
278.15	1645.823	5.66923	8.6090	16.169	192	1.2
288.15	1552.455	5.60066	7.3850	10.749	252	1.7
298.15	1491.121	5.29811	5.8904	8.107	282	3.7
313.15	1380.628	4.89345	3.3706	3.212	282	1.0
323.15	1296.804	5.14398	5.3315	6.529	282	2.5

[a] Mean deviation of the experimental values of V_p/V_0 from the values calculated with Eq. (2).

The coefficients of Eq. (2) are given in Table II. As we have noted previously, relationships of the form of Eq. (2) provide a very good representation of the pressure dependence of V_p/V_0 at a constant temperature. However, for purposes of extrapolation to pressures higher than the maximum experimental pressure at each temperature, it is preferable to express V_p/V_0 in terms of the Tait equation in the form utilized by Gibson and co-workers, *viz.*,

$$1 - V_p/V_0 = C \ln\{(B+p)/B\} \tag{3}$$

The coefficients of Eq. (3) are given in Table III and it appears from the values of δ in Tables II and III that Eq. (2) is, overall, a slightly better representation of the variation of V_p/V_0 with pressure than is Eq. (3). It

Table III. Coefficients of Eq. (3) for $1 - V_p/V_0$ for Bromobenzene

T(K)	$10^2 C$	B (MPa)	$10^3 \delta$(%)[a]	B (Ref. 3)[b]
278.15	9.592	159.3470	3.2	(155.28)[c]
288.15	9.655	151.7373	5.6	(147.75)[c]
298.15	9.690	145.0572	3.0	140.44
313.15[d]	9.608	131.5113	4.2	128.93[e]
323.15	9.773	127.1147	2.5	121.40[e]

[a] Mean deviation of the experimental values of V_p/V_0 from the values calculated with Eq. (3).

[b] Calculated with the constraint $C = 0.09377$ at all temperatures; $0.1 \leqslant p \leqslant 101.3$ MPa.

[c] Extrapolated from a linear fit of B versus T.

[d] The values $C = 0.09740$ and $B = 134.2321$ are more consistent with the values at the other temperatures than are the best-fit values.

[e] Interpolated from a linear fit of B versus T.

should be noted that Gibson and Loeffler [3] adopted a value for C which was temperature independent and the same for a number of liquids. In fitting the present data to Eq. (3) we have relaxed the constraint of a constant value of C. Nonetheless, the assumption made in Ref. 3 (that the temperature dependence of V_p/V_0 is embodied in the variation of B with temperature) is essentially verified, in that although C apparently increases slightly with increasing temperature, the temperature coefficient of C is only about 0.04% K^{-1}, compared with about 0.5% K^{-1} for B.

Another relationship which has been used to express the pressure dependence of volume at constant temperature is the Hudleston equation [7], used by Doolittle and Doolittle [8] in the form

$$\ln\{p v_p^{\frac{2}{3}}/(v_0^{\frac{1}{3}} - v_p^{\frac{1}{3}})\} = A + B(v_0^{\frac{1}{3}} - v_p^{\frac{1}{3}}) \tag{4}$$

where v_0 and v_p are specific volumes at zero pressure and pressure p. In terms of volume ratios Eq. (4) can be written

$$\ln\{p v_0^{\frac{1}{3}} k^{\frac{2}{3}}/(1 - k^{\frac{1}{3}}) = A + B v_0^{\frac{1}{3}}(1 - k^{\frac{1}{3}}) \tag{5}$$

where $k = V_p/V_0$, and we have fitted the data for bromobenzene to Eq. (5). The best-fit values of v_0 from these fits are close to literature values for the specific volume at 0.1 MPa, but Eq. (5) fits the experimental volume ratio data considerably less well than does Eq. (2) or Eq. (3). We conclude that, at least in the case of bromobenzene, there is no advantage in representing the volume ratio data with the Hudleston equation.

Isothermal compressibilities, κ, defined by

$$\kappa = -(1/V)(\partial V/\partial p)_T = -(1/k)(\partial k/\partial p)_T \tag{6}$$

were calculated from the coefficients of Eq. (2) using the relationship

$$\kappa = -\{1/(p - K)\}\{1 - (p/K)(\partial K/\partial p)_T\} \tag{7}$$

and from the coefficients of Eq. (3) using

$$\kappa = \{Z/(Z - p)\}\{C/(B + p)\} \tag{8}$$

where

$$Z = p/C \ln\{(B + p)/p\} \tag{9}$$

Values of κ derived from Eqs. (2) and (3) are compared with values calculated from the Tait equation coefficients of Gibson and Loeffler [3] in Table IV. The probable uncertainty in κ is estimated to be ±1% for pressures above 50 MPa, increasing to ±2% at pressures approaching

Table IV. Isothermal Compressibilities for Bromobenzene

T(K)	p(MPa)	$10^4 \kappa(\mathrm{MPa}^{-1})$		
		Eq. (2)	Eq. (3)	Ref. 3
278.15	0.1	6.07	6.02	(6.00)[a]
	10.0	5.72	5.70	
	20.0	5.41	5.41	
	50.0	4.68	4.71	
	100.0	3.88	3.88	
	101.3	3.87	3.86	(3.80)[a]
	150.0	3.33	3.31	
	200.0	2.86	2.90	
288.15	0.1	6.44	6.36	(6.32)[a]
	10.0	6.05	6.01	
	20.0	5.70	5.69	
	50.0	4.89	4.92	
	100.0	4.02	4.03	
	101.3	4.00	4.01	(3.94)[a]
	150.0	3.44	3.43	
	200.0	3.01	2.99	
	250.0	2.62	2.65	
298.15	0.1	6.70	6.68	6.68
	10.0	6.30	6.29	
	20.0	5.95	5.95	
	50.0	5.10	5.11	
	100.0	4.16	4.17	
	101.3	4.14	4.15	4.09
	150.0	3.54	3.53	
	200.0	3.08	3.07	
	250.0	2.68	2.72	
	275.0	2.50	2.57	
313.15	0.1	7.24	7.30	7.29[b]
	10.0	6.81	6.84	
	20.0	6.42	6.43	
	50.0	5.48	5.46	
	100.0	4.40	4.39	
	101.3	4.38	4.37	4.32[b]
	150.0	3.69	3.68	
	200.0	3.17	3.18	
	250.0	2.78	2.81	
	275.0	2.61	2.65	
323.15	0.1	7.71	7.68	7.75[b]
	10.0	7.20	7.18	
	20.0	6.75	6.74	
	50.0	5.69	5.70	
	100.0	4.55	4.56	
	101.3	4.53	4.54	4.47[b]
	150.0	3.83	3.82	
	200.0	3.31	3.29	
	250.0	2.89	2.90	
	275.0	2.69	2.74	

[a] Extrapolated from quadratic fits of κ versus T at each pressure.

[b] Interpolated from quadratic fits of κ versus T at each pressure.

0.1 MPa. The agreement with the literature values [3] is within the combined uncertainties.

Densities at 0.1 MPa from the literature [9] and volume ratios from Eq. (2) were used to calculate isobaric expansivities, α, by evaluating the molar volume (V_M) as a function of temperature at each pressure, fitting V_M to a quadratic in T, then calculating α from

$$\alpha = (1/V_M)(\partial V_M/\partial T)_p \tag{10}$$

Values of α are given in Table V: the probable uncertainty in α is estimated to be ±2–3%. It is interesting to note that unlike toluene, dichloromethane, and acetonitrile, for instance, for which $(\partial\alpha/\partial T)_p > 0$ at pressures up to 275 MPa [10], for bromobenzene $(\partial\alpha/\partial T)_p$ changes sign at an intermediate pressure (about 100 MPa). A similar variation in sign is found with trichloromethane [10], *N*-methylformamide [11], and *N*, *N*-dimethylformamide [11], although the pressure at which $(\partial\alpha/\partial T)_p$ changes sign is much lower for these liquids.

Internal pressures, π, calculated using the relationships

$$\pi = T(\partial p/\partial T)_v - p \tag{11}$$

$$(\partial p/\partial T)_v = \alpha/\kappa \tag{12}$$

from the values for κ and α in Tables IV (column 3) and V are shown in Table VI. The probable uncertainty in π is of the order 2–3%. At 298 K (the only temperature at which a direct comparison can be made) and pressures up to 101.3 MPa, the values of π in Table VI agree with those of Gibson and Loeffler [12] to within 1–2 MPa.

The freezing pressure at each temperature for which volume ratios were measured was estimated as follows. The freezing pressures reported by

Table V. Isobaric Expansivities for Bromobenzene

	$10^4\,\alpha$ (K^{-1}) at p						
T (K)	0.1 MPa	10 MPa	20 MPa	50 MPa	100 MPa	150 MPa	200 MPa
278.15	8.84	8.58	8.31	7.62	6.77	6.21	5.71
288.15	8.95	8.65	8.37	7.64	6.75	6.16	5.66
298.15	9.05	8.73	8.42	7.66	6.74	6.11	5.62
313.15	9.21	8.84	8.51	7.68	6.72	6.05	5.56
323.15	9.32	8.92	8.56	7.70	6.70	6.00	5.52

Table VI. Internal Pressures for Bromobenzene

	π (MPa) at p					
T (K)	0.1 MPa	20 MPa	50 MPa	100 MPa	150 MPa	200 MPa
278.15	405	407	403	385	369	355
288.15	400	403	400	384	366	342
298.15	403	402	398	383	365	344
313.15	398	395	389	378	363	349
323.15	391	390	387	376	356	339

Bridgman [6] were adjusted by adopting the suggestion of Babb [13] that Bridgman's freezing pressure for mercury at 278.15 K was 76 $\mathrm{kg \cdot cm^{-2}}$ low and, hence, applying a correction increasing linearly from zero at 1.02 $\mathrm{kg \cdot cm^{-2}}$ (i.e., 0.1 MPa) to 76 $\mathrm{kg \cdot cm^{-2}}$ at 7640 $\mathrm{kg \cdot cm^{-2}}$. The corrected freezing pressures were then fitted to a quadratic in T, which was interpolated at the temperatures of interest. Values of V_p/V_0 at the freezing pressure at each temperature were then calculated from Eq. (3) and used in conjunction with molar volumes at 0.1 MPa to calculate the molar volume at the freezing pressure for each temperature. Finally, the equivalent hard-sphere diameter for bromobenzene was calculated at each temperature from the relationship [14]

$$\sigma = 0.11611\, V_\mathrm{M}^{\frac{1}{3}} \tag{13}$$

Table VII. Equivalent Hard-Sphere Diameters for Bromobenzene

T (K)	P_f[a] (MPa)	ρ_0[b] ($\mathrm{g \cdot cm^{-3}}$)	V_p/V_0[c]	V_M[d] ($\mathrm{cm^3 \cdot mol^{-1}}$)	σ (nm)
278.15	195.34	1.51527	0.92325	95.669	0.531_0
288.15	257.07	1.50184	0.90431	94.545	0.529_0
298.15	322.24	1.48838	0.88664	93.536	0.527_1
313.15	426.44	1.46813	(0.8612)[e]	(92.10)	(0.524)
323.15	500.20	1.45458	(0.8440)	(91.11)	(0.523)

[a] Freezing pressure.

[b] Density at 0.1 MPa.

[c] Volume ratio at pressure P_f.

[d] Molar volume at pressure P_f.

[e] The parenthesized values were derived by extrapolation of Eq. (3) beyond the experimental pressure range.

where σ is in nm and V_M is in $cm^3 \cdot mol^{-1}$. The values of σ are given in Table VII together with the data used for the calculation. It is notable that even though estimation of V_p/V_0 at the freezing pressure at 313 and (particularly) 323 *K* involves lengthy extrapolations of Eq. (3), it is only at 323 K that the estimated value of σ deviates significantly from a smooth curve through the values for the lower temperatures. Excluding the estimated value at 323 K, the temperature variation of $\sigma(278\ K \leqslant T \leqslant 313\ K)$ can be expressed by

$$\sigma = 0.6216 - 4.476 \times 10^{-4} T + 4.38 \times 10^{-7} T^2 \qquad (14)$$

where σ is in nm and T is in K.

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