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Thermodynamic Properties of 2,2,4-Trimethylpentane

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p, V, T data for 2,2,4-trimethylpentane (TMP) have been obtained in the form of volume ratios for six temperatures in the range 278.15 to 338.15 K for pressures up to 280 MPa. Isothermal compressibilities, isobaric expansivities, and internal pressures have been evaluated from the volumetric data. There are strong indications that the combination of the present results with literature data at 348 and 373 K enable accurate extrapolations in the liquid range up to 473 K, and possibly to as low as 170 K, for pressures up to 980 MPa; use of only the present results with the requirement that the *B* coefficient of the Tait equation should become equal to the negative of the critical pressure at the critical temperature provides interpolations and extrapolations of comparable accuracy. It is suggested that 2,2,4-trimethylpentane is a suitable secondary reference material (because of its large liquid range at atmospheric pressure and the similarity of its volumetric properties to a wide range of fluids) for calibration of measuring cells used for determining volumes of fluids under pressure.

KEY WORDS: compressibility; high pressure; *p, V, T* data; reference material; Tait equation of state; 2,2,4-trimethylpentane.

1. INTRODUCTION

The objective of the present investigation was to provide accurate *p, V, T* data for 2,2,4-trimethylpentane (TMP) at temperatures from 278 to 338 K for use in our continuing studies of the volumetric properties of liquid mixtures under pressure. The accurate determination of excess thermodynamic quantities from these studies requires that the temperature intervals be 10 to 15 K.

Some methods of measuring volumetric properties of fluids under pressure rely on calibration of the measuring cell with a reference fluid.

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Although accurate high-pressure density data are available for water [1], it has a limited liquid range at ambient pressures which are the most convenient for initiating experimental high-pressure measurements. 2,2,4-trimethylpentane is a recommended reference material for atmospheric pressure measurements of density [2], shear viscosity [3], thermal conductivity [4], and refractive index [5]. It has a liquid range of 206 K (165.8 to 372.4 K) at 0.1 MPa and, as it is a much more compressible fluid than water, has similar volumetric properties to a substantially wider range of fluids.

In addition to the present volume ratio measurements there are those of Dymond *et al.* [6], who estimated their accuracy to be ±0.1% for temperatures in the range 298.15 to 373.15 K at 25-K intervals and the less accurate (±0.5%) results of Bridgman [7] at 273.15, 323.15, and 368.15 K.

2. EXPERIMENTAL

The 2,2,4-trimethylpentane was BDH HiPerSolv-grade material of stated purity minimum 99.8 mol % and was used without further purification, except for storage over Type 4A molecular sieves for several weeks before use to remove water and other low molecular weight impurities.

Volume ratios, k $(=V_p/V_{0.1}$, where $V_{0.1}$ and V_p are the volumes of a fixed mass of TMP at 0.1 MPa and pressure p, with p the pressure relative to atmospheric pressure), were measured at 278.15, 288.15, 298.15, 313.15, 323.15, and 338.15 K using a bellows volumometer [8–10]. The procedures followed in the present work were virtually identical to those described previously [9] and are summarized briefly here. The pressure range was from about 2.5 to 280 MPa; the position of the bellows was determined at 20-MPa intervals from 280 to 100 MPa, at 10-MPa intervals from 100 to 30 MPa, at 5-MPa intervals from 30 to 5 MPa, and at about 2.5 MPa. The position of the bellows at 0.1 MPa and, thus, the displacements of the bellows were obtained from the intercept of a sixth-order polynomial fit in pressure of the bellows positions. The displacements thus determined were used to obtain the volume ratios from calibration values [9]. Pressures were measured using Heise–Bourdon gauges calibrated to ±0.05% using deadweight gauges. Temperatures were measured accurately to within ±0.01 K and during measurements at each temperature the bath was constant to within ±0.004 K. The overall accuracy of the measured volume ratios are estimated as about ±0.02–0.04% for pressures above 50 MPa, increasing to ±0.1% at pressures approaching 0.1 MPa.

There were two series of measurements: series 1, which included the temperatures 278.15, 288.15, 298.15, 313.15, and 323.15 K, for which the bellows volumometer had been calibrated using water and heptane as the calibrating fluids [8], and series 2, which used a new volumometer cell (calibrated by the same method [8]) at 323.15 and 338.15 K. However, for the new volumometer cell it was found that its characteristics were well defined [11] using water only as the calibration fluid. (A sensitive test illustrating this is included in Fig. 1, where the volume ratios obtained at 323.15 K in both series are compared; the differences between volume ratios at the same pressures are less than ±0.03%.)

Densities of TMP were measured at 0.1 MPa using an Anton Paar Model DMA 602 densimeter at 278.15, 288.15, 298.15, and 313.15 K with a maximum uncertainty of $\pm 0.02\ \mathrm{kg\cdot m^{-3}}$.

3. RESULTS AND DISCUSSION

3.1. Volumetric Data

The experimental values for the density at 0.1 MPa ($\rho_{0.1}$) agree very well with the literature values: at 278.15 K, 704.16 (this work) and $704.20\ \mathrm{kg\cdot m^{-3}}$ [12]; at 298.15, 687.33, 687.85 [2], and $687.81\ \mathrm{kg\cdot m^{-3}}$

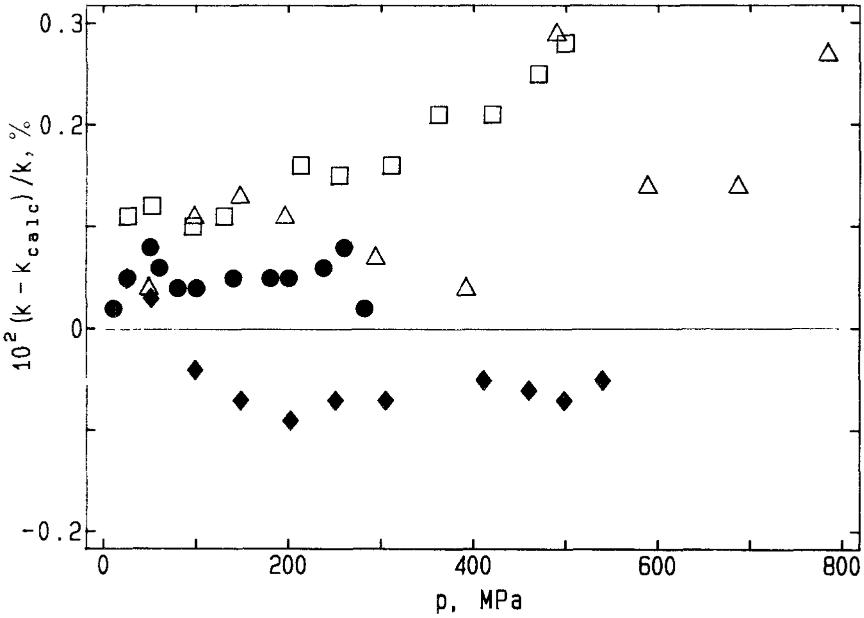

Fig. 1. Comparison of experimental volume ratios with those obtained using optimized Tait coefficients. At 298.15 or 323.15 K: ——, Eq. (3) using coefficients (Table I). At 298.15 K: ◆, [6]. At 323.15 K: ●, series 1 (this work); □, [6]; △, [7]. At 323.15 K the solid line represents data for volumetric cell 2 (series 2).

[13]; and at 313.15 K, 675.33, 675.33 [13], and 675.35 $\mathrm{kg \cdot m^{-3}}$ [2]. The density of 696.03 $\mathrm{kg \cdot m^{-3}}$ at 288.15 K compared well with the extrapolated value of 696.04 $\mathrm{kg \cdot m^{-3}}$ from the equation given in Ref. 2 for densities of TMP (recommended as a secondary reference material for densities at 0.1 MPa for the temperature range 293 to 323 K). The combined data (this work and the literature values [2]) over the combined temperature range can be represented by a third-degree polynomial,

$$\rho_{0.1} = 936.721 - 1.0040\,T + 1.1034 \times 10^{-3}\,T^2 - 1.797 \times 10^{-6}\,T^3$$
$$(278.15 \leqslant T \leqslant 323.15) \qquad (1)$$

where $\rho_{0.1}$ is in $\mathrm{kg \cdot m^{-3}}$ and T is in K. The uncertainty limit is $\pm 9 \times 10^{-3}\ \mathrm{kg \cdot m^{-3}}$. The density used for TMP at 0.1 MPa to calculate the thermal expansivities at 338.15 K was 654.18 $\mathrm{kg \cdot m^{-3}}$; this was obtained from interpolation of the densities fitted in the range 313 to 366 K [12].

The secant bulk modulus (SBM), $K = [= p/(1-k)$, where k is the experimentally determined volume ratio], was represented by cubic equations

$$K = \sum_{i=0}^{3} A_i p^i \qquad (2)$$

The A_i of Eq. (2) are listed in Table I with the coefficients B and C of the modified Tait equation [14] expressed here as

$$1 - k = C \log[(B + p)/(B + p_0)] \qquad (3)$$

where p_0 is the reference pressure, usually 0.1 MPa, and the constants B and C are adjustable parameters. The maximum deviation for a set of volume ratios at any temperature was generally at the highest pressure of the measurements and the worst deviation between the calculated and the experimental measurements was 0.087% at 274 MPa and 338.15 K. Equation (2) gives the more accurate representation of the experimental volume ratios; the fit is well within the estimated experimental precision.

The density at pressure p, ρ_p, can be calculated using Eq. (4)

$$\rho_p = \rho_{0.1}/k = \rho_{0.1}/[1 - (p/K)] \qquad (4)$$

and Eq. (1) with k from either Eq. (2) or Eq. (3).

The Tait equation has been shown to give for substances an accurate extrapolation of the volume ratios for pressures outside the actual experimental pressure range [15]. Figure 1 shows the deviations of the

Table 1. Coefficients of Eq. (2) for SBM and of Eq. (3) for the Tait Equation

T (K)	A_0 (MPa)	A_1	$-A_2$ (GPa^{-1})	A_3 (GPa^{-2})	r^a	B (MPa)	C	r^b	r^c
				Series 1					
278.15	769.35	5.4543	7.2151	9.216	0.008	69.2	0.2060	0.02	0.02
288.15	712.01	5.3441	6.9742	8.880	0.009	63.8	0.2062	0.02	0.04
298.15	671.11	5.0599	5.1284	4.825	0.008	59.2	0.2058	0.05	0.02
313.15	597.13	4.8856	4.3525	3.264	0.012	51.6	0.2041	0.03	0.06
323.15	552.65	5.0853	4.0586	7.516	0.011	48.2	0.2084	0.01	0.03
				Series 2[d]					
323.15	554.14	5.1421	6.5058	7.514	0.017	49.0	0.2051	0.03	0.06
338.15	486.48	5.0394	6.4350	7.475	0.022	42.6	0.2043	0.04	0.06

[a] rmsd (%) in calculated $V_p/V_{0.1}$ using SBM coefficients of Eq. (2).

[b] rmsd (%) in calculated $V_p/V_{0.1}$ using optimized coefficients B and C from columns 7 and 8, respectively, in Eq. (3).

[c] rmsd (%) in calculated $V_p/V_{0.1}$ using Eq. (5) to obtain B for a fixed value of $C = 0.205$ in Eq. (3).

[d] New volumometer cell.

calculated volume ratios, using optimized coefficients B and C (Table I) in Eq. (3), from the literature volume ratios at 298.15 [6] and 323.15 K [6, 7] for pressures extending to 800 MPa, which is 500 MPa above (or nearly three times) our maximum experimental pressure. The zero line indicates the volume ratios obtained using optimized coefficients at 298.15 or 323.15 K (series 2), respectively, in Table I. The maximum deviation between the volume ratios obtained from the Tait equation fitted to this work and the experimental volume ratios of Dymond et al. [6] at 298.15 K is less than ±0.1% for pressures up to 540 MPa (260 MPa above the maximum pressure of measurement in this work). Similarly, the deviations at 323.15 K are within ±0.1% for pressures up to 200 MPa, after which there is a systematic increase in the difference with pressure at this temperature. The cross-sectional area of the bellows used in Ref. 6 apparently was calibrated at only one reference temperaure, 298.15 K [16], and an equation [Eq. (1) in Ref. 6, involving the appropriate coefficients of thermal expansion and the linear coefficient of compressibility] used to predict the area at other temperatures; this procedure may not be completely accurate. The deviation between this work and the other set of measurements at 323 K [7] is less than ±0.1% for pressures up to 280 MPa, and the difference between the predicted and the experimental volume ratios [7] for pressures above 280 MPa and up to 800 MPa is within the experimental uncertainties.

3.2. The Tait Equation of State

The significance and the use of the Tait equation of state to correlate volumetric data for liquids over wide pressure and temperature ranges have been reviewed recently [17]. A necessary feature for interpolation of densities (or volumes) at intermediate temperatures [18, 19] is the use of a temperature-independent value of C and representation of the temperature dependence of the B values by a suitable equation. The present measurements can be represented by

$$C = 0.205 \tag{5a}$$

$$B = 329.69 - 1.3658\,T + 1.533 \times 10^{-3}\,T^2 \qquad (278.15 \leqslant T \leqslant 338.15) \tag{5b}$$

where B is in MPa and T is in K. The standard deviation is 0.40. The value of C was chosen to give the best fit to the whole data set; this set does not include the optimized value of B for Series 1 at 323.15 K, which was omitted intentionally to avoid the use of weightings in the curve fit. (The two sets of data at 323.15 K agree within ±0.03% in the volume ratio.) The deviation of the calculated volume ratio from the experimental value at any temperature was at a maximum of less than $\pm 0.14\%$ at the highest pressure of the measurements, with the exception of a deviation of 0.16% for 100 MPa at 323.15 K. The deviations for pressures up to 200 MPa are marginally worse than those which occur when the isotherms are represented by individual optimized coefficients B and C. However, the correlation with C fixed not only reproduces the measured data satisfactorily but also enables interpolation of volume ratios within the maximum experimental uncertainty.

The Tait equation has been considered reliable for extrapolating data to temperatures outside the experimental range [15, 20]. However, Eq. (5b) for B does not enable prediction of volume ratios for TMP at 348.15 and 373.15 K within the experimental uncertainty of the literature data [6]: the maximum deviation between the predicted and the literature data is of the order of $\pm 0.4\%$. This disagreement is not surprising since these temperatures are not only close to the normal boiling point of the fluid where the extrapolation is known to be unreliable [21], but also close to a reduced temperature T_r ($= T/T_c$, where T_c is the critical temperature) of 0.66, which is a region to which the Tait equation for n-alkanes [21] did not extrapolate within the experimental uncertainty. However, the B values for a fixed value of C ($=0.205$), representing the literature data for TMP [6] at each experimental temperature in the range 298.15 to 373.15 K, within their experimental uncertainty of $\pm 0.1\%$ in the volume, combine smoothly with the B values of this work.

The combined B values (this work and those for Ref. 6 at 348.01 and 372.95 K) are represented as a quadratic function of temperature:

$$B = 261.18 - 0.9123\,T + 7.8508 \times 10^{-4}\,T^2 \qquad (278.15 \leqslant T \leqslant 373.15) \quad (6)$$

where B is in MPa and T is in K. The standard deviation is 0.49. The calculated volume ratios using the combined data are compared with the literature values [7] up to a maximum pressure of 588 MPa at 273.15 K and up to 980 MPa at 368.15 K in Table II. The volume ratios agree at 273.15 K within the maximum experimental uncertainty of Ref. 7 ($\pm 0.5\%$ [22]), demonstrating the use of the Tait equation of state outside the temperature and pressure range of the measurements. The accurate prediction of volume ratios for pressures up to 980 MPa at 368.15 K shows that the equation can be used successfully for estimation of densities at pressures well outside the experimental range. Equation (6) was also used to obtain volume ratios up to 473.15 K (100 K above the highest temperature for the combined B data) which agreed with the literature values [23] for the temperature range of 373 to 473 K at 25-K intervals up to their maximum pressure of 30 MPa within the estimated experimental uncertainty of

Table II. Comparison of the Predicted[a] and Literature Volume Ratios at 273.15 and 368.15 K

p (MPa)	$V_p/V_{0.1}$ (273.15 K)		$V_p/V_{98.07}$[b] (368.15 K)	
	Eq. (6)	Ref. 7	Eq. (6)[c]	Ref. 7
49.03	0.9529	0.9532		
98.07	0.9526	0.9221		
147.10	0.8999	0.9001	0.9674	0.9675
196.13	0.8818	0.8825	0.9427	0.9433
294.20	0.8540	0.8558	0.9062	0.9081
392.27	0.8328	0.8356	0.8795	0.8815
490.30	0.8157	0.8161	0.8584	0.8581
588.40	0.8013	0.8037	0.8408	0.8433
686.47			0.8259	0.8284
784.50			0.8129	0.8145
882.60			0.8013	0.8020
980.70			0.7909	0.7913

[a] Using Eq. (6).
[b] $V_p/V_{98.07}$ is volume ratio of volumes at pressure p and 98.07 MPa, respectively.
[c] $V_p/V_{98.07} = (V_p/V_{0.1})/(V_{98.07}/V_{0.1})$.

±0.3% [23]. B is expected to become equal to $-P_c$ (P_c = critical pressure) as T approaches T_c [24]; the extrapolation of the present curve [using Eq. (6)] to T_c (543.9 K [25]) gives a P_c of 2.8 MPa compared to the literature value of 2.6 MPa [25].

The usefulness of the Tait equation for extrapolation well outside the experimental range of temperatures can be shown by combining the present B data for 278–338 K (with a fixed C of 0.205) with the theoretical requirement that $B = -P_c$ at T_c. The least-squares fitted values of B can be represented by the equation

$$B = -2.589 - 6.3387 \times 10^{-2}(T - T_c) + 7.6169 \times 10^{-4}(T - T_c)^2 \qquad (7)$$

with a standard deviation of 0.48. The differences between the predicted [Eq. (2)] and the experimental volume ratios [6, 7, 23] for the individual isotherms are always within the estimated experimental error, being ±0.2% except at 398 K, where it is 0.3%. The overall difference is only slightly worse than was obtained using Eq. (6). [Use of the combined values of B from this work and Ref. 6 with the theoretical value at T_c to obtain an equation similar to Eq. (7) produces only trivial changes in the differences between the correlated and experimental volume ratios.]

The Tait equation of state for toluene [15], obtained from experimental densities in the temperature range 298 to 373 K ($T_r = 0.5$ to 0.63) for pressures up to 300 MPa, was able to predict density ratios for temperatures down to 180 K ($T_r = 0.3$) agreeing well within the experimental uncertainty ($\pm 0.2\%$) of the literature data [26] which were for a maximum pressure of 10 MPa at that temperature. Equation (7) is therefore expected to be suitable for generating volume ratios of TMP up to high pressures for temperatures in the range from the normal freezing point at 166 K up to 273 K ($T_r = 0.3$ to 0.5), although no data for such conditions exist in the literature. [It may be noted that if the data for 278 and 288 K are omitted from the combined data (this work and temperatures above 338.15 K from Ref. 6), the resulting Tait equation for the range 298 to 373 K provides extrapolated values of the volume ratio at 273, 278, and 288 K which agree within the uncertainty of the present and the literature data from Ref. 7. However, the representation by a Tait equation of the data of Ref. 6 alone does not provide such an accurate prediction of the volume ratios at 278 K.]

3.3. Compressibilities and Expansivities

Isothermal compressibilities, κ_T, given in Table III, were calculated from the SBM coefficients given in Table I for Eq. (2) by using the relationship [27]

$$\kappa_T = -[1/(p-K)][1-(p/K)(\partial K/\partial p)_T] \tag{8}$$

Table III. Isobaric Expansivities (α, in K^{-1}) and Isothermal Compressibilities (κ_T, in MPa^{-1})

		p(MPa)								
T(K)	Property	0.1	10	20	50	100	150	200	250	275
278.15	$10^3\alpha$	1.13	1.06	0.99	0.84	0.69	0.62	0.58	0.54	0.51
	$10^4\kappa_T$	13.00	11.51	10.31	7.85	5.71	4.57	3.83	3.24	2.96
288.15	$10^3\alpha$	1.17	1.08	1.01	0.85	071	064	0.59	0.55	0.52
	$10^4\kappa_T$	14.04	12.35	11.00	8.27	5.94	4.72	3.93	3.31	3.02
298.15	$10^3\alpha$	1.20	1.10	1.03	0.87	0.72	0.65	0.60	0.56	0.54
	$10^4\kappa_T$	14.95	13.12	11.65	8.67	6.11	4.81	4.01	3.43	3.18
313.15	$10^3\alpha$	1.25	1.14	1.05	0.88	0.75	0.65	0.62	0.57	0.56
	$10^4\kappa_T$	16.74	14.57	12.84	9.35	6.42	4.96	4.11	3.56	3.35
322.15	$10^3\alpha$	1.28	1.15	1.06	0.89	0.76	0.68	0.63	0.59	0.57
	$10^4\kappa_T$	18.01	15.41	13.41	9.58	6.56	5.12	4.25	3.60	3.31
338.15	$10^3\alpha$	1.32	1.15	1.09	0.91	0.78	0.70	0.64	0.60	0.59
	$10^4\kappa_T$	20.52	17.26	14.81	10.28	6.89	5.32	4.39	3.70	3.39

Isobaric expansivities, α, were calculated fitting V_m at a constant pressure, p, to a quadratic in T and using

$$\alpha = (1/V_m)(\partial V_m/\partial T)_p \tag{9}$$

The molar volumes, V_m, were evaluated as a function of temperature at eight pressures (10, 20, 50, 100, 150, 200, 250, and 275 MPa) from the densities at 0.1 MPa given by Eq. (1), and volume ratios from the SBM given by Eq. (2) using the coefficients in Table I. The expansivities and compressibilities are listed in Table III. The probable uncertainties in κ_T and α are ± 1–2 and ± 2–3%, respectively. The isothermal compressibilities at 0.1 MPa are in reasonable agreement with literature values: at 298.15 K, 15.0×10^{-4} (this work), 15.0×10^{-4} [6], and 15.4×10^{-4} MPa^{-1} [13]; at 313.15 K, 16.7×10^{-4} (this work) and 17.6×10^{-4} MPa^{-1} [13]; and at 323.15 K, 18.0×10^{-4} (this work) and 18.1×10^{-4} MPa^{-1} [6].

An indication of the accuracy of the p, V, T data from the present work and Ref. 6 is obtained by comparing the isothermal compressibilities at the same pressures. Isothermal compressibilities for TMP for temperatures 298.15, 323.15, 348.01, and 372.95 K were calculated for pressures (0.1, 20, 50, 100, 150, 200, and 250 MPa) from the coefficients of Eq. (2) given in Table III of Ref. 6. The compressibilities at 298.15 and 323.15 K, temperatures which were common to both this work and Ref. 6, agree well within the expected uncertainty of ± 2%; they also show a smooth continuation to the compressibilities at 348.15 and 372.95 K. The compressibilities at constant pressure (this work and those of Ref. 6 at 348.01 and 372.96 K) can be represented by a quadratic function of temperature

$$10^4 \kappa_T = \sum_{i=0}^{2} \kappa_i T^i \tag{10}$$

Table IV. Coefficients of Eq. (10) for Isothermal Compressibilities

p (MPa)	κ_0 (MPa^{-1})	$10^3\kappa_1$ (MPa$^{-1}\cdot$K^{-1})	$10^6\kappa_2$ (MPa$^{-1}\cdot$K^{-2})	rmsd	Max. dev. (%)
0.1	87.958	−593.11	1166.30	0.16	1.7
20.0	34.466	−220.70	482.61	0.14	1.4
50.0	9.883	−47.32	144.52	0.09	1.3
100.0	1.956	8.79	17.18	0.02	0.6
150.0	1.010	13.92	−3.90	0.03	1.0
200.0	1.006	11.51	−4.82	0.03	1.2
250.0	0.573	11.06	−5.19	0.02	1.0

The coefficients κ_i are listed, along with the accuracy of the least-squares fit, in Table IV. The calculated compressibilities [6] are plotted in Fig. 2.

A comparison of the compressibilities at 298.15 and 323.15 K for both sets of data is given in Fig. 3. The compressibilities calculated from the SBM coefficients in Ref. 6 are consistent with the compressibilities of the present work up to the maximum pressure of the latter of 280 MPa. Compressibilities were also calculated using the relationship [20]

$$\kappa_T = \frac{1}{2.3026k} \frac{C}{(B+p)} \tag{11}$$

where $C = 0.205$ for TMP, k is calculated using Eq. (3), and B is calculated from Eq. (6). Values of κ_T calculated from Eq. (11) have a maximum devia-

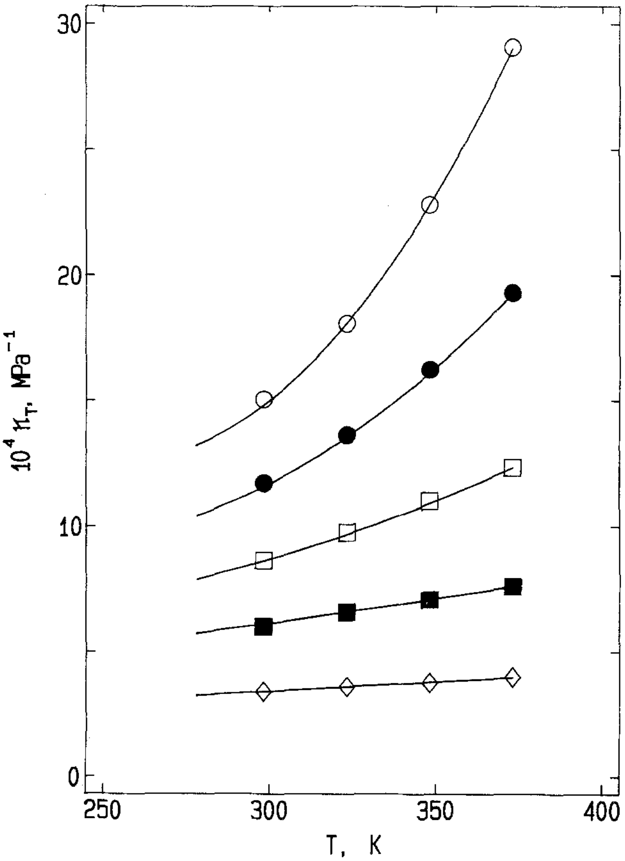

Fig. 2. Isothermal compressibilities as a function of temperature. ——, Eq. (10). Compressibilities calculated from Ref. 6: ○, 0.1 MPa; ●, 20 MPa; □, 50 MPa; ■, 100 MPa; ◇, 250 MPa.

tion from the corresponding compressibilities in Table III of less than 3%. However, it should be reasonable to use Eq. (11) to calculate isothermal compressibilities with a probable uncertainty of ±3% in the temperature range 278 to 373 K for pressures up to 300 MPa.

3.4. Internal Pressure

The internal pressure p_{int} is related to the thermal pressure coefficient $(\partial p/\partial T)_v$, by

$$p_{\mathrm{int}} = T(\partial p/\partial T)_v - p \qquad (12)$$

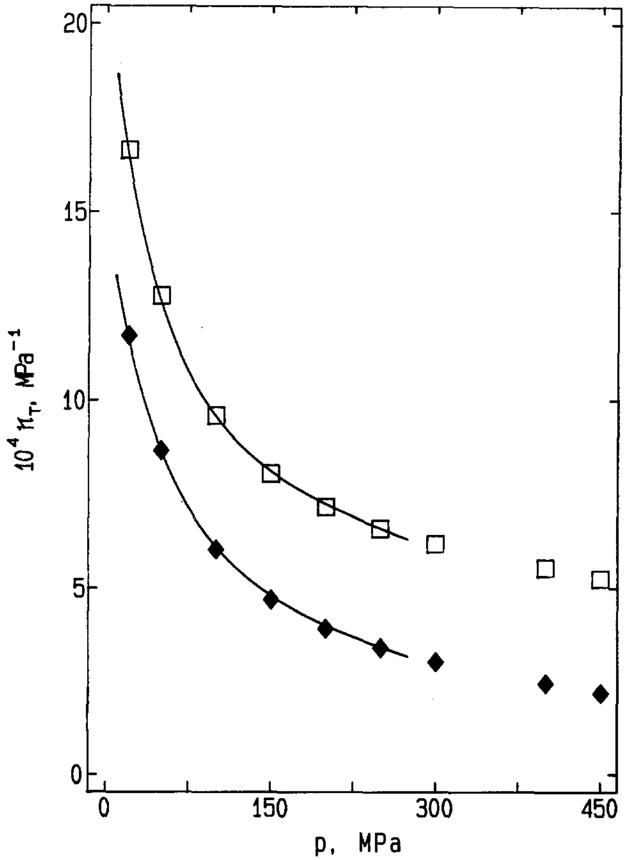

Fig. 3. Isothermal compressibilities as a function of pressure. ——, the solid line smooth curve through the compressibilities of this work; ◆, 298.15 K [6]; □, 323.15 K [6].

Table V. Internal Pressure (p_{int}, in MPa)

	T(K)					
V_m($cm^3 \cdot mol^{-1}$)	278.15	288.15	298.15	313.15	323.15	338.15
144	221	234	246	266	280	301
147	230	240	250	267	278	296
150	235	243	252	265	274	288
153	238	244	251	261	268	279
156	240	244	249	256	261	268
159	240	243	246	250	253	258
162	240	241	242	244	245	247

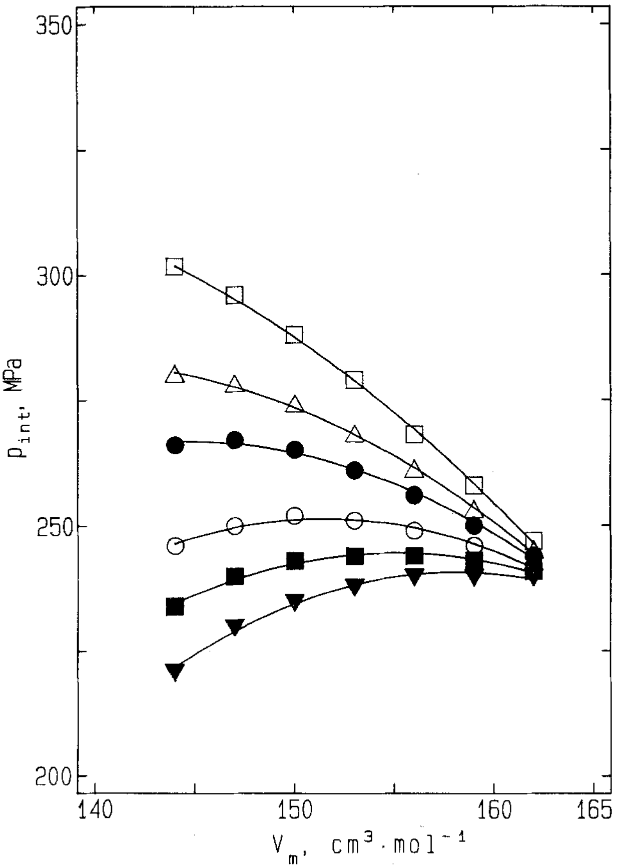

Fig. 4. Volume and temperature dependence of the internal pressure calculated using volume ratios obtained from Eq. (3): ▼, 278 K; ■, 288 K; ○, 298 K; ●, 313 K; △, 323 K; □, 338 K. Solid lines are curves fitted to the points.

Thermal pressure coefficients $(\partial p/\partial T)_v$ for selected values of V_m were calculated as described in Ref. 20; the values of p_{int} are listed in Table V, and they are estimated to have a probable uncertainty of the order of ±3%. The data of Ref. 6 at 348.15 and 372.95 K were not included in the calculations of internal pressures. The inclusion of these data significantly decreases the quality of the quadratic fit of pressure as a function of temperature used to obtain the internal pressure.

The volume dependence of the internal pressure for TMP, at constant temperature, is shown in Fig. 4. The temperature effect on the internal pressure as a function of volume is contrary to that observed by Eduljee et al. [28] for normal hydrocarbons (hexane, heptane, and octane); they observed that the internal pressure for different temperatures, plotted as a function of volume, were on one curve, suggesting that the pressure coefficient $(\partial p/\partial T)_v$ was a function of volume alone.

4. CONCLUSION

The use of the Tait equation of state to represent data for TMP has been examined in detail in this paper for the temperature range 273 to 373 K. The measurements in this work and Ref. 6 have been combined so as to extend the temperature range up to 373 K and to provide a Tait equation of state (expressed in the form of a constant prelogarithmic factor with a temperature-dependent B term). This equation should enable prediction of properties covering the temperature range 170 to 473 K (some ±100 K outside the temperature range of the combined measurements) for pressures up to a maximum of 980 MPa with an accuracy in the volume ratio of ±0.3%. However, by adding to the B values from only this work the theoretical requirement that $B(T_c) = -P_c$ gives an equation essentially the same in predictive power. TMP is recommended as a secondary calibration fluid for temperatures in the range 273.15 to 373.15 K with a maximum deviation in the volume ratio of up to ±0.1% for pressures up to 300 MPa or up to ±0.2% for pressures in the range from 300 to 500 MPa.

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