

Thermodynamic Properties and Excess Volumes of 2,2,4-Trimethylpentane + *n*-Heptane Mixtures from 298 to 338 K for Pressures up to 400 MPa

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(p, V, T) data for mixtures of 2,2,4-trimethylpentane (TMP) and heptane have been obtained in the form of volume ratios for four temperatures in the range 298.15 to 338.15 K for pressures up to 390 MPa. The data have been represented by the Tait equation of state for the purposes of interpolation and extrapolation. The atmospheric pressure densities of both pure components and their mixtures for three temperatures have been measured and used to determine the excess molar volumes. Isothermal compressibilities have been evaluated from the volumetric data.

KEY WORDS: compressibility; excess volume; high pressure; p, V, T data; 2,2,4-trimethylpentane + heptane.

1. INTRODUCTION

This work was done to provide information on the effect of pressure and temperature on the volume of three mixtures of 2,2,4-trimethylpentane (TMP) and *n*-heptane to assist in the interpretation of thermal conductivity measurements for such mixtures which are reported in an earlier paper [1]. In addition to the measurements at high pressures, data are given for densities of the pure components and the mixtures for three temperatures at atmospheric pressure to enable determination of excess molar volumes both for interpolation of densities at intermediate compositions and for extrapolation to higher temperatures.

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2. EXPERIMENTAL

The *n*-heptane was American Burdick and Jackson High Purity Solvent and the 2,2,4-trimethylpentane BDH HiPerSolv (99.8%); they were used without further purification except for storage over Type 4A molecular sieves for several weeks.

Volume ratios, $k (= V_p/V_{0.1})$, where V_p and $V_{0.1}$ are the volumes of a fixed mass of liquid at pressure p and 0.1 MPa, respectively, were determined for the mixtures with a bellows volumeter described previously [2-4]. The measurements were made at 298.15, 313.15, 323.15, and 338.15 K for the pressure range from about 2.5 to 400 MPa. The overall accuracy of the measured volume ratios is estimated to be ± 0.02 – 0.04% for pressures above 50 MPa, varying to $\pm 0.1\%$ at pressures approaching 0.1 MPa.

Densities at 0.1 MPa were measured with an Anton Paar Model 60 digital densimeter using a DMA602HT external cell. Temperatures were maintained to ± 0.02 K or better and were monitored with platinum resistance thermometers at the inlet and outlet. The temperatures were read at 1-s intervals and averaged over the duration of each densimeter measurement of 10^4 periods of vibration; 10 such densimeter readings were used to interpolate a value at exactly the temperature required. Results obtained with this procedure were stable to a density equivalent of $\pm 2 \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ or better. The calibrating fluids were air or ultra-high-purity nitrogen and freshly prepared degassed, deionized distilled water: the assumption of a linear relationship between the square of the period and the density was found to be reliable to $\pm 1 \times 10^{-2} \text{ kg} \cdot \text{m}^{-2}$ using sucrose solutions. The pure solvents were dried by stirring over a 4-Å molecular sieve, degassed with helium sparging, and sampled under reduced pressure through 10- μm stainless steel filters into gas-tight glass and Teflon syringes. The mixtures were individually prepared gravimetrically with small vapor space in 25-cm³ vessels; each mixture was sampled only once, immediately after preparation, and injected into the densimeter through inert 0.45- μm filters. The maximum uncertainty in the density of the mixtures is estimated to be 20 ppm.

3. RESULTS AND DISCUSSION

3.1. Atmospheric Pressure Densities and Excess Volumes

The densities are given in Table I together with excess molar volumes, V^E , defined by

$$V^E = V_m - V^{\text{id}} \quad (1)$$

Table I. The Densities and Excess Volume of the Mixture TMP + *n*-Heptane (2) at 0.1 MPa and 298.15 and 323.15 K

<i>T</i> (K)	Mole fraction, <i>x</i> ₂	ρ (kg · m ⁻³)	V^E (cm ³ · mol ⁻¹)
298.15	0.0	687.84	0.0
	0.1895	686.56	-0.008
	0.2394	686.22	-0.013
	0.4572	684.67	-0.026
	0.5226	684.17	-0.027
	0.7009	682.75	-0.023
	0.7353	682.46	-0.020
	1.0	680.16	0.0
313.15	0.0	675.35	0.0
	0.1170	674.51	-0.001
	0.2001	673.94	-0.013
	0.3090	673.16	-0.024
	0.3822	672.61	-0.028
	0.5088	671.61	-0.030
	0.5649	671.17	-0.034
	0.7169	669.87	-0.024
	0.7689	669.41	-0.020
	0.9072	668.14	-0.006
	1.0	667.28	0.0
338.15	0.0	653.94	0.0
	0.5223	649.74	-0.034
	1.0	645.14	0.0

with

$$V_m = (x_1 M_1 + x_2 M_2) / \rho_{\text{mix}} \quad (2)$$

and

$$V^{\text{id}} = V^0(1) - x_2 [V^0(1) - V^0(2)] \quad (3)$$

mole fractions x_1 and x_2 . M_i ($i = 1, 2$) are the molecular weights, ρ_{mix} is the density of the mixture, and $V^0(i)$ is the molar volume of pure component i ($= M_i / \rho_i$).

Table I shows that the excess volumes are independent of temperature within the estimated error of $\pm 0.006 \text{ cm}^3 \cdot \text{mol}^{-1}$, and the result at 338.15 K indicates that the data can be extrapolated with confidence by 25 K. To predict densities of the liquid mixtures at temperatures above 338.15 K, it is necessary to have only the densities of the pure components to use with the excess volume from Table I in Eq. (2). Without the excess

volumes the density of the mixtures can be predicted within about $\pm 0.03 \text{ kg} \cdot \text{m}^{-3}$ from the densities of the pure components. For *n*-heptane the densities are available from [5] and for TMP from [6]. For the approximately equimolar mixture at 298.15 K the excess volume of $-0.03 \text{ cm}^3 \cdot \text{mol}^{-1}$ compares well with the literature value at 293.15 K of $-0.04 \text{ cm}^3 \cdot \text{mol}^{-1}$ [7] within the combined experimental uncertainties.

The excess molar volumes (Table I) for the mixtures at 298.15 and 313.15 K were fitted to the equation

$$V^E = x_1 x_2 \sum_{k=1}^3 A_{k-1} (x_1 - x_2)^{k-1} \quad (4)$$

The parameters A_{k-1} and the standard deviation s are $A_1 = -0.10621$, $A_2 = -0.01959$, $A_3 = 0.0860$, and $s = 0.0004$ at 298.15 K and $A_1 = -0.13530$, $A_2 = -0.02669$, $A_3 = 0.13172$, and $s = 0.0020$ at 313.15 K. (The fit, obtained using only two values of A , is also within the estimated error of the data.)

3.2. High-Pressure Volumetric Data

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

$$K = \sum_{i=0}^3 A_i p^i \quad (5)$$

The coefficients of Eq. (5) are listed in Table II; the maximum root mean square deviation (rmsd) between the calculated and the experimental volume ratios at any temperature was 0.032%. The maximum deviation for a set of volume ratios at any temperature for any mole fraction was 0.065%.

The measured volume ratios were also fitted to the modified Tait equation [8], expressed here as

$$1 - k = C \log[(B + p)/(B + p_0)] \quad (6)$$

where p_0 is the reference pressure, usually 0.1 MPa, and the constants B and C are adjustable parameters. The coefficients B and C of Eq. (6) are given in Table II; the maximum rmsd between the calculated and the experimental volume ratios at any temperature for any mole fraction was 0.037%. The maximum deviation for a set of volume ratios at any temperature was generally at the highest pressure of the measurement and the largest deviation between the calculated and the experimental measurement was 0.085% for 60 MPa at 338.15 K for the equimolar mixture.

Table II. Coefficients of Eq. (5) for SBM and of Eq. (6) 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
0.8131 TMP + 0.1869 heptane									
298.15	697.88	5.0866	5.0463	4.498	0.017	62.6	0.2082	0.026	0.029
313.15	624.27	4.9097	4.6338	3.955	0.019	55.4	0.2082	0.027	0.030
323.15	555.11	5.1626	6.2175	6.316	0.027	49.9	0.2067	0.033	0.040
338.15	486.86	5.0285	5.9843	6.004	0.031	43.2	0.2057	0.036	0.044
0.5040 TMP + 4960 heptane									
298.15	706.35	5.0690	5.1276	4.732	0.013	93.9	0.2097	0.022	0.025
313.15	630.32	4.9011	4.6950	4.027	0.020	56.8	0.2106	0.028	0.030
323.15	574.86	4.8920	4.9443	4.481	0.023	51.3	0.2090	0.030	0.037
338.15	511.10	4.7307	4.6466	4.101	0.032	45.2	0.2096	0.035	0.040
0.2580 TMP + 0.7420 heptane									
298.15	697.09	5.2839	6.2029	6.159	0.018	65.0	0.2118	0.032	0.035
313.15	616.01	5.1472	6.0125	5.967	0.021	56.7	0.2110	0.031	0.033
323.15	567.63	5.0568	5.9090	5.870	0.024	52.1	0.2112	0.031	0.034
338.15	493.48	5.0075	6.0497	6.114	0.030	44.8	0.2093	0.037	0.042

^a rmsd (%) in calculated $V_p/V_{0.1}$ using SBM coefficients of Eq. (5).

^b rmsd (%) in calculated $V_p/V_{0.1}$ using optimized coefficients, B and C , from columns 7 and 8, respectively, in Eq. (6).

^c rmsd (%) in calculated $V_p/V_{0.1}$ using fixed value of C and coefficients (Table III) of Eq. (7) to obtain B in Eq. (6).

Equation (5), in comparison to Eq. (6), is a more accurate representation of the pressure dependence of the experimental volume ratios at constant temperature (Table II). However, the Tait equation, which has been extensively used for interpolating densities of pure liquids at intermediate temperature [9–11], also has the advantage of reliably extrapolating the temperature and pressure dependence of their experimental volume ratios beyond the experimental temperature and pressure range [6, 12]. It has also been employed to correlate p - V - T data for mixtures of alkanes [13] which behave like nearly ideal mixtures.

B values obtained from the present measurements can be represented by a fixed value of C chosen to give the best fit to the whole data set of $V_p/V_{0.1}$ values for each mole fraction, with B expressed as a function of temperature,

$$B(\text{MPa}) = \sum_{i=0}^2 B_i T(K)^i \quad (7)$$

The coefficients for Eq. (7) are given in Table III. The percentage rmsd between the calculated and the experimental volume ratios using Eq. (7) to obtain B in Eq. (6) is given in column 10 (Table II) and is not much different in comparison to those (column 9, Table II) obtained using optimized coefficients in Eq. (6). The temperature dependence of B in its reduced form was shown to extrapolate volume ratios for TMP [6] and 2,2,2-trifluoroethanol [14] to temperatures well outside the range of measurement. However, experience with the Tait equation of state, Eq. (7) has shown that it can be used to obtain volume ratios up to 15 K above the maximum experimental temperature.

3.3. Compressibilities

Isothermal compressibilities, κ_T , given in Table IV, were calculated from the coefficients given in Table II for Eq. (5) by using the relationship [15]

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

The compressibilities which have a probable uncertainty of $\pm 1-2\%$ are given in Table IV. The compressibilities at each mole fraction are constant for the same temperature within the estimated uncertainty for pressures above 100 MPa.

Compressibilities were also calculated using the relationship [15]

$$\kappa_T = \frac{1}{2.3026 k} \frac{C}{(B + p)} \quad (9)$$

where B is calculated using Eq. (7) with the coefficients from Table III. Values of the calculated compressibilities from Eq. (9) have a maximum deviation from the corresponding compressibilities in Table IV of less than 2% for pressures up to 200 MPa; for pressure above 200 MPa and up to 350 MPa the maximum deviation is up to 5%.

Table III. Coefficients for Tait Equation of State, Eq. (7), for the Mixture TMP (1) + *n*-Heptane (2)

x_2	C	B_0	B_1	$B_2 \times 10^3$	rmsd
0.1869	0.207	322.984	-1.24665	1.2455	0.06
0.4960	0.210	362.985	-1.47615	1.5890	0.01
0.7420	0.210	394.861	-1.67530	1.8964	0.01

Table IV. Isothermal Compressibilities for the Mixture TMP + *n*-Heptane

x_2	T (K)	κ (10^{-4} MPa $^{-1}$) at p (MPa) of									
		0.1	20	50	100	150	200	250	300	350	375
0.1869	298.15	14.31	11.28	8.48	6.01	4.73	3.96	3.43	3.02	2.66	2.49
	313.15	16.00	12.40	9.14	6.35	4.94	4.10	3.54	3.12	2.75	2.58
	323.15	17.98	13.37	9.52	6.50	5.08	4.25	3.67	3.19	2.72	2.49
	338.15	20.50	14.80	10.25	6.84	5.28	4.40	3.79	3.28	2.80	2.55
0.4960	298.15	14.14	11.19	8.44	6.01	4.75	3.98	3.45	3.02	2.65	
	313.15	15.84	12.32	9.11	6.35	4.95	4.13	3.57	3.14	2.78	2.60
	323.15	17.37	13.21	9.58	6.57	5.09	4.23	3.65	3.19	2.79	2.60
	338.15	19.53	14.55	10.32	6.93	5.31	4.38	3.77	3.30	2.89	2.69
0.7420	298.15	14.33	11.20	8.38	5.97	4.75	4.02	3.50	3.07	2.66	2.46
	313.15	16.21	12.39	9.06	6.32	4.97	4.18	3.63	3.17	2.74	2.52
	323.15	17.59	13.23	9.52	6.55	5.13	4.30	3.72	3.24	2.79	2.56
	338.15	20.23	14.68	10.23	6.86	5.32	4.44	3.84	3.33	2.84	2.59

3.4. Excess Volumes

Excess volumes were calculated for 20, 50, 100, 150, 200, and 250 MPa at 298.15 K using the present results with data for the pure substances [5, 6] and are given in Table V. Because the p - V - T data for TMP do not extend past 280 MPa, the excess volumes were not calculated above 250 MPa, although this could be done, if necessary, by using the Tait equation to extrapolate the data [6]. The excess volumes are small and negative; they increase with increase in pressure. A comparison with excess

Table V. Excess Molar Volume V^E at 298.15 and 323.15 K for $\{(1-x_2)i-C_8H_{18}+x_2C_7H_{16}\}$

x_2	T (K)	V^E (cm 3 ·mol $^{-1}$) at p (MPa) of						
		0.10	20	50	100	150	200	250
0.1869	298.15	-0.009	0.102	0.194	0.274	0.322	0.356	0.378
	313.15	-0.010	0.134	0.239	0.298	0.314	0.323	0.338
0.4960	298.15	-0.027	0.071	0.132	0.176	0.204	0.230	0.254
	313.15	-0.034	0.099	0.165	0.186	0.190	0.202	0.220
0.7618	298.15	-0.017	-0.019	0.009	0.058	0.090	0.105	0.109
0.7420	313.15	-0.023	-0.005	0.016	0.042	0.051	0.051	0.050

volumes for the system octane + 2,2,4-trimethylpentane [16] to examine the effect of increased length of the *n*-alkane chain is not possible because the values of the secant bulk modulus reported for that system are not of sufficient accuracy.

4. CONCLUSION

The volumetric behavior of *n*-heptane and TMP mixtures approximate that of an ideal mixture at atmospheric pressure, and even without the excess volumes the densities of the mixture can be predicted within $\pm 0.03 \text{ kg} \cdot \text{m}^{-3}$. The volume ratios for the present work can be represented at each mole fraction by using a fixed value of *C* and temperature-dependent *B* in the Tait equation. The equation can also be used to obtain volume ratios at the intermediate temperature or to extrapolate them by 15 K.

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