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Freezing Pressures, *p*, *V*, *T*, and Self-Diffusion Data at 298 and 313 K and Pressures up to 300 MPa for 1,3,5-Trimethylbenzene

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Measurements are reported for the melting point of 1,3,5-trimethylbenzene at pressures up to 345 MPa. Self-diffusion coefficients and *p*, *V*, *T* data have been obtained at 298 and 313 K for pressures up to 280 MPa. Isothermal compressibilities have been calculated from the *p*, *V*, *T* results. The freezing pressures at 0.1 MPa correspond to previously reported values for modification III of trimethylbenzene. Equivalent hard-sphere diameters estimated from the melting point and *p*, *V*, *T* data are used to apply the rough hard-spheres theory to the self-diffusion data; the calculations indicate that there is random packing of the particles.

KEY WORDS: freezing pressure; high pressure; isothermal compressibility; *p*, *V*, *T* data; self-diffusion; 1,3,5-trimethylbenzene.

1. INTRODUCTION

The measurement and interpretation of tracer and self-diffusion coefficients for liquids have been the subject of a number of communications from this laboratory. The application of hard-spheres theory for liquid-state transport properties to experimentally determined transport (particularly diffusion) data has been of considerable interest both in this laboratory and elsewhere.

As has been noted in recent papers [1, 2], the rough hard-spheres (RHS) theory due to Chandler [3], in conjunction with molecular dynamics (MD) simulation results, provides a very useful theoretical basis

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for interpretation of the density dependence of diffusion coefficients. Our recent applications of the RHS theory have differed in one important respect from Chandler's original treatment, in that we have chosen to remove some arbitrariness from the selection of numerical values for equivalent hard-spheres diameters, σ, by estimating σ for pure liquid from experimental data which have been determined independently of diffusion data. This has been done by calculating σ from liquid densities at the freezing pressure, at the temperatures of interest. This approach has been used for methane, carbon tetrachloride, benzene, octamethylcyclotetrasiloxane, and water in particular: for several other liquids the required freezing pressure and/or p, V, T data are not available at the temperatures at which diffusion coefficients have been measured.

The present study is an extension of our previous work to a liquid (1,3,5-trimethylbenzene) with roughly spherical molecules and easily attainable freezing pressures in the temperature range for which we are able to determine conveniently p, V, T data and self-diffusion coefficients as a function of pressure.

2. EXPERIMENTAL

The 1,3,5-trimethylbenzene (mesitylene) was Fluka "puriss"-grade material which was dried with molecular sieve prior to fractional distillation under reduced pressure.

The melting point was measured for 16 pressures at approximately 20-MPa steps in the range 0.1 to about 345 MPa, using the differential thermal analysis (DTA) technique which has been described previously [4]. Melting points were determined with an accuracy of ±0.2 K using a calibrated copper–constantan thermocouple, and pressures were determined to ±0.1 MPa using a 400-MPa Heise bourdon tube gauge which had been calibrated against a deadweight tester.

Volume ratios, k, defined by

$$k = V_p / V_o \tag{1}$$

where V_p and V_o are volumes at 0.1 MPa and pressure p, respectively, were determined at pressures from about 2.5 to about 280 MPa using the bellows volumometer whose construction, calibration, and operation have been previously described [5, 6]. Temperatures were controlled to within ±0.005 K and measured to ±0.01 K using a calibrated platinum resistance thermometer. Above 25 MPa pressures were measured with an uncertainty of ±0.1 MPa with a calibrated 400-MPa Heise gauge. In the 0- to 25-MPa region a calibrated 25-MPa gauge was used, with an accuracy of

±0.01 MPa. The overall uncertainty of the volume-ratio determinations corresponds to about ±0.04% in density at pressures above 50 MPa, increasing to about ±0.1% at pressures close to 0.1 MPa. Experimentally determined volume ratios were expressed as the secant bulk modulus, K, defined by

$$K = p/(1-k) \tag{2}$$

and fitted to cubic equations of the form

$$K = \sum_{i=0}^{3} A_i p^i \tag{3}$$

Densities at 0.1 MPa were obtained from the literature at 293 and 298 K and by pycnometry with an uncertainty of ±0.002% at 288 K and digital densimetry (using an Anton Paar densimeter) with an uncertainty of ±0.005% at 313 K.

Self-diffusion coefficients, D, were determined using the nmr spin-echo technique as described previously [7], except that an all-PTFE sample cell [8] was utilized in place of the metal bellows cell. Temperatures were measured to ±0.02 K and pressures to ±0.4 MPa, and the overall accuracy of the diffusion measurements should be within ±2%.

3. RESULTS

Experimental values for the density at 0.1 MPa are given in Table I, together with literature data. The combined data are represented by the equation

$$\rho = 0.998229\text{-}1 - 1.10884 \times 10^{-4} T - 1.17035 \times 10^{-6} T^2 \tag{4}$$

(ρ in $\mathrm{g \cdot cm^{-3}}$; T in K) with rms deviation of the experimental points from the calculated curve 2.4×10^{-5} (0.003%).

Table I. Densities at 0.1 MPa

T (K)	ρ ($\mathrm{g \cdot cm^{-3}}$)	Ref.[a]
288.15	0.86909	a
293.15	0.86518	b
298.15	0.86111	b
313.15	0.84874	a

[a] (a) Ref. 9; (b) this work.

The measured melting points are represented by the equation

$$T = 221.1088 + 0.2689p - 6.6962 \times 10^{-5}p^2 \qquad (0.1 \leqslant p < 345) \qquad (5)$$

(T in K; p in MPa) with rms deviation 0.19. Interpolation of Eq. (5) at several pressures yields for the temperature dependence of the freezing pressure the relationship

$$p = -776.0806 + 3.7929T - 3.5247 \times 10^{-3}T^2 + 1.0153 \times 10^{-5}T^3 \qquad (220 < T < 310) \qquad (6)$$

The experimentally determined liquid ↔ solid equilibrium curve is shown in Fig. 1.

The coefficients of Eq. (3) are listed in Table II. Isothermal compressibilities, κ, were calculated from these coefficients at each temperature, using the relationships

$$\kappa = (1/V)(\partial V/\partial p)_T = -[1/(p-K)][1-(p/K)(\partial K/\partial p)_T] \qquad (7)$$

The values of κ, with a probable uncertainty of $\pm 1\%$ at pressures above 50 MPa, increasing to $\pm 2\%$ at 0.1 MPa, are given in Table III.

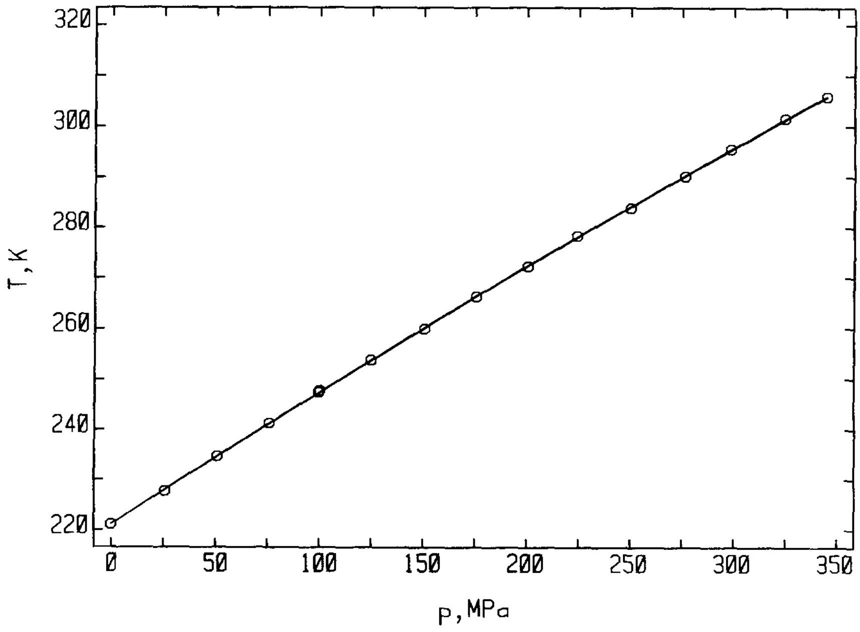

Fig. 1. Melting point of 1, 3, 5-trimethylbenzene as a function of pressure.

Table II. Coefficients of Eq. (3) for Secant Bulk Modulus

T (K)	A_0 (MPa)	A_1	$10^3 A_2$ (MPa^{-1})	$10^6 A_3$ (MPa^{-2})	100 ($\delta K/K$)[a]
298.15	1227.298	5.468723	−5.602960	6.460002	0.052
313.15	1113.099	5.368432	−5.072776	6.081064	0.034

[a] K in this heading defined by Eq. (2); $\delta K = K$[Eq. (3)] − K(measured).

Table III. Isothermal Compressibilities

p (MPa)	$10^4 \kappa$ (MPa^{-1})	
	298.15 K	313.15 K
0.1	8.1_4	8.9_8
20	7.0_1	7.6_4
50	5.8_0	6.2_2
100	4.5_3	4.7_7
150	3.76	3.88
200	3.22	3.27
250	2.80	2.80
275	2.61	2.59

Table IV. Self-Diffusion Coefficients

298.15 ± 0.02 K		313.15 ± 0.02 K	
p (MPa)	$10^9 D$ (m^2·s^{-1})	p (MPa)	$10^9 D$ (m^2·s^{-1})
0.1	1.61	0.1	1.97
22.0	1.35	24.6	1.67
51.5	1.09	49.9	1.39
102.6	0.77	100.5	1.04
149.3	0.59	150.8	0.76
199.0	0.43_4	200.4	0.58
241.3	0.33_8	280.7	0.37_4
281.2	0.26_3		

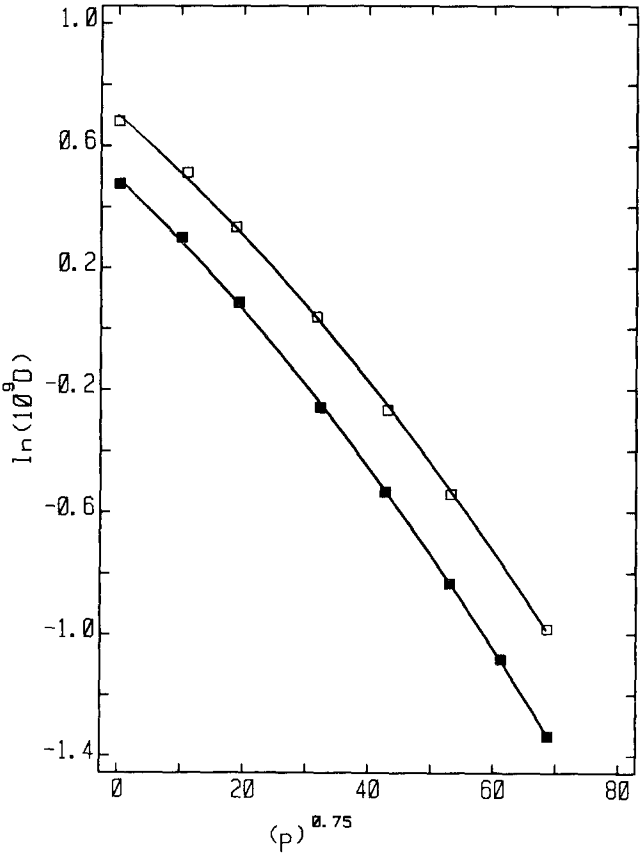

Fig. 2. Pressure dependence of the self-diffusion coefficient at (■) 298.15 K and (□) 313.15 K, where D is in $m^2 \cdot s^{-1}$ and p is in MPa.

Self-diffusion coefficients are given in Table IV and shown in Fig. 2 in the form of graphs of $\ln(D)$ against $p^{0.75}$. The pressure and temperature dependence of D is represented to within the probable experimental uncertainty by an equation of the form

$$\ln D = B_0 + \sum_{i=1}^{2} B_{1i}(1000/T)^i + \sum_{i=1}^{3} B_{2i}(p^{0.75})^i + B_3(1000/T)(p^{0.75}) \quad (8)$$

(for D in $10^9\ m^2 \cdot s^{-1}$). The coefficients of Eq. (8) are given in Table V.

Table V. Coefficients of Eq. (8) for Self-Diffusion Coefficient

$B_0 = 160.0174$	$B_{11} = -96.21957$	$B_{21} = 2.24371 \times 10^{-2}$	$B_3 = -1.18040 \times 10^{-2}$
	$B_{12} = 14.5000$	$B_{22} = -1.97789 \times 10^{-4}$	
		$B_{23} = 9.38495 \times 10^{-7}$	
σ[a] $= 8.29 \times 10^{-3}$			

[a] The rms deviation corresponds to a mean difference of 0.70% between the experimental values of D and those calculated from Eq. (6). The maximum difference is 1.5%.

4. DISCUSSION

The observed melting point at 0.1 MPa, *viz.*, 221.1$_4$ K, is in good agreement with the freezing point (221.34 K) reported by Hirschler and Faulconer [10] for modification III of 1,3,5-trimethylbenzene, even though modification III is evidently not usually the stable crystal form. The melting-point determinations were done by freezing the sample under elevated pressure, extensive supercooling invariably being observed, then reducing the pressure before subsequent heating of the solid. It appears that under these conditions (and possibly also as a result of specific impurities being present in the liquid), modification III of the solid was always produced. No indication of solid ↔ solid transitions was detected in any of the DTA traces.

For a smooth hard-sphere fluid, the reduced density, ρ^*, at the freezing point is given by

$$\rho^* = n\sigma^3 = 0.943 \tag{9}$$

where n is the number density and σ the molecular diameter. For 1,3,5-trimethylbenzene at 298.15 K, the freezing pressure from Eq. (6) is 310.5$_7$ MPa, and at this pressure the density [from Eqs. (3) and (8)] is $0.9800\ \mathrm{g \cdot cm^{-3}}$ so that the molar volume, V_m, is $122.64_9\ \mathrm{cm^3 \cdot mol^{-1}}$. Equation (9) can be written

$$\sigma = 0.11611 (V_\mathrm{m})^{\frac{1}{3}} \tag{10}$$

(σ in nm; V_m in $\mathrm{cm^3 \cdot mol^{-1}}$), from which the value $\sigma = 0.576_9$ nm is obtained for 1,3,5-trimethylbenzene at the freezing pressure at 298.15 K. A value for σ at 313.15 K cannot be reliably estimated via extrapolation of Eq. (8) to the freezing pressure [377.$_8$ MPa from extrapolation of Eq. (6)] at this temperature. A more reliable estimate can be obtained by assuming that the temperature dependence of σ is approximately the same as has been found for other liquids. On the basis of the temperature dependence of

σ for benzene and carbon tetrachloride [11] (in each case from freezing pressure and p, V, T data), we assume that for 1,3,5-trimethylbenzene σ is 0.3% smaller at 313.15 K than at 298.15 K and the value $\sigma = 0.575$ nm is thus assigned at 313.15 K. It should be noted that since the temperature dependence of σ is in any event small, the estimated value at 313.15 K is unlikely to be significantly in error.

The application of hard-spheres theory to self-diffusion provides the relationship

$$D = A_D D_{\mathrm{SHS}} \tag{11}$$

where D is the experimental diffusion coefficient, A_D $(0 < A_D \leqslant 1)$ is a factor which accounts for coupling of rotational and translational motion, and

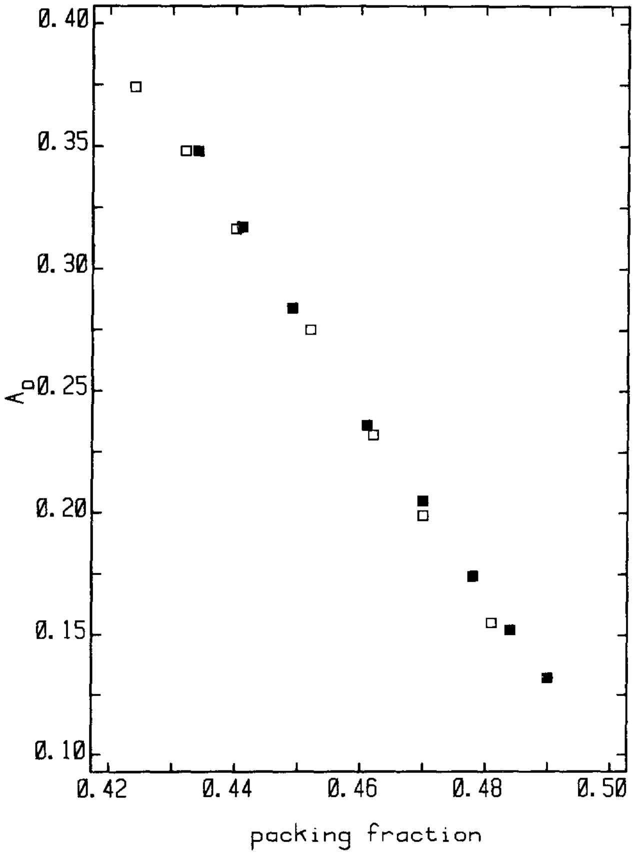

Fig. 3. The rotational-translation coupling factor for self-diffusion at (■) 298.15 K and (□) 313.15 K.

D_{SHS} is the Enskog dense-fluid diffusion coefficient corrected by the inclusion of MD simulation results, so that

$$D_{\mathrm{SHS}} = C_D D_E = C_D (nD)_{\mathrm{o}}/g(\sigma)\, n = C(nD)_{\mathrm{o}}/n \tag{12}$$

where $g(\sigma)$ is the radial distribution function at contact, C_D is a factor derived from the MD simulations, and $(nD)_{\mathrm{o}}$ is given by

$$(nD)_{\mathrm{o}} = (3/8)(RT/\pi M)^{\frac{1}{2}}/\sigma^2 \tag{13}$$

(where M is molar mass). Recent simulation data [12] are represented by

$$\begin{aligned} C = C_D/g(\sigma) = {} & -9.90916 + 15.3290(V/V_{\mathrm{o}}) - 7.87485(V/V_{\mathrm{o}})^2 \\ & + 1.78403(V/V_{\mathrm{o}})^3 - 0.15015(V/V_{\mathrm{o}})^4 \end{aligned} \tag{14}$$

with $V_{\mathrm{o}} = L\sigma^3/2^{\frac{1}{2}}$, where L is Avogadro's constant. Assuming that σ is density independent at constant temperature, the application of Eqs. (11) to (14) to the self-diffusion data for 1,3,5-trimethylbenzene at 298.15 K and 313.15 K yields the two sets of A_D values shown in Fig. 3 as a function of the packing fraction defined by $Z = \pi\rho^*/6$. The significant result is that A_D is density dependent but for a given packing fraction independent of temperature. This behavior was found previously for carbon tetrachloride [11] and is in marked contrast to that exhibited by benzene [11], for which A_D is both density and temperature dependent. The implication is that the molecular packing in 1,3,5-trimethylbenzene is random, whereas in benzene the molecules pack in preferred configurations [13].

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