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p, V, T and Derived Thermodynamic Data for Toluene, Trichloromethane, Dichloromethane, Acetonitrile, Aniline, and *n*-Dodecane

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Experimentally determined p,V,T data are reported for toluene, trichloromethane, dichloromethane, acetonitrile, aniline, and *n*-dodecane at 278, 288, 298, 313, and 323 K, except for dichloromethane, for which the highest temperature was 298 K. At each temperature, measurements were done at pressures up to about 280 MPa or (for aniline and *n*-dodecane) at a lower pressure slightly below the freezing pressure at the temperature of measurement. Values of the isobaric expansivity isothermal compressibility and (for toluene, trichloromethane, dichloromethane, and acetonitrile) internal pressure, derived from the p,V,T data, are presented.

KEY WORDS: acetonitrile; aniline; dichloromethane; high pressure; *n*-dodecane; p,V,T data; toluene; trichloromethane.

1. INTRODUCTION

During the past several years a bellows volumometer technique for determining volume ratios (i.e., volumes at elevated pressure relative to the volume at normal atmospheric pressure) has been developed in this laboratory [1]. The purpose of that development was to determine volume ratios with sufficient accuracy (of the order of $\pm 0.1\%$) to provide ancillary data for the measurement and interpretation of tracer and self-diffusion coefficients of liquids under pressure. However, the accuracy of the volumometer exceeds the original expectation and the instrument yields p,V,T data which can be used to derive reliable values of isothermal com-

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pressibility, isobaric expansivity, and internal pressure. The accuracy of p,V,T data obtained with the volumometer for water + acetonitrile mixtures at 298 K was demonstrated in an earlier paper [2] by a stringent test, viz., comparison of indirectly determined excess volumes with directly measured values [3]. The agreeement was within the probable uncertainty of the directly measured data. In subsequent work the temperature and pressure ranges of the volumometer were increased, and the water + methanol system has been studied at temperatures from 278 to 323 K and pressures up to about 280 MPa [4, 5].

The objectives of the present investigation were to extend the temperature and/or pressure ranges at which p,V,T data are currently available for a number of pure liquids, all of which are relevant to our experimental program on diffusion in liquids under pressure. In this report we present volume-ratio data for six liquids, viz., toluene, trichloromethane, dichloromethane, acetonitrile, aniline, and *n*-dodecane, and derived values of compressibility, expansivity, and (except for aniline and *n*-dodecane) internal pressure for these liquids.

There are features of these derived quantities which are particularly interesting and justify the present grouping of these otherwise diverse substances.

2. EXPERIMENTAL

2.1. Measurements

Materials used were AnalaR or equivalent grade, used without further purification except for storage over molecular sieve, to remove water and other low molecular weight impurities, for several weeks before use. The trichloromethane, as received, contained 1–2% by volume ethanol (added as stabilizer), which was not removed.

Volume ratios, k, defined by

$$k = V_p/V_0 \tag{1}$$

where V_0 and V_p are volumes at 0.1 MPa and pressure p, respectively, were determined using the bellows volumometer, whose construction, calibration, and use have been described previously [1, 4]. The measurements were done at 278.15, 288.15, 298.15, 313.15, and 323.15 K (the temperatures at which the volumometer had been calibrated), except for dichloromethane, for which, owing to the low boiling point (approximately 313 K) at 0.1 MPa, the highest temperature was 298.15 K. The pressure range for the measurements was from about 2.5 MPa to either about 280 MPa or (for aniline and *n*-dodecane) a lower pressure slightly below the freezing pressure at the temperature of measurement.

Temperatures were controlled to within ±0.005 K and the uncertainty of temperature measurement (with a calibrated platinum resistance thermometer) was ±0.01 K. Pressures were measured with two Heise bourdon-tube gauges. Above 25 MPa pressures were measured with a maximum uncertainty of ±0.4 MPa with a 400-MPa gauge: in the region of 0–25 MPa a 25-MPa gauge was used, with an accuracy of ±0.025 MPa. The overall accuracy of the volume ratio determinations corresponds to about ±0.05% in density except (as for aniline and *n*-dodecane at 278 K) where the experimental pressure range at a given temperature does not exceed about 50 MPa. In such cases the uncertainty is likely to be greater than 0.05% in density.

2.2. Treatment of Experimental Data

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

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

We have found in the present and in previous work that Eq. (3) is a very good representation of the pressure dependence of experimental volume ratios at constant temperature. It should not, however, be extrapolated to pressures which substantially exceed the highest experimental pressure. The form of the Tait equation which has been extensively utilized by other workers, viz.,

$$K = p/C \ln[(B+p)/(B+p_0)] \tag{4}$$

where p_0 is normal atmospheric pressure, gives an inferior fit of volume-ratio data but, unlike Eq. (3), can be reliably extrapolated to pressures beyond the experimental pressure range.

Isothermal compressibilities, κ, were calculated from the coefficients of Eq. (3) at each temperature by using the relationships

$$\begin{aligned} \kappa &= -(1/V)(\partial V/\partial p)_T = -(1/k)(\partial k/\partial p)_T \\ \kappa &= -[1/(p-K)][1-(p/K)(\partial K/\partial p)_T] \end{aligned} \tag{5}$$

The probable uncertainty in κ is believed to be ± 1–2% for pressures higher than 50 MPa, provided that the experimental pressure range for volume-ratio measurement is at least 150 MPa.

The densities of the liquids at 0.1 MPa were taken from Timmermans [6] and from Gibson and Loeffler [7] for aniline at temperatures above 298 K. Isobaric expansivities, α, were calculated from densities at 0.1 MPa and volume ratios from Eq. (3) by evaluating the molar volume (V_m) as a function of temperature at 25, 50, 100, 150, 200, 250, and 275 MPa, fitting V_m to a quadratic in T (or to a linear equation in T where volume ratios at a given pressure were measured at fewer than three temperatures), then utilizing the relationship

$$\alpha = (1/V_\mathrm{m})(\partial V_\mathrm{m}/\partial T)_p \tag{6}$$

The probable uncertainty in α is estimated to be ± 2–3% for pressures higher than 50 MPa and where the experimental pressure range at a given temperature was at least 150 MPa.

Internal pressures, π, were calculated for toluene, trichloromethane, dichloromethane, and acetonitrile from the equation

$$\pi = T(\partial p/\partial T)_v - p \tag{7}$$

For each liquid, at each temperature the values of p corresponding to selected values of V_m were determined by interpolation of cubic spline fits of 10 values of p against V_m. The thermal pressure coefficients $(\partial p/\partial T)_v$ and hence π were evaluated from quadratic fits of these values of p against T. The probable uncertainty in π is of the order of $\pm 3\%$. For aniline and n-dodecane, since the experimental pressure range was considerably smaller at low temperatures than at high temperatures, π was not calculated.

3. RESULTS

The coefficients of Eq. (3) are listed in Table I, expansivities and compressibilities in Table II, and internal pressures in Table III. It should be noted that the entries in Table II for aniline and n-dodecane at temperatures of less than 298 K are approximate values, owing to the restricted accessible pressure range for these liquids at low temperatures. Internal pressures for aniline and n-dodecane are not tabulated. Values can be obtained via the thermal pressure coefficient by using Eq. (7) and the relationship

$$(\partial p/\partial T)_v = \alpha/\kappa \tag{8}$$

Table I. Coefficients of Eq. (3)[a]

Liquid		T (K)	A_0 (MPa)	A_1	$-A_2$ (GPa^{-1})	A_3 (GPa^{-2})	$10^2 \langle \delta K/K \rangle$
Toluene		278.15	1240.79	5.6750	7.2690	9.7534	0.07
		288.15	1167.21	5.3025	6.1898	8.0613	0.05
		298.15	1084.32	5.3667	6.6888	8.4588	0.05
		313.15	996.541	4.9102	4.3686	5.7504	0.08
		323.15	908.426	5.1330	4.8945	4.1892	0.07
Trichloromethane		278.15	1100.78	5.7640	9.3894	15.368	0.11
		288.15	1025.31	5.6766	9.1515	14.093	0.08
		298.15	975.825	5.0293	5.2667	6.1509	0.04
		313.15	858.196	5.0693	6.3688	10.231	0.08
		323.15	796.042	4.8800	4.5710	4.2987	0.08
Dichloromethane		278.15	1151.01	4.9519	3.5910	2.8158	0.10
		288.15	1058.52	5.0910	5.8763	7.7719	0.03
		298.15	981.106	4.9424	5.3929	6.6088	0.05
Acetonitrile		278.15	1077.05	4.1102	2.5157	5.6879	0.39
		288.15	940.535	4.8242	6.2657	8.6833	0.24
		298.15	902.385	4.3936	4.2773	5.1005	0.22
		313.15	794.229	4.4943	5.6775	10.045	0.44
		323.15	731.013	4.4217	4.4485	4.8915	0.79
	$p_{\max}$ (MPa)						
Aniline	53	278.15	2157.96	24.0247	56.083	—[b]	0.53
	102	288.15	2263.93	4.4906	−4.4516	−19.555	0.04
	153	298.15	2082.22	7.1766	2.9439	99.271	0.19
	240	313.15	1952.16	5.5601	5.9044	8.0600	0.10
	280	323.15	1935.48	3.8393	−5.7267	−16.658	0.06
Dodecane	59	278.15	1075.70	10.4642	153.06	—[c]	0.50
	103	288.15	999.236	8.1367	48.201	222.06	0.16
	155	298.15	1036.10	4.3470	−5.7354	−36.924	0.29
	240	313.15	903.703	5.6083	8.6670	14.482	0.06
	281	323.15	863.013	5.1483	4.5397	3.3011	0.10

[a] Maximum pressure approximately 280 MPa except where specified.

[b] $A_3 = 5164.9$ GPa^{-2}.

[c] $A_3 = 1329.3$ GPa^{-2}.

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

		p (MPa)							
T (K)	Property	0.1	25	50	100	150	200	250	275
(a) Toluene									
278.15	$10^4\alpha$	10.5	9.47	8.54	7.03	5.89	5.08	4.55	4.38
	$10^4\kappa$	8.05	6.68	5.74	4.63	4.09	3.90	3.93	4.02
288.15	$10^4\alpha$	10.7	9.48	8.54	7.12	6.14	5.44	4.95	4.77
	$10^4\kappa$	8.56	7.11	6.11	4.89	4.28	4.01	3.98	4.03
298.15	$10^4\alpha$	10.8	9.50	8.53	7.22	6.38	5.81	5.37	5.17
	$10^4\kappa$	9.21	7.54	6.41	5.09	4.47	4.23	4.26	4.35
313.15	$10^4\alpha$	11.0	9.52	8.52	7.36	6.76	6.39	6.02	5.79
	$10^4\kappa$	10.0	8.20	6.93	5.36	4.51	4.05	3.82	3.78
323.15	$10^4\alpha$	11.2	9.53	8.81	7.45	7.02	6.77	6.44	6.20
	$10^4\kappa$	11.0	8.74	7.24	5.48	4.58	4.12	3.94	3.92
(b) Trichloromethane									
278.15	$10^4\alpha$	12.3	11.2	10.2	8.66	7.67	7.00	6.48	6.22
	$10^4\kappa$	9.08	7.36	6.26	5.09	4.66	4.68	5.06	5.39
288.15	$10^4\alpha$	12.4	11.0	9.98	8.47	7.52	6.88	6.37	6.11
	$10^4\kappa$	9.74	7.81	6.59	5.31	4.84	4.86	5.26	5.60
298.15	$10^4\alpha$	12.5	10.9	9.79	8.27	7.36	6.76	6.27	6.01
	$10^4\kappa$	10.2	8.31	7.00	5.44	4.64	4.26	4.14	4.16
313.15	$10^4\alpha$	12.6	10.8	9.49	7.96	7.12	6.58	6.11	5.86
	$10^4\kappa$	11.6	9.19	7.63	5.90	5.12	4.85	4.92	5.06
323.15	$10^4\alpha$	12.7	10.6	9.29	7.74	6.95	6.45	5.99	5.73
	$10^4\kappa$	12.5	9.81	8.02	5.97	4.95	4.43	4.22	4.20
(c) Dichloromethane									
278.15	$10^4\alpha$	13.3	11.8	10.7	9.15	7.66	6.33	5.47	5.34
	$10^4\kappa$	8.68	7.26	6.23	4.88	4.09	3.60	3.32	3.23
288.15	$10^4\alpha$	13.5	11.9	10.8	9.18	7.95	6.94	6.16	5.88
	$10^4\kappa$	9.44	7.76	6.62	5.26	4.58	4.28	4.24	4.29
298.15	$10^4\alpha$	13.7	12.1	10.8	9.21	8.24	7.57	6.87	6.43
	$10^4\kappa$	10.2	8.31	7.03	5.51	4.74	4.39	4.30	4.34
(d) Acetonitrile									
278.15	$10^4\alpha$	13.2	11.4	10.2	8.61	7.25	5.84	4.38	3.67
	$10^4\kappa$	9.28	7.94	6.92	5.53	4.66	4.10	3.73	3.61
288.15	$10^4\alpha$	13.5	11.7	10.49	8.83	7.60	6.45	5.32	4.77
	$10^4\kappa$	10.6	8.65	7.35	5.85	5.17	4.95	5.04	5.19
298.15	$10^4\alpha$	13.8	12.0	10.7	9.06	7.98	7.09	6.28	5.90
	$10^4\kappa$	11.1	9.11	7.74	6.07	5.18	4.73	4.55	4.54
313.15	$10^4\alpha$	14.3	12.4	11.0	9.42	8.54	8.06	7.77	7.66
	$10^4\kappa$	12.6	10.1	8.43	6.60	5.78	5.50	5.60	5.76
323.15	$10^4\alpha$	14.6	12.7	11.3	9.66	8.93	8.71	8.76	8.81
	$10^4\kappa$	13.7	10.7	8.85	6.68	5.61	5.11	4.95	4.96

Table II. *(Continued)*

		p (MPa)							
T (K)	Property	0.1	25	50	100	150	200	250	275
				(e) Aniline					
278.15	$10^4\alpha$	(8.3)	(7.7)	(7.4)					
	$10^4\kappa$	(4.6)	(3.8)	(3.4)					
288.15	$10^4\alpha$	(8.4)	(7.9)	(7.5)	(6.8)				
	$10^4\kappa$	(4.4)	(4.0)	(3.7)	(3.1)				
298.15	$10^4\alpha$	8.53	7.99	7.56	6.75	6.52			
	$10^4\kappa$	4.80	4.21	3.84	3.34	2.73			
313.15	$10^4\alpha$	8.66	8.19	7.68	7.00	6.49	6.23	5.59	
	$10^4\kappa$	5.12	4.54	4.09	3.44	2.99	2.64	2.34	
323.15	$10^4\alpha$	8.75	8.32	7.76	7.16	6.46	6.19	5.56	
	$10^4\kappa$	5.16	4.72	4.31	3.58	3.05	2.71	2.56	
				(f) Dodecane					
278.15	$10^4\alpha$	(9.6)	(8.6)	(7.9)					
	$10^4\kappa$	(9.3)	(7.2)	(6.1)					
288.15	$10^4\alpha$	(9.6)	(8.5)	(7.8)	(6.6)				
	$10^4\kappa$	(10)	(7.6)	(6.4)	(4.6)				
298.15	$10^4\alpha$	9.68	8.47	7.66	6.56	5.76			
	$10^4\kappa$	9.64	8.02	6.73	5.07	4.43			
313.15	$10^4\alpha$	9.76	8.41	7.49	6.39	6.04	5.68	4.35	
	$10^4\kappa$	11.0	8.63	7.10	5.34	4.32	3.56	2.87	
323.15	$10^4\alpha$	9.81	8.38	7.37	6.28	6.22	5.64	4.35	
	$10^4\kappa$	11.6	9.08	7.43	5.46	4.38	3.71	3.26	

but values of π calculated in that fashion are more uncertain than the values listed for toluene, trichloromethane, dichloromethane, and acetonitrile.

3.1. Comparisons with Literature Data

3.1.1. Toluene

The density of toluene at four temperatures (223, 248, 273, and 298 K) and pressures up to about 200 MPa has been determined by Mopsik [8] and expressed in terms of a Tait-type equation at each temperature. Volume ratios evaluated from the parameters given by Mopsik at several pressures at 298.15 K are compared with those obtained in the present work in Table IV, which includes a comparison of values, interpolated at

Table III. Internal Pressures (π, in MPa)

	$T(K)$				
V_m ($cm^3 \cdot mol^{-1}$)	278.15	288.15	298.15	313.15	323.15
(a) Toluene					
95.01	253	277	298	327	355
95.97	265	286	307	336	361
96.92	283	300	316	340	359
97.88	303	314	324	340	352
98.84	322	327	332	340	345
99.80	338	338	338	338	339
100.76	350	347	343	337	333
101.72	360	353	347	337	330
102.68	365	358	349	336	328
103.64	368	360	351	336	327
104.59	369	360	351	337	327
(b) Trichloromethane					
71.09	406	383	358	315	292
71.85	387	371	355	327	310
72.61	383	369	355	333	318
73.37	386	372	358	337	321
74.13	391	376	362	339	322
74.89	396	381	365	341	323
75.64	400	384	367	342	323
76.40	401	385	368	343	324
77.16	399	384	368	343	326
77.92	395	381	366	344	328
78.68	389	377	364	344	331
(c) Dichloromethane					
55.93	273	322	372		
56.62	313	347	383		
57.30	357	373	389		
57.99	394	393	393		
58.67	417	408	398		
59.36	429	416	404		
60.04	432	420	408		
60.72	431	421	411		
61.41	427	420	413		
62.09	424	418	412		
62.78	422	416	409		
(d) Acetonitrile					
46.39	286	312	336	373	403
46.89	303	323	342	371	394
47.40	317	333	347	371	387
47.90	329	341	352	370	383
48.40	338	348	355	370	379
48.91	346	353	358	369	376
49.41	353	358	361	368	372
49.92	360	363	363	366	368
50.42	367	367	365	364	363
50.93	375	371	367	361	357
51.43	383	377	369	358	350

278.15 and 288.15 K from Mopsik's parameters, with our data. The two sets of data are clearly in very good agreement at pressures up to at least 100 MPa; the only significant divergence is at pressures approaching the upper limit of Mopsik's experimental pressure range.

The compressibility of toluene at 0.1 MPa has been measured over a wide temperature range, and literature data [9–11] are compared with values from Eq. (5) in Fig. 1. The present data are in close agreement with the literature data, even though our values of κ for pressures below 50 MPa are less accurate than at higher pressures.

3.1.2. Trichloromethane and Dichloromethane

Volume ratios for these liquids at 298 K have been reported by Newitt and Weale [12] for pressures up to about 100 MPa and their values at selected pressures are compared with our data in Table IV. The two sets of values for both liquids agree to within about 0.1 %, which we believe to be the accuracy of the previous data.

Compressibilities for trichloromethane at 0.1 MPa are compared with literature data [12–14] in Fig. 2. The agreement is within the probable uncertainty in our values of κ at 0.1 MPa. Compressibilities for both trichloromethane and dichloromethane at 298 K and 100 MPa agree with values from Newitt and Weale [12] to within the expected uncertainty in κ.

It is interesting to note that Newitt and Weale reported identical values for the volume ratios (and hence κ) of trichloromethane and dichloromethane at 298 K. The very close similarity at low pressures has been confirmed in the present work, but at higher pressures (and particularly at low temperatures) those properties of these two liquids diverge significantly.

3.1.3. Acetonitrile

Relative densities (i.e., values of $1/k$) for acetonitrile at 283, 298, and 313 K and pressures up to 250 MPa have been reported by Srinivasan and Kay [15], and their data (expressed as volume ratios) are compared with values from the present work in Table IV. There are discrepancies of up to about 0.8 % between the two sets of data, and the magnitude of the discrepancies is not easily accounted for in view of the established reliability of the bellows volumometer used in the present work. We believe that there are practical problems associated with the piston-type volumometer which was used by Srinivasan and Kay and that, despite the calibration check

Table IV. Comparison of Volume Ratios with Literature Data

	T (K)							
p (MPa)	278.15		288.15		298.15		313.15	323.15
				(a) Toluene				
	a^{a}	Ref. 8	a	Ref. 8	a	Ref. 8		
25	0.9794	0.9793	0.9807	0.9806	0.9819	0.9818		
50	0.9626	0.9625	0.9647	0.9646	0.9668	0.9666		
100	0.9360	0.9360	0.9392	0.9392	0.9427	0.9423		
150	0.9151	0.9156	0.9189	0.9195	0.9235	0.9231		
200	0.8978	0.8989	0.9022	0.9030	0.9075	0.9071		
				(b) Trichloromethane				
					a	Ref. 12		
25					0.9772	0.9782		
50					0.9588	0.9602		
100					0.9302	0.9314		
				(c) Dichloromethane				
					a	Ref. 12		
5					0.9773	0.9782		
50					0.9589	0.9602		
100					0.9300	0.9314		

(d) Acetonitrile

	a	Ref. 15	a	Ref. 15
50	0.9550	0.9559	0.9503	0.9532
100	0.9233	0.9252	0.9165	0.9212
150	0.8988	0.9016	0.8909	0.8969
200	0.8788	0.8825	0.8707	0.8773
250	0.8621	0.8670	0.7546	0.8610

(e) Aniline[b]

	a	Ref.	a	Ref. 17	a	Ref. 17
25	0.9889	0.9890	0.9880	0.9882	0.9877	0.9875
50	0.9790	0.9792	0.9774	0.9776	0.9766	0.9765
100	0.9616	0.9621	0.9593	0.9595	0.9576	0.9577

(f) Dodecane[c]

	a	Ref. 19	a	Ref. 18	a	Ref. 19
25	0.9780	0.9779	0.9765	0.9761	0.9746	0.9746
50	0.9604	0.9603	0.9579	0.9577	0.9546	0.9549
100	0.9329	0.9335	0.9292	0.9304	0.9249	0.9257
150	0.9113	0.9128	0.9070	0.9099	0.9028	0.9039

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[a] (a) This work.

[b] The values from Ref. 17 were interpolated from data at other temperatures.

[c] The temperatures are 298.27, 310.95, and 323.35 K. The data from this work were interpolated using the parameters in Table I.

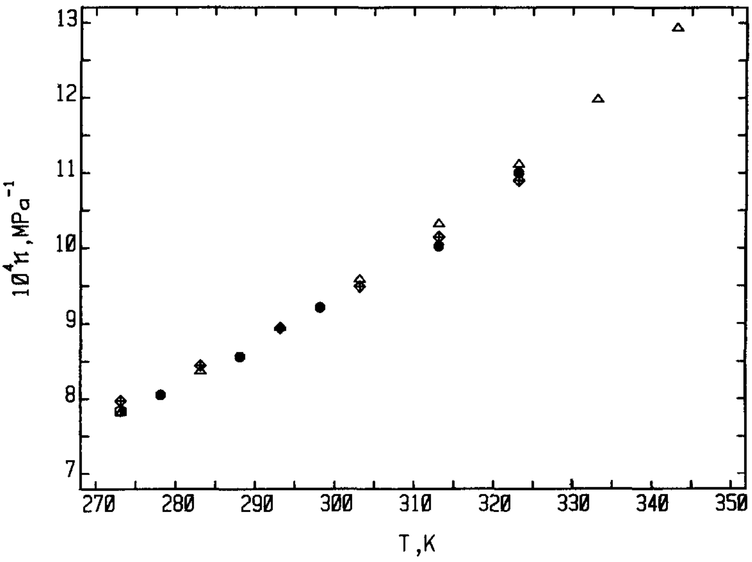

Fig. 1. Isothermal compressibility for toluene at 0.1 MPa. ●. This work; △, Ref. 9; ◈, Ref. 10; ◑, Ref. 11.

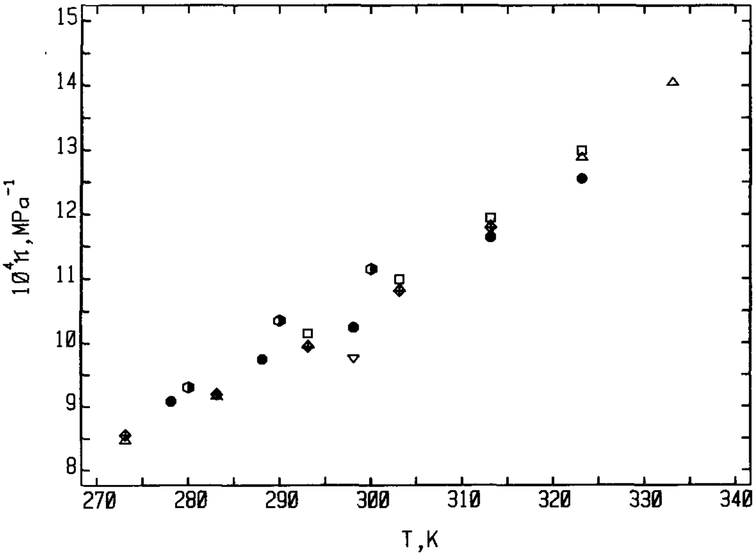

Fig. 2. Isothermal compressibility for trichloromethane at 0.1 MPa. ●, This work; △, Ref. 9; ◈, Ref. 10; ▽, Ref. 12; □, Ref. 13; ◑, Ref. 14.

which was made, using water, by these workers, their volume-ratio data for acetonitrile are significantly in error.

The compressibility of acetonitrile at 0.1 MPa has been directly measured by Grant-Taylor and MacDonald [16]: their values of κ at 298.15 and 318.15 K, 11.54×10^{-4} and 13.00×10^{-4} MPa^{-1}, respectively, are in good agreement with the values (11.07×10^{-4} and 13.18×10^{-4} MPa^{-1}, the latter value obtained by interpolation) from the present work.

3.1.4. Aniline

Volume ratios for aniline at temperatures from 298 to 358 K and pressures up to 100 MPa have been reported by Gibson and Loeffler [7, 17]. Data from those sources are compared with our data in Table IV. The agreement is good: only at 100 MPa and 298.15 K does the discrepancy exceed 0.02 %.

Compressibilities at 0.1 MPa are compared with literature data [5, 18] in Fig. 3. The agreement is satisfactory except possibly at 298 K, where the discrepancy is larger than we would have expected. Values of κ at 100 MPa are compared with values from Gibson and Loeffler in the inset in Fig. 3. The agreement is within the uncertainty in κ, except at 298 K. It appears that, for reasons which are not apparent, our values of κ at 298 K may be 2–3 % high.

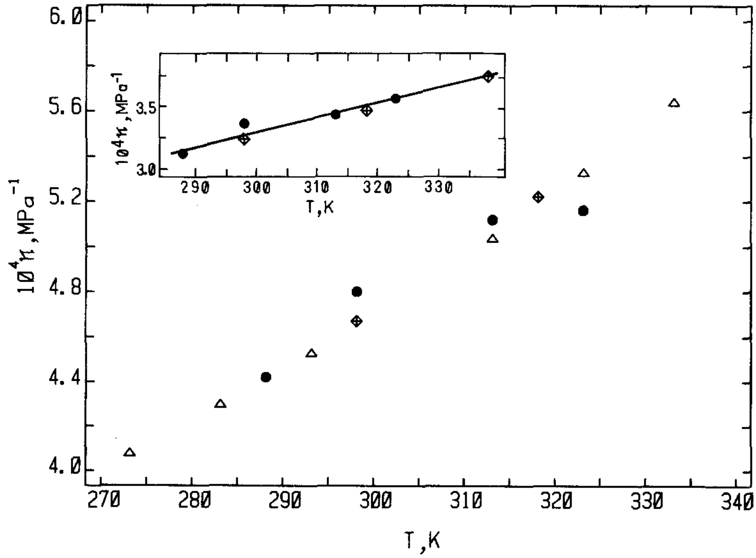

Fig. 3. Isothermal compressibility for aniline at 0.1 MPa and (inset) 100 MPa. ●, This work; △, Ref. 9; ⊕, Ref. 7.

3.1.5. n-*Dodecane*

p,*V*,*T* data for *n*-dodecane have been reported by Cutler and co-workers [18] and by Dymond and co-workers [19], for temperatures of 298.17 K and above. Volume ratios calculated from these data are compared with values from the present work interpolated at 298.27 and 310.95 K and extrapolated to 323.35 K in Table IV. The agreement is satisfactory for pressures up to 50 MPa but at higher pressures there is an increasing divergence between the sets of data. In view of the general concordance between our volume ratio-ratio data (or derived values for quantities such as excess volume) and literature data, for liquids other than *n*-dodecane at pressures up to 250 MPa, we believe that there is some doubt concerning the reliability of the literature data for *n*-dodecane at elevated pressures. We have previously commented on the necessity to calibrate bellows-type volumometers over the whole pressure range at which they are to be used. The discrepancies which are apparent in the data in Table IV may be due to the fact that the (bellows-type) volumometers which were used to obtain the previous data for *n*-dodecane were calibrated only at 0.1 MPa.

Compressibilities at 0.1 MPa are compared with literature data [18, 20] in Fig. 4. The agreement is within 2.5% with the directly measured values [20]. As for aniline, our values at the lower temperatures

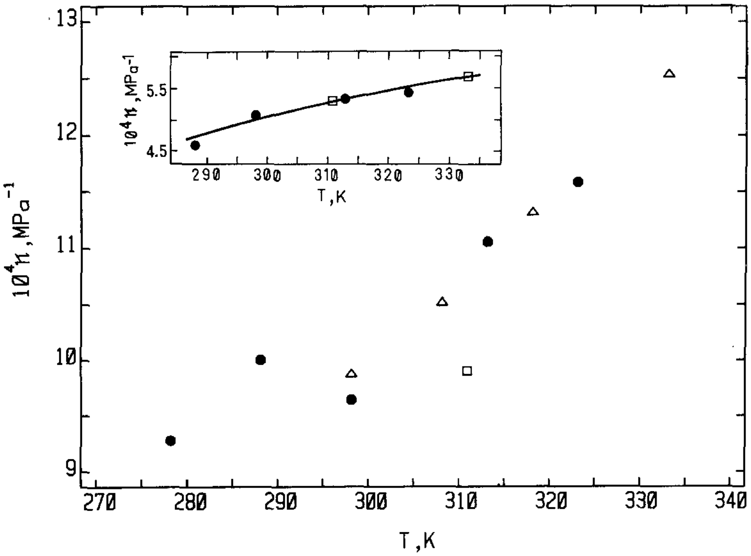

Fig. 4. Isothermal compressibility for *n*-dodecane at 0,1 MPa and (inset) 100 MPa. ●, This work; △, Ref. 20; □, Ref. 18.

are only approximate, owing to the limited accessible pressure range. The agreement between our values of κ and literature data at 100 MPa, shown by the inset in Fig. 4, is good.

4. DISCUSSION

The volume dependence at constant temperature of the internal pressure of toluene is shown in Fig. 5 and has some striking features. At large (molar) volumes, i.e., low pressures, the V,T dependence of π is essentially that of a typical nonassociated liquid. However, this behavior is not preserved as the volume is decreased, and $(\partial\pi/\partial T)_v$ changes sign at about 100 cm$^3\cdot$mol^{-1}. At elevated pressures (roughly above 75 MPa at 278 K and 125 MPa at 323 K) π becomes quite strongly temperature dependent and the behavior becomes more like that of an associated liquid. The

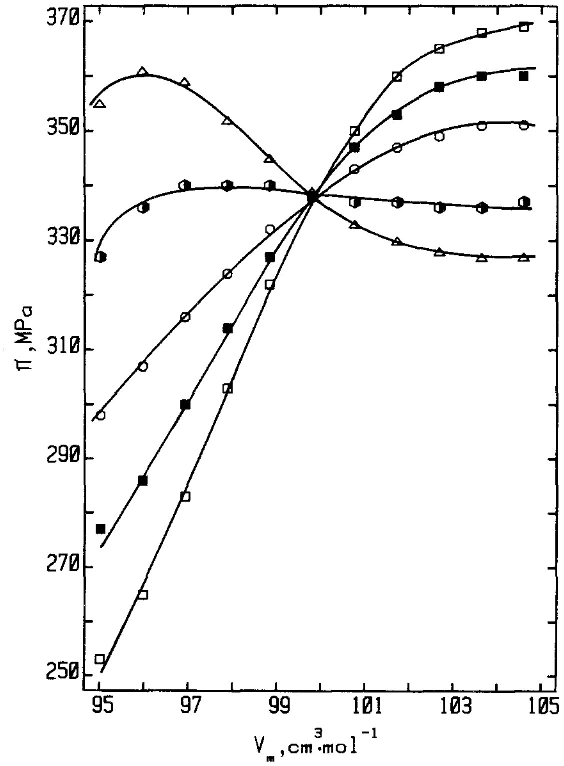

Fig. 5. Volume and temperature dependence of the internal pressure for toluene. □, 278 K; ■, 288 K; ○, 298 K; ◑, 313 K; △, 323 K.

behavior at high pressures is consistent with strong short-range intermolecular interactions becoming effective as the average interparticle separation decreases. No specific chemical (e.g., hydrogen-bonding) interactions can occur in toluene and the molecule has only a small dipole moment, but the quadrupole moment is relatively large. It seems likely therefore, that multipole–multipole interactions are moderately strong in compressed toluene.

For dichloromethane, the volume and temperature dependence of π (Fig. 6) is qualitatively similar to that of toluene. At large average interparticle distances the behavior is characteristic of nonassociated liquids, but when interparticle distances are sufficiently reduced by the application of pressure, short-range intermolecular interactions can evidently become significant. The dipole moment of dichloromethane is substantial (about

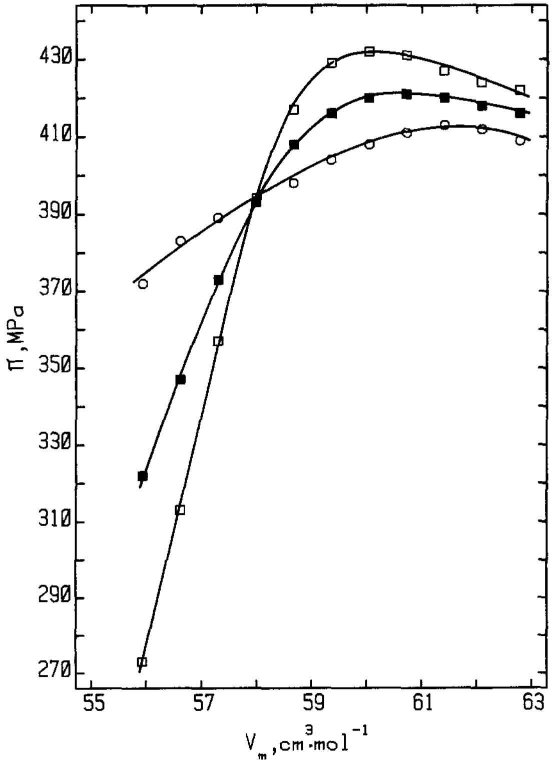

Fig. 6. Volume and temperature dependence of the internal pressure for dichloromethane. Symbols as in the legend to Fig. 5.

5×10^{-30} Cm) so that the variation of π with V and T at high pressures can be ascribed principally to dipole–dipole interactions.

The progressive change in the V,T dependence of π shown in Figs. 5 and 6, including the increase in $(\partial\pi/\partial T)_v$ at low volume, is even more pronounced for acetonitrile (Fig. 7), for which there is only a small volume range (at low pressure) where behavior typical of a nonassociated liquid [i.e., $(\partial\pi/\partial T)_v > 0$] is observed. The behavior of acetonitrile, compared with toluene and dichloromethane, is consistent with the larger dipole moment (of the order 13×10^{-30} Cm) for acetonitrile. It is interesting to note that for the extensively hydrogen-bonded liquid methanol, for which internal pressure calculated from the p,V,T data in Ref. 4 are shown in Fig. 8, the volume dependence of π is very like that of acetonitrile (except for some complexities near the highest experimental pressures), but there is virtually no volume range for which nonassociated liquid behavior is obser-

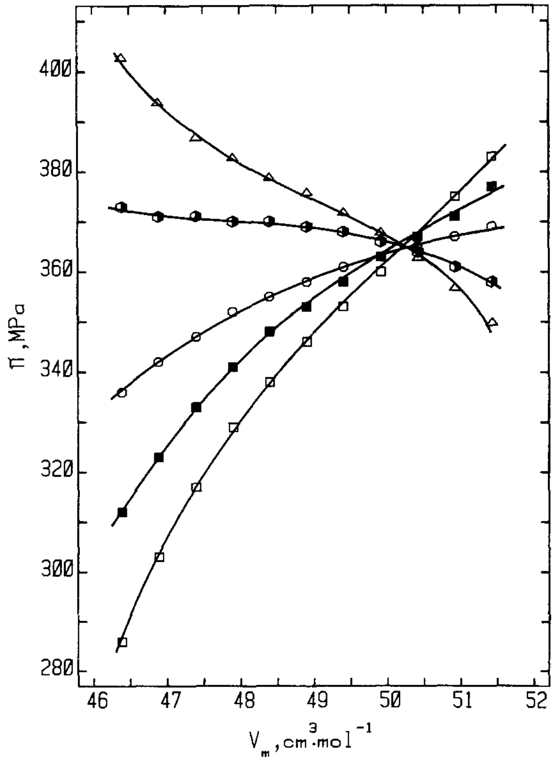

Fig. 7. Volume and temperature dependence of the internal pressure for acetonitrile. Symbols as in the legend to Fig. 5.

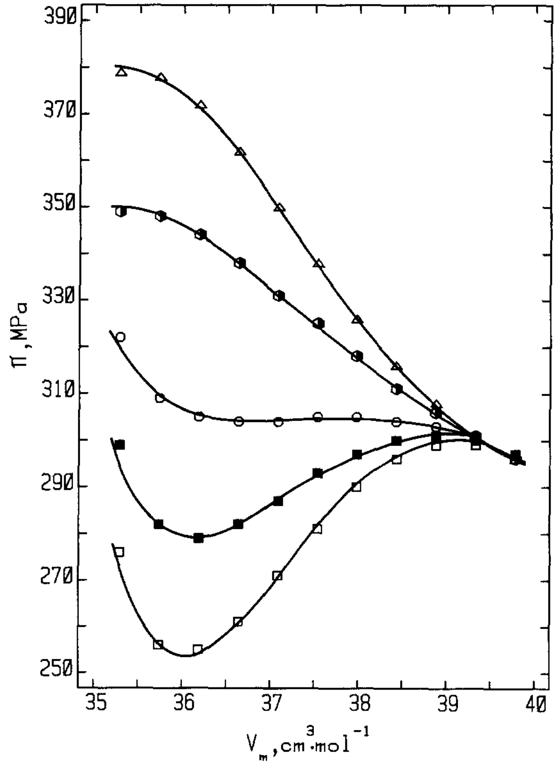

Fig. 8. Volume and temperature dependence of the internal pressure for methanol. Symbols as in the legend to Fig. 5.

ved (for pressures up to about 280 MPa). The extreme case of associated liquid behavior is that shown by water (Fig. 9), for which π was evaluated from literature data [21–23]. A feature of the V,T dependence of π for water is that $(\partial\pi/\partial T)_v$ decreases with increasing pressure, presumably due to, first, distortion and, eventually, disruption of the hydrogen-bonded network structure as the pressure is increased. It seems, from Fig. 8, that a similar effect occurs in methanol when the molar volume is reduced to less than about 36 $cm^3 \cdot mol^{-1}$. Apparently at higher densities the molecules are forced to pack in such a manner that fewer extended hydrogen-bonded structures can exist.

Following the analyses due to Wiehe and Bagley [24] and Bagley and co-workers [25], it is instructive to compare the product πV_m with the cohesive energy calculated as $E_v + 3/2RT$, where E_v is the energy of vaporization evaluated from $\Delta H_v - RT$. Such a comparison, based on ΔH_v

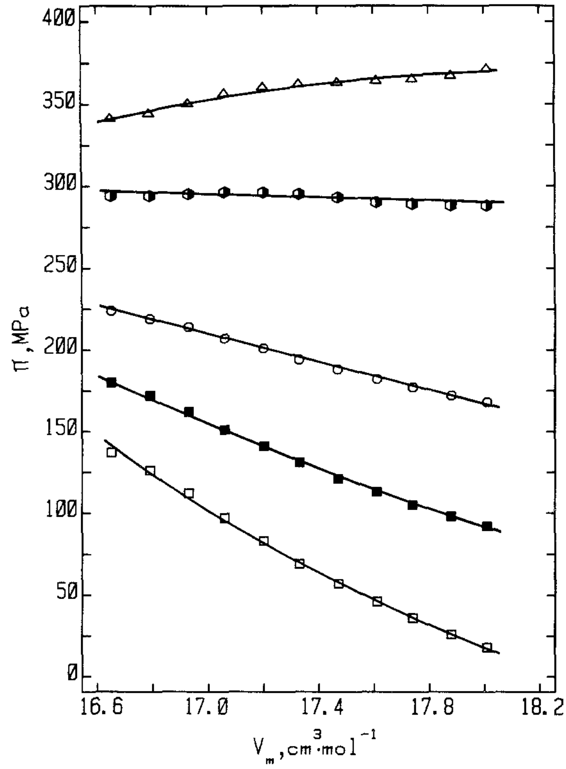

Fig. 9. Volume and temperature dependence of the internal pressure for water. Symbols as in the legend to Fig. 5.

values from Ref. 6, is presented in Table V (for 298 K and 0.1 MPa). The quantity of interest in Table V is δ, the difference between $E_v + 3/2RT$ and πV_m expressed as a percentage of $E_v + 3/2RT$. For the nonpolar, nonasociated carbon tetrachloride δ is almost zero, and πV_m accounts for virtually the whole magnitude of the cohesive energy. The increase in δ from toluene to dichloromethane, acetonitrile, and methanol, which can be interpreted as an increase in the contribution from dipole–dipole (or higher-order multipole) interactions to the cohesive energy, is consistent with the change in the observed V,T dependence of π for these liquids.

The negative value of δ in Table V for *n*-dodecane is difficult to explain, since the uncertainty in π at 298 K and 0.1 MPa should not be sufficiently large to lead to an error of 15% in πV_m.

The case of trichloromethane is clearly anomalous. The V,T dependence of π (Fig. 10) is complex but, nonetheless, typical of a nonassociated rather than an asociated liquid. As for toluene, $(\partial\pi/\partial T)_v$ increases rapidly

Table V. Comparison of the Product $\pi V_m{}^a$ with Cohesive Energy,[a] at 298 K and 0.1 MPa

Liquid	$\Delta E_v{}^b + (3/2)RT$	πV_m	δ (%)[c]
Methanol	38.67	11.87	69
Acetonitrile	34.46	19.76	43
Trichloromethane	34.55	29.85	14
Aniline	57.00	49.83	13
Dichloromethane	29.80	27.09	9
Toluene	39.23	37.61	4
Carbon tetrachloride[d]	33.65	33.38	1
n-Dodecane	62.54	71.78	−15

[a] In $kJ \cdot mol^{-1}$.

[b] Calculated as $\Delta H_v - RT$, where ΔH_v is the enthalpy of vaporization. ΔH_v values from Ref. 6.

[c] The difference between $\Delta E_v + (3/2)RT$ and πV_m, expressed as a percentage of $\Delta E_v + (3/2)RT$.

[d] Molar volume and internal pressure from Ref. 26.

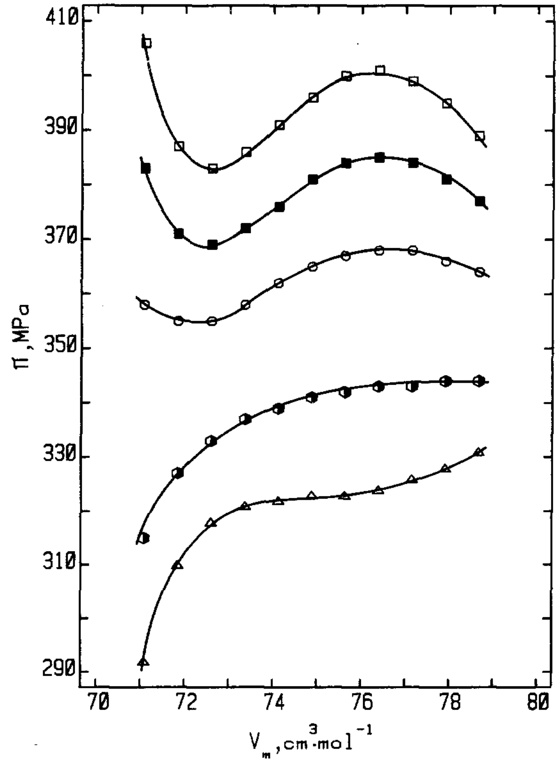

Fig. 10. Volume and temperature dependence of the internal pressure for trichloromethane. Symbols as in the legend to Fig. 5.

in magnitude as the volume is decreased (below about 73 $\mathrm{cm^3 \cdot mol^{-1}}$ for trichloromethane), but unlike toluene the negative temperature coefficient of π is maintained as the pressure is increased. In view of the substantial value of δ in Table V, it is surprising that the V,T dependence of π is not intermediate between that of dichloromethane and that of acetonitrile.

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