Temperature and Density Dependence of the Viscosity of Toluene

Kenneth R. Harris*

School of Chemistry, University College, University of New South Wales, Australian Defence Force Academy, Canberra, ACT 2600, Australia

New measurements have been made for the viscosity of toluene between 255 K and 323 K at pressures up to approximately 400 MPa with a falling-body viscometer. These extend earlier high-pressure measurements below 298 K. The measurements form part of an intercomparison of high-pressure viscometers by the IUPAC Physical Chemistry Division, Commision 1.2, Subcommittee on Transport Properties. A revised correlation function is used to represent the results with a repeatability of ±0.5%. The uncertainty is estimated at ±1%.

Introduction

New measurements have been made for the viscosity (η) of toluene between 255 K and 323 K at pressures up to approximately 400 MPa using a falling-body viscometer. These extend past high-pressure measurements below 298 K. The work forms part of a comparison of high-pressure viscometers of different types by the IUPAC Physical Chemistry Division, Commission 1.2, Subcommittee on Transport Properties. It is intended that toluene can become a standard reference substance for such instruments.

Here we report only data obtained with our apparatus. They complement earlier measurements from this laboratory done at 298 and 323 K as a check on accuracy as part of a study on the viscosity of octane.[1] In that paper, a correlation was produced using the best available data in the literature valid at pressures to 200 MPa. The equations employed reproduced individual data sets well but showed large residuals at high densities (where $(d\eta/d\rho)$ is large), when all the available data sets were combined together. The present extension of the high-pressure falling-body data set to lower temperatures has been used to partially improve this situation.

An account of the comparison of data sets obtained with falling-body, vibrating wire, torsionally oscillating crystal, and capilliary viscometers is to be published elsewhere.[2]

Experimental Section

The toluene was High Purity Solvent grade from Burdick and Jackson (Muskegan, MI) (manufacturer's analysis: >99.8% by GLC), dried over sodium wire. The density was determined, using matched pycnometers, to be (0.862 21 ± 0.000 01) g/mL at 25.00$_0$ °C. This compares well with the value obtained from the equation of state used in this and the previous work, 0.8622$_3$ g/mL, which is based on several sets of reliable experimental data.[3] The molar mass was taken to be 92.1408 g/mol.

The high-pressure viscometer and its operation have been described elsewhere.[4] Temperatures below ambient were produced by cooling the thermostat fluid (Shell Diala B) with a heat exchanger coil through which cold alcohol from a Lauda UKW1500 refrigerated circulating unit was pumped. An on−off heater was controlled by a bridge circuit employing a sensitive thermistor as one arm of the bridge to maintain temperatures constant to ±0.005 K. The uncertainty of the primary Pt resistance thermometer (Tinsley Instruments, U.K.) employed is estimated at ±0.01 K. The primary pressure gauge (400 MPa Heise CM, Dresser Instruments, Stratford, CT) was calibrated against a dead weight tester to ±0.05%.

The viscometer is automatic. New software using Microsoft Visual Basic replaced earlier Turbo-Pascal based software. Data are obtained in the following way. Under computer control, replicate (usually 3) measurements at a set temperature are made at atmospheric pressure. (The viscometer pressure vessel is inverted by a stepper motor to return the slug after each fall time is measured.) Then the viscometer is manually pumped up to a pressure a little above the maximum value required for the isotherm. Control is returned to the computer program, and the pressure is adjusted automatically to the highest of a set of pressures contained in a table in the computer program. This adjustment is accomplished by driving out the piston of a screw injector (model 37-5.75-60, High Pressure Equipment Co., Erie, PA) connected to the viscometer pressure vessel but lying outside the viscometer bath. A Wika model 891.01.2002 pressure transducer (Alexander Wiegand GmbH & Co., Klingenberg am Main, Germany) is used to monitor the pressure during this process. After a time interval sufficient for temperature and pressure equilibration, replicate (again usually 3) fall times are measured and the process is repeated through the series of set pressure points (see Table 2) until atmospheric pressure is reached.

The calibration method was changed from that used previously which relied on an atmospheric pressure correlation for toluene over a range of temperatures recommended by Nieto de Castro and Dymond.[5] Instead, a group of liquids was used for this purpose, with all calibrations being done at the single temperature, 25 °C. The liquids included a set of calibration standards obtained from the Cannon Instrument Co. (State College, PA) (Table 1) and samples of toluene, octane, and cyclohexane. The viscosity used for toluene was that used previously.[1,5] The viscosities of the octane and cyclohexane samples were determined to ±0.2% in an independently calibrated, flared-capillary glass Ubbelohde viscometer with a negligible kinetic energy correction.

* To whom correspondence should be sent. E-mail: k.harris@adfa.edu.au. Fax: 61 2 6268 8017.

10.1021/je000024l CCC: $19.00
Published on Web 08/16/2000

Table 1. Calibration Data at 298.15 K[a]

substance	η/mPa s	ρ/g mL^{-1}	t/s	$t(1-\rho/\rho_s)$/s	Re	$10^{-3}A$/Pa^{-1}
N4 (hexane)[b]	0.3081	0.663 60	9.816	8.922	2177	28.958
octane	0.5136[c,d]	0.698 60	16.342	14.775	823.5	28.767
toluene	0.5542	0.862 19	18.043	15.908	855.6	28.704
N8 (xylenes)	0.6268	0.861 60	20.445	18.027	667.1	28.760
cyclohexane	0.8980[d]	0.773 89	28.850	25.785	296.4	28.740
N1 (mixed HCs)	1.0030	0.789 60	32.313	28.811	241.7	28.725
S3 (mineral oil)	3.4250	0.841 10	111.170	98.335	21.92	28.711
S6 (mineral oil)	7.6800	0.856 90	249.520	220.170	4.437	28.668
N10 (polybutene)	15.1800	0.865 10	493.530	434.923	1.146	28.651
S20 (mineral oil)	29.0000	0.853 90	940.620	830.367	0.3106	28.633
average (disregarding N4)						28.707 ± 0.17%

[a] Sinker diameter = 6.3 mm; density, ρ_s = 7.285 g/mL. [b] N4, S1, and so forth are Cannon viscosity standard numbers. Calibration viscosity values used are those supplied by Cannon for their materials. [c] The sample used is described in ref 1. The viscosity differs from that recommended in ref 12. [d] These values were determined with a glass Ubbelohde flared-capillary viscometer calibrated at 25 °C with water and aqueous sucrose solutions.[13]

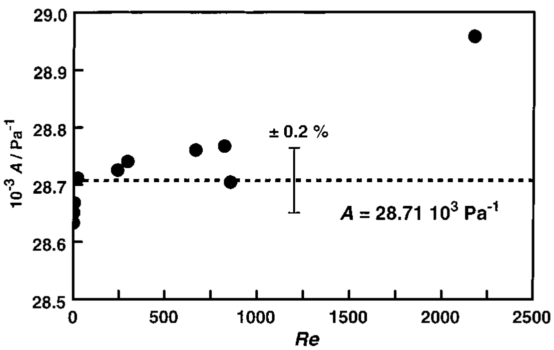

Figure 1. Calibration plot: viscometer constant for various calibration fluids at 25 °C as a function of Reynolds number, *Re*.

The working equation for the falling-body viscometer is[4,6,7]

$$\eta(p,T) = \frac{t(1-\rho/\rho_s)}{A[(1+2\alpha(T-T_{ref})][1-2\beta(p-p_{ref})/3]} \quad (1)$$

where t is the fall time, ρ is the density of the fluid, ρ_s is that of the sinker, α is the coefficient of thermal expansion (1.6×10^{-5} K^{-1}) and β is the bulk compressibility (2×10^{-6} MPa^{-1}) of the sinker and tube material, in this case 316 stainless steel. (The factor $^2/_3$ in the second term of the denominator is incorrectly given as 2 in ref 4. The effect of this error is negligibly small.) A is the calibration constant. The sinker density was corrected for changes in T and p from the calibration state point, T_{ref} = 298.15 K and p_{ref} = 0.1 MPa, using the relation[8]

$$\rho_s = \frac{\rho_s(T_{ref},p_{ref})}{[1+3\alpha(T-T_{ref})][1-\beta(p-p_{ref})]} \quad (2)$$

Some workers[6] express A in terms of the quantity $[t(1-\rho/\rho_s)]^N$, where N is an arbitrary constant. For example, Malhotra et al.,[4] calibrating with various fluids, used $N = 1$. However in this work, A was found to be constant ($N = 0$) within the experimental scatter (average deviation, ±0.2%; maximum deviation, ±0.3%).

Figure 1 is a plot of A against the Reynolds number, *Re*. Equation 5 is not exact at high Reynolds numbers, and the point at which turbulence can occur is dependent on the value of the viscometer constant A. Inspection of graphs given by Isdale and Spence[6] suggests the critical *Re* value is about 1000 to 2000 for A in the range 30 000 to 38 000 Pa^{-1}, dropping to about 5 at $A \sim 3300$ Pa^{-1}. The value of A for the sinker used here was 28 707 Pa^{-1}, which can be expected to be valid for $Re < 1000$ at least. The point for hexane (the least viscous calibrant), which is somewhat high and for which $Re \sim 2180$, was not included in this calibration average.

For toluene, densities were obtained from an equation of state used previously.[3] The uncertainty, based on comparisons with other high-pressure equations of state, is <0.1%.

The accuracy of the high-pressure viscosity measurements is estimated to be ±1% on the basis of the precision of the (best) correlation below, ±0.5%, and that of the calibration. The accuracy relative to the results of other techniques and laboratories is discussed elsewhere.[2]

Results

The results are presented in Table 2. Only a single point was obtained at the lowest temperature, 255 K, due to the very high viscosity of the thermostat bath fluid (Shell Diala B) and the resultant difficulty of maintaining adequate stirring.

At 323.15 K, the lower density points correspond to $1000 < Re < 1450$, where there is the possibility of turbulent flow. However the 0.1 MPa point agrees very well with a value interpolated from the recent vibrating wire viscometer measurements of Assael et al.,[9] 0.4205 mPa s (±0.5%). This value in turn lies in the middle of the best recent determinations at this state point, cited in Assael's work, so it seems that our viscometer calibration can be used to at least $Re \sim 1500$.

Discussion

The equations employed for the original correlation[1,10] were

$$1/\eta^* = \phi^* = \zeta_1 + \zeta_2 V_r/(1 + \zeta_3/V_r) \quad (3)$$

where η^* is the Dymond reduced viscosity[11] and V_r is expressed in terms of molar volume V and temperature T by

$$V_r = V(1 - \xi_1(T-T_r) - \xi_2(T-T_r)^2) \quad (4)$$

T_r being any convenient reference temperature (usually 273.15 K). η^* is defined by

$$\eta^* = \frac{\eta}{\eta^\infty}\left(\frac{V}{V_0}\right)^{2/3} \quad (5)$$

where η^∞ is the Chapman–Enskog expression for the viscosity of the dilute hard-sphere gas and V_0 ($=L\sigma^3/\sqrt{2}$)

Table 2. Viscosity of Toluene from 255 K to 323 K

T/K	p/MPa	V/(cm^3 mol^{-1})	ρ/(g cm^{-3})	η/(mPa s)	Re	T/K	p/MPa	V/(cm^{3}mol^{-1})	ρ/(g cm^{-3})	η/(mPa s)	Re
255.12	0.1	102.14	0.902 10	1.044	251.1						
258.15	0.1	102.47	0.899 22	1.000	272.8	258.15	0.1	102.47	0.899 22	0.9882	279.6
	0.3	102.45	0.899 37	1.009	268.0		0.1	102.47	0.899 22	0.9871	280.2
	3.5	102.21	0.901 49	1.032	256.9		0.1	102.47	0.899 22	0.9871	280.2
	6.6	102.00	0.903 34	1.052	247.8		0.1	102.47	0.899 22	0.9841	281.9
	10.5	101.74	0.905 65	1.085	233.4		5.2	102.10	0.902 47	1.032	257.1
	11.2	101.69	0.906 09	1.089	231.5		9.3	101.82	0.904 94	1.066	241.6
	26.0	100.76	0.914 46	1.224	185.0		13.3	101.56	0.907 30	1.102	226.4
	26.2	100.75	0.914 55	1.224	184.8		24.4	100.86	0.913 58	1.204	191.0
	29.5	100.55	0.916 37	1.266	173.0		25.4	100.80	0.914 12	1.213	188.1
	49.6	99.45	0.926 50	1.460	131.4		49.6	99.45	0.926 55	1.458	131.8
	50.2	99.41	0.926 84	1.470	129.7		49.7	99.44	0.926 61	1.459	131.7
	72.4	98.33	0.937 08	1.722	95.4		72.8	98.31	0.937 25	1.724	95.2
	73.1	98.30	0.937 38	1.718	95.8		75.5	98.19	0.938 43	1.756	91.8
	100.9	97.10	0.948 96	2.101	64.8		98.2	97.21	0.947 88	2.056	67.6
	103.1	97.01	0.949 82	2.132	63.0		102.2	97.05	0.949 46	2.113	64.0
	128.2	96.05	0.959 26	2.527	45.2		126.0	96.13	0.958 46	2.482	46.8
	150.0	95.30	0.966 87	2.916	34.2		129.1	96.02	0.959 59	2.533	45.0
	177.1	94.44	0.975 66	3.481	24.2		148.8	95.34	0.966 46	2.884	34.9
	196.6	93.87	0.981 59	3.956	18.8		149.5	95.31	0.966 71	2.895	34.7
	205.9	93.61	0.984 31	4.199	16.7		175.4	94.49	0.975 14	3.430	24.9
	228.5	93.01	0.990 64	4.858	12.6		178.5	94.40	0.976 10	3.496	24.0
	233.2	92.89	0.991 91	5.013	11.8		195.6	93.90	0.981 30	3.902	19.3
	246.3	92.57	0.995 39	5.451	10.0		196.1	93.88	0.981 44	3.919	19.2
	249.9	92.48	0.996 32	5.569	9.6		219.4	93.25	0.988 14	4.552	14.3
							226.0	93.08	0.989 95	4.742	13.2
							240.1	92.72	0.993 75	5.190	11.0
							244.4	92.61	0.994 89	5.329	10.5
268.15	0.1	103.52	0.890 04	0.8359	387.1	268.15	0.1	103.52	0.890 04	0.8392	384.1
	0.1	103.52	0.890 04	0.8366	386.5		3.2	103.29	0.892 06	0.8588	367.5
	6.4	103.04	0.894 19	0.8807	350.1		5.3	103.13	0.893 44	0.8735	355.7
	11.1	102.70	0.897 17	0.9173	323.7		10.3	102.76	0.896 66	0.9100	328.7
	25.7	101.71	0.905 90	1.027	260.2		25.7	101.71	0.905 92	1.025	261.2
	50.7	100.23	0.919 30	1.234	182.6		50.8	100.22	0.919 39	1.232	183.4
	77.3	98.87	0.931 92	1.482	128.1		75.2	98.97	0.930 98	1.457	132.4
	100.9	97.81	0.942 04	1.726	95.3		100.9	97.81	0.942 04	1.727	95.2
	149.1	95.95	0.960 28	2.338	52.8		126.7	96.77	0.952 15	2.033	69.3
	199.0	94.35	0.976 56	3.167	29.2		148.0	95.99	0.959 89	2.324	53.4
	250.1	92.96	0.991 16	4.286	16.1		150.7	95.90	0.960 84	2.361	51.8
	293.3	91.94	1.002 21	5.546	9.7		200.9	94.30	0.977 14	3.195	28.7
							225.9	93.59	0.984 47	3.712	21.4
							250.5	92.95	0.991 26	4.304	16.0
							284.8	92.13	1.000 12	5.290	10.7
							297.5	91.84	1.003 23	5.696	9.2
278.15	0.0	104.61	0.880 79	0.7165	522.0	278.15	0.1	104.61	0.880 79	0.7212	515.2
	0.1	104.61	0.880 80	0.7203	516.5		0.1	104.61	0.880 80	0.7211	515.4
	0.2	104.61	0.880 80	0.7178	520.0		0.1	104.61	0.880 80	0.7210	515.4
	2.4	104.42	0.882 41	0.7302	503.3		5.1	104.18	0.884 44	0.7506	477.2
	5.1	104.20	0.884 30	0.7462	482.9		10.3	103.78	0.887 85	0.7820	441.2
	19.1	103.12	0.893 53	0.8309	393.0		10.6	103.76	0.888 02	0.7846	438.4
	24.9	102.71	0.897 10	0.8724	357.7		25.7	102.66	0.897 53	0.8791	352.4
	49.8	101.13	0.911 11	1.041	254.5		25.7	102.66	0.897 53	0.8792	352.3
	75.0	99.76	0.923 62	1.232	183.9		26.2	102.62	0.897 88	0.8833	349.2
	99.9	98.57	0.934 74	1.444	135.4		27.5	102.54	0.898 58	0.8904	343.8
	124.9	97.51	0.944 94	1.680	100.9		50.9	101.07	0.911 65	1.052	249.6
	149.8	96.56	0.954 28	1.947	75.7		52.3	100.99	0.912 38	1.060	246.0
	174.4	95.70	0.962 86	2.242	57.6		75.9	99.72	0.924 00	1.242	181.1
	199.5	94.89	0.971 03	2.584	43.6		99.9	98.57	0.934 78	1.444	135.4
	224.6	94.15	0.978 66	2.970	33.2		100.8	98.53	0.935 15	1.454	133.5
	250.3	93.45	0.986 01	3.425	25.2		151.6	96.49	0.954 93	1.971	74.0
	276.2	92.79	0.992 99	3.949	19.0		152.1	96.47	0.955 12	1.973	73.8
	302.6	92.17	0.999 73	4.570	14.3		193.9	95.06	0.969 25	2.509	46.2
	328.1	91.60	1.005 93	5.267	10.8		200.3	94.87	0.971 23	2.596	43.3
	352.6	91.08	1.011 67	6.028	8.3		219.3	94.30	0.977 11	2.887	35.1
	374.5	90.63	1.016 68	6.776	6.6		241.6	93.68	0.983 58	3.267	27.6
							249.5	93.47	0.985 79	3.425	25.2
							290.9	92.44	0.996 78	4.298	16.1
							300.2	92.22	0.999 12	4.520	14.6
288.15	0.1	105.72	0.871 53	0.6375	653.1	298.15	0.1	106.86	0.862 23	0.5557	851.3
	0.1	105.72	0.871 53	0.6274	673.3		12.1	105.73	0.871 44	0.6085	716.7
	5.1	105.27	0.875 26	0.6539	622.2		25.7	104.60	0.880 89	0.6733	591.0
	10.1	104.84	0.878 84	0.6803	576.9		51.6	102.76	0.896 69	0.8027	422.3
	24.8	103.69	0.888 64	0.7593	467.5		73.8	101.42	0.908 54	0.9241	322.3
	49.8	101.98	0.903 54	0.9038	334.8		100.3	100.02	0.921 22	1.082	238.1
	51.0	101.92	0.904 02	0.9169	325.4		122.4	98.99	0.930 85	1.226	187.0
	74.5	100.58	0.916 13	1.061	245.9		152.7	97.72	0.942 94	1.447	135.9
	100.5	99.27	0.928 15	1.247	179.9		175.7	96.85	0.951 43	1.632	107.6
	102.6	99.18	0.929 06	1.260	176.4		202.4	95.92	0.960 62	1.872	82.5
	126.1	98.14	0.938 89	1.445	135.3		252.1	94.39	0.976 16	2.395	51.2
	149.2	97.21	0.947 83	1.645	105.2		270.6	93.88	0.981 50	2.621	42.9

Table 2. (Continued)

T/K	p/MPa	V/(cm^3 mol^{-1})	ρ/(g cm^{-3})	η/(mPa s)	Re	T/K	p/MPa	V/(cm^{3}mol^{-1})	ρ/(g cm^{-3})	η/(mPa s)	Re
288.15	154.7	97.00	0.949 88	1.698	99.1	298.15	303.7	93.02	0.990 53	3.077	31.4
	200.5	95.42	0.965 66	2.173	61.3		353.3	91.86	1.003 05	3.897	19.8
	204.3	95.30	0.966 89	2.221	58.7		372.0	91.45	1.007 53	4.259	16.6
	239.4	94.25	0.977 66	2.665	41.2		373.5	91.42	1.007 90	4.297	16.4
	247.4	94.00	0.980 20	2.781	37.9		390.0	91.07	1.011 78	4.644	14.0
	272.3	93.36	0.986 97	3.157	29.6		393.5	91.00	1.012 59	4.719	13.6
	294.9	92.79	0.992 99	3.551	23.5						
	296.9	92.74	0.993 52	3.581	23.1						
	322.3	92.15	0.999 94	4.079	17.9						
	329.1	91.99	1.001 63	4.224	16.7						
	351.7	91.49	1.007 10	4.739	13.4						
	387.3	90.75	1.015 37	5.6803	9.4						
	390.4	90.68	1.016 09	5.7716	9.1						
	392.3	90.64	1.016 52	5.8255	8.9						
323.15	202.3	97.37	0.946 32	1.343	158.4	323.15	0.1	109.86	0.838 73	0.4215	1443
	225.3	96.55	0.954 30	1.490	129.7		0.1	109.86	0.838 73	0.4224	1444
	250.6	95.72	0.962 59	1.668	104.3		0.1	109.86	0.838 73	0.4225	1442
	275.5	94.96	0.970 28	1.857	84.7		5.1	109.26	0.843 32	0.4399	1337
	296.4	94.37	0.976 41	2.030	71.2		10.3	108.68	0.847 84	0.4584	1237
	301.5	94.23	0.977 87	2.075	68.3		15.5	108.13	0.852 15	0.4772	1147
	326.2	93.57	0.984 69	2.300	55.9		20.3	107.65	0.855 95	0.4940	1074
	341.8	93.18	0.988 84	2.457	49.1		29.6	106.78	0.862 90	0.5278	947.6
	352.5	92.92	0.991 61	2.567	45.1		50.9	105.05	0.877 11	0.6075	725.4
	375.8	92.37	0.997 49	2.828	37.4		51.4	105.01	0.877 41	0.6096	720.6
	393.2	91.98	1.001 75	3.035	32.6		75.3	103.38	0.891 27	0.7042	547.4
	399.6	91.84	1.003 29	3.117	30.9		76.3	103.32	0.891 81	0.7088	540.6
							101.0	101.88	0.904 45	0.8132	415.7
							126.9	100.54	0.916 44	0.9330	319.4
							156.9	99.17	0.929 10	1.084	239.5
							176.1	98.37	0.936 64	1.188	200.6

Table 3. Coefficients of Nonlinear Least Squares Fits

quantity fitted	η^*	η		η
equations	3 and 4	3, 4, and 6		7 and 8
ζ_1	−0.444 080	−10.8424	$10^{-2}\zeta_1$/(K$^{0.5}$/(mPa s))	8.295 07
$10^2\zeta_2$/(mol cm^{-3})	0.257 241	6.212 94	$10^{-2}\zeta_2$/(K$^{0.5}$ mol/(mPa s cm^3))	−0.194 056
$10^{-2}\zeta_3$/(cm^3 mol^{-1})	−0.432 201	−0.437 137	ζ_3/(K$^{0.5}$ mol^2/(mPa s cm^6))	0.113 620
			$10^2\zeta_4$/(K$^{0.5}$ mol^3/(mPa s cm^9))	0.873 380
$10^3\xi_1$/K^{-1}	−0.646 370	−0.623 107	$10\xi_1$/(cm^3/(K mol))	−0.605 661
$10^5\xi_2$/K^{-2}	0.127 466	0.125 517	$10^3\xi_1$/(cm^3/(K^2 mol))	0.138 663
T range/K	255−323	255−323		255−323
stand. devn/%	0.4	0.7		0.5
max. devn/%	3.7	2.2		1.3

is the volume of random close-packing of equivalent spherical molecules of diameter σ. In terms of practical quantities, eq 5 can be rewritten as

$$\eta^* = (20.929 \times 10^3)\eta\left(\frac{1000}{MT}\right)^{1/2} V^{2/3} \qquad (6)$$

where η has units of Pa s, V has units of cm^3/mol, M has units of g/mol, and T has units of K. The data obtained here have been fitted to eqs 3 and 4 by nonlinear least-squares methods. In earlier work, the Dymond reduced viscosity η^* (eq 6) was fitted directly as a function of V and T. However, strictly speaking, this procedure is not correct, as η^* is computed using V and T, and this must bias the weightings of errors. To avoid this effect, here $\eta(V,T)$ was fitted by minimizing its squared residuals rather than those of η^*. The coefficients of the fit are given in Table 3 together with those of the fit of η^* for comparison. Figures 2 and 3 are deviation plots for the two fitting procedures.

It is clear from these figures that, over the temperature range now available, eqs 3 and 4 are not entirely satisfactory over the whole density range. The fit of η^* (Figure 2) appears to be very good at all but the highest densities (V > 93 cm^3/mol), but there is a systematic upswing in the residuals below this molar volume where the terms $\zeta_2 V_r/(1 + \zeta_3/V_r)$ and ζ_1, which are of opposite sign, approach one another in magnitude. The unbiased fit of η (Figure 3) reduces the upswing and the scatter between isotherms at higher densities at the expense of the scatter at lower densities. Though the small range of the residuals is quite good, within ±2%, the precision is clearly better, and the lack of randomness in the residuals shows that eqs 3 and 4 are not truly satisfactory in reproducing the data for this system. This was an unresolved question in our earlier study.[1]

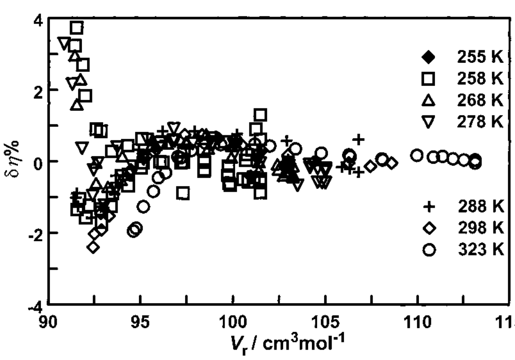

Figure 2. Residuals for the indirect fit of the viscosity of toluene to eqs 3 and 4 obtained by fitting the Dymond reduced viscosity (η^*) as a function of reference molar volume, V_r: (◆) 255 K; (□) 258 K; (△) 268 K; (▽) 278 K; (+) 288 K; (◇) 298 K; (○) 323 K.

Some effort has been expended to find an alternative set of equations to fit the data. Attempts were made to employ eq 3 with different forms of V_r: for example, (a) $V_r = V/V_0$,

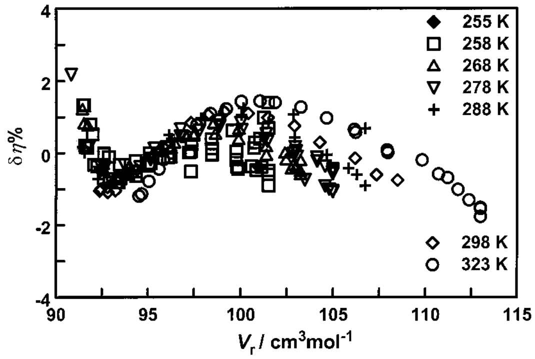

Figure 3. Residuals for the direct fit of the viscosity of toluene to eqs 3, 4, and 6 as a function of reference molar volume, V_r: symbols as in Figure 2.

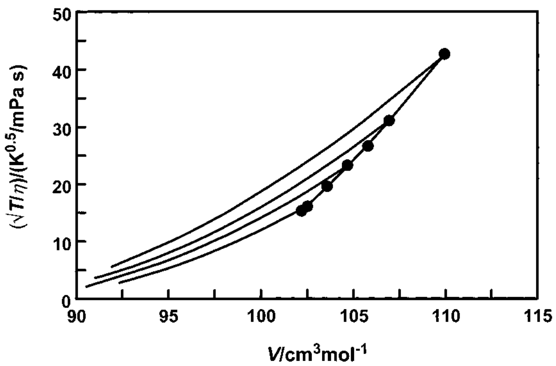

Figure 4. Plot of the quantity $\sqrt{T}/\eta$ against molar volume, V. The isotherms shown, from top to bottom, are 323, 298, 278, and 258 K. Also shown is the curve linking the 0.1 MPa points for all the experimental isotherms.

$V_0 = L\sigma^3/\sqrt{2}$, and $\sigma = \sigma_0 + \sigma_1\sqrt{T} + \sigma_2 T$; and (b) $V_r = V/V_0$ and $V_0 = a + b(T - T_r) + c(T - T_r)^2$. It was possible to obtain satisfyingly small residuals and standard deviations with these forms for V_r, but the errors in the fitted coefficients were large and the values obtained varied considerably depending on the initial estimates made. In other words, the minima in the n-dimensional parameter surface were very shallow. Therefore, a variant of an equation successfully used with self-diffusion coefficients was tried.

Figure 4 shows fluidity ($\phi = 1/\eta$) isotherms reduced by factoring out the primary kinetic theory $1/\sqrt{T}$ dependence. The isotherms are similar in the geometric sense, like those for the corresponding self-diffusion coefficient function $D/\sqrt{T}$.[3,10] Also shown is the curve linking the 0.1 MPa points for all the experimental isotherms: this is nonlinear. $(\sqrt{T}/\eta)/(\sqrt{K}/(\mathrm{mPa\ s})) = 457.963 - 11.6496(V/(\mathrm{cm^3\,mol^{-1}})) + (7.16053 \times 10^{-2})(V/\mathrm{cm^3\,mol^{-1}})^2$ with a standard deviation of $\pm 1.0\%$. For the complete data set, the best simple empirical function found was a Padé approximation combined with a simple mapping of the isotherms onto a single reference isotherm:

$$\sqrt{T}/\eta = (\zeta_1 + \zeta_2 V_r' + \zeta_3 V_r'^2)/(1 + \zeta_4 V_r') \qquad (7)$$

$$V_r' = V - \xi_1(T - T_r) - \xi_2(T - T_r)^2 \qquad (8)$$

The coefficients are also listed in Table 3, and the residual plot is shown as Figure 5. The residuals cluster about the axis and are now better distributed (though not perfectly randomly) within a range of $\pm 1.3\%$ and a standard deviation of $\pm 0.5\%$. Equations 7 and 8 therefore appear sufficient for the task in this case.

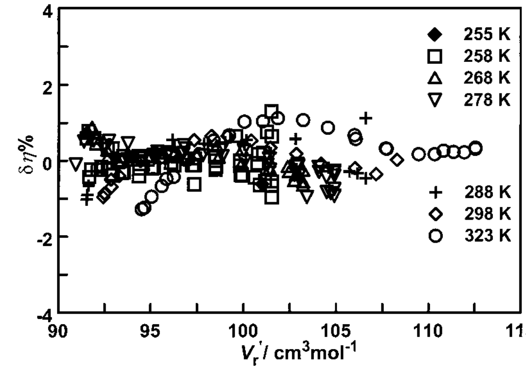

Figure 5. Residuals for the direct fit of the viscosity of toluene to eqs 7 and 8 as a function of reference molar volume, V_r': symbols as in Figure 2.

Acknowledgment

I am grateful to other members of the IUPAC Division of Physical Chemistry, Commission 1.2, Subcommittee on Transport Properties, for helpful discussions. I particularly thank Prof. Marc Assael and Prof. JoãoFareleira as well as Prof. Akira Nagashima for his comment on the importance of checking Reynolds numbers when calibrating with low-viscosity fluids. Dr. Lawrie Woolf is thanked for criticism and advice. It is a pleasure to thank Mr. Shane Murtagh for assisting with the viscometer calibration and Messrs Kerry Richens and Ken Piper for electronics and mechanical workshop services, respectively.

Literature Cited

(1) Harris, K. R.; Malhotra, R.; Woolf, L. A. Temperature and Density Dependence of the Viscosity of Octane and Toluene. *J. Chem. Eng. Data* **1997**, *42*, 1254−1260.

(2) Assael, M. J.; Avelino, H. M. T.; Dalaouti, N. K.; Fareleira, J. M. N. A.; Harris, K. R. Standard Reference Data for the Viscosity of Toluene over a Wide Range of Temperatures and Pressures. *Int. J. Thermophys.*, submitted for publication.

(3) Harris, K. R.; Alexander, J. J.; Goscinska, T.; Malhotra, R.; Woolf, L. A.; Dymond, J. H. Temperature and Density Dependences of the Self-diffusion Coefficients of Liquid *n*-Octane and Toluene. *Mol. Phys.* **1993**, *78*, 235−248.

(4) Malhotra, R.; Price, W. E.; Woolf, L. A.; Easteal, A. J. Thermodynamic and Transport Properties of 1,2-Dichloroethane. *Int. J. Thermophys.* **1990**, *11*, 835−861.

(5) Nieto de Castro, C. A.; Dymond, J. H. Private communication, Sept. 1996.

(6) Isdale, J. D.; Spence, C. M. A Self-Centering Falling Body Viscometer for High Pressures. National Engineering Laboratory Report No. 592; Department of Industry, U.K., 1975.

(7) Isdale, J. D.; Easteal, A. J.; Woolf, L. A. Shear Viscosity of Methanol and Methanol + Water Mixtures Under Pressure. *Int. J. Thermophys.* **1985**, *6*, 439−450.

(8) Dymond, J. H.; Young, K. J.; Isdale, J. D. Transport Properties of Nonelectrolyte Liquid Mixtures. II. Viscosity Coefficients for *n*-Hexane + *n*-Hexadecane System at Temperatures from 25 to 100 °C at Pressures up to the Freezing Pressure or 500 MPa. *Int. J. Thermophys.* **1980**, *1*, 345−373.

(9) Assael, M. J.; Dalaouti, N. K.; Dymond, J. H. The Viscosity of Toluene in the Temperature Range 210 to 370 K and at Pressures up to 30 MPa. *Int. J. Thermophys.* **1999**, *20*, 1367−1377.

(10) Harris, K. R. Temperature and Density Dependence of the Self-diffusion Coefficients of *n*-Hexane from 223 to 333 K and up to 400 MPa. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2265−2275.

(11) Dymond, J. H. The Interpretation of Transport Coefficients on the Basis of the van der Waals Model. I. Dense Fluids. *Physica A* **1974**, *79*, 100−114.

(12) Dymond, J. H.; Øye, H. A. Viscosity of Selected Liquid *n*-Alkanes. *J. Phys. Chem. Ref. Data* **1994**, *23*, 41−53.

(13) James, C. J.; Mulcahy, D. E.; Steel, B. J. *J. Phys. D: Appl. Phys.* **1984**, *17*, 225−230.

Received for review January 24, 2000. Accepted June 7, 2000. This work was supported in part by grants from the Australian Research Council and the University College.

JE000024L