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Temperature and Density Dependence of the Viscosity of Octane and Toluene

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Fluids of larger polyatomic molecules do not well fit the hard sphere model of dense fluids as their liquid range, reduced in terms of relative molecular volumes, usually extends well beyond the freezing density of the hard sphere fluid. Even where overlap occurs, the density dependence is observed to be not as simple as that of the model. It is for this reason that empirical functions for the density dependence of the transport properties have been developed. Application of such correlations has thrown some doubt on previous high-pressure measurements of the viscosity of liquid octane and toluene. New measurements have been made for octane between 283 K and 348 K and for toluene at 298 K and 323 K at pressures up to approximately 375 MPa with a falling-body viscometer. These are supplemented by *pVT* measurements for octane between 278 K and 298 K, which have been used to improve an earlier equation of state. The viscosity results are compared with earlier data using a general correlation method for molecular liquids.

Introduction

This contribution reports high-pressure viscosity (η) data for the liquids octane and toluene. We have previously reported high-pressure self-diffusion coefficients (D) for these two systems (Harris et al., 1993). The density dependence of the self-diffusion coefficient and the fluidity (reciprocal viscosity, $\phi = 1/\eta$) is known to be similar for many molecular fluids. For atomic and some near-spherical molecular fluids, such as methane, it is possible to fit experimental data to computer simulation results for the hard sphere fluid using the molecular diameter and a translational−rotational coupling factor as fitted parameters (see, for example, Harris (1992)). However such correlation methods are of little help with the majority of molecular fluids, including toluene and octane, as they are liquid at reduced densities well above the freezing point of the hard sphere fluid used as the reference model. In addition, the quantities ($D/\sqrt{T}$) and ($\sqrt{T}/\eta$) generally show a strong nonlinear volume dependence at the highest densities, inconsistent with the hard sphere model simulation results.

In our original paper on the self-diffusion coefficients of toluene and octane (Harris et al., 1993), we sought to employ simple correlation equations used earlier (Harris, 1982) to fit viscosities and self-diffusion coefficients for hexane. The two properties were fitted simultaneously to take advantage of the similar volume dependence of the fluidity and the self-diffusion coefficient. The equations employed were

$$1/\eta^* = \phi^* = \zeta_4 + \zeta_5 V_r/(1 + \zeta_6/V_r) \tag{1}$$

and

$$D^* = \zeta_1 + \zeta_2 V_r/(1 + \zeta_3/V_r) \tag{2}$$

where V_r is expressed in terms of molar volume V and temperature T by

$$V_r = V\,(1 - \xi_1(T - T_r) - \xi_2(T - T_r)^2) \tag{3}$$

T_r being any convenient reference temperature. η^* is the reduced viscosity coefficient introduced by Dymond (1974) and defined by

$$\eta^* = \frac{\eta}{\eta^\infty}\left(\frac{V}{V_0}\right)^{2/3} \tag{4}$$

where $^\infty$ indicates the dilute-gas value for the hard-sphere fluid, V is the molar volume and V_0 is the volume of random close packing, $L\sigma^3/\sqrt{2}$, for a molecule of diameter σ. D^* is the self-diffusion analogue:

$$\mathrm{D}^* = \frac{(nD)}{(nD)^\infty}\left(\frac{\mathrm{V}}{\mathrm{V}_0}\right)^{2/3} \tag{5}$$

These equations were introduced to take into account the curvature of $D^* - V$ and $\phi^* - V$ plots in a simple way, to provide a means to represent and interpolate data, and to compare results from different sources, even when obtained at different state points. The method is similar in intent to that of Assael et al. (1992, 1994) but differs in detail.

Both methods fit the Dymond reduced coefficients rather than the experimental quantities from which these are derived. When the appropriate dilute gas factors are substituted in eqs 4 and 5, one obtains expressions in terms of experimental quantities; thus

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

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$$D^* = 17.44 \times 10^9 \frac{D}{V^{1/3}}\left(\frac{M}{1000T}\right)^{1/2} \qquad (7)$$

where D has units of $m^2\ s^{-1}$, η of Pa s, V of $cm^3\ mol^{-1}$, M of g mol^{-1}, and T of K.

In our original work (Harris et al., 1993), we examined the deviations for literature viscosities from the correlation eqs 1 and 3. These were much greater than expected for those data sets obtained with a falling-body viscometer at the UK National Engineering Laboratory (Dymond et al., 1981, 1991), than for data obtained by other types of viscometer, albeit over rather shorter ranges of density. This contrasted with the situation for hexane and hexadecane, where good joint diffusion coefficient-viscosity fits were obtained, though these viscosity data sets had also been obtained with the NEL apparatus over a similar range of pressures, and with that for trichloromethane where the data were obtained from the viscometer used in this work (Harris et al., 1990). The situation was further confused by the different methods of calibration used with different viscometer types. The falling-body type viscometers depend on calibration, usually at atmospheric pressure, with a number of fluids encompassing the range of viscosities to be examined. The other methods for viscosity measurement depend on calibration at a few, well-determined state points or along the liquid−vapor coexistence curve with water or other fluids, but not necessarily at high viscosity. The oscillating disk, oscillating crystal, and vibrating wire techniques are also more accurate (±0.3−0.5%) than the falling body type (±2−4%), though the precision of fall times for a good falling-body apparatus may be better than ±0.5%.

In an attempt to clarify the situation, we have measured the viscosity of octane from 283 K to 348 K to pressures approaching 375 MPa. In addition two isotherms for toluene at 298 K and 323 K have been obtained for comparison with the extensive new data sets now available for that substance, including a new NEL series (Dymond et al., 1995).

Experimental Section

The octane sample was the same as that used for self-diffusion measurements (Harris et al., 1993). The toluene was High Purity Solvent grade from Burdick and Jackson (Muskegan, MI). The molar masses have been taken to be 114.231 and 92.1408 g/mol, respectively.

The high-pressure viscometer, its calibration, and the operational procedures have been described elsewhere (Malhotra et al., 1990). Pressure gauges were calibrated against a dead-weight tester to ±0.05%. Temperatures were maintained constant to ±0.005 K and had an accuracy of ±0.01 K. Viscosities were measured relative to atmospheric pressure values taken from the literature; for octane, the data of Dymond and Øye (1994) and for toluene, those recommended by Nieto de Castro (1997), which are given by the formula

$$\ln\left(\frac{\eta(T)}{\eta(298.15\ \mathrm{K})}\right) = -\,5.1451 + 8.7002/T^* - 5.5568/(T^*)^2 + 2.0014/(T^*)^3 \qquad (8)$$

where $\eta(298.15\ \mathrm{K}) = 0.5542$ mPa s, $218 < T/\mathrm{K} < 393$, and $T^* = T/(298.15\ \mathrm{K})$. The accuracy of the viscosity measurements is estimated to be ±2%, whereas the precision is somewhat better than this, ±0.5 %.

In our earlier work (Harris et al., 1993), densities were calculated from a Hayward equation of state incorporating data from several sources. Below 298 K, the only available data were points at 273 K due to Bridgman (1931) and smoothed Tait equations for several isotherms due to Scaife and Lyons (1980). The Bridgman data did not well fit the Hayward equation of state, so this could only be used at and above 298 K, with diffusion measurements below this temperature being confined to those isotherms for which Scaife and Lyons had provided equations.

Table 1. Volume Ratios, *k*, for Octane

p/MPa	k	p/MPa	k	p/MPa	k	p/MPa	k
			$T = 278.15$ K				
2.547	0.9973	30.39	0.9717	138.38	0.9112	273.84	0.8670
4.996	0.9947	38.67	0.9654	157.83	0.9034	296.94	0.8611
9.576	0.9901	58.09	0.9520	178.46	0.8958	321.34	0.8551
14.728	0.9852	77.69	0.9403	197.98	0.8891	347.27	0.8492
19.374	0.9810	98.03	0.9295	222.99	0.8812	364.64	0.8456
23.639	0.9773	116.56	0.9207	247.22	0.8742		
			$T = 288.15$ K				
2.547	0.9971	29.43	0.9707	135.43	0.9081	272.38	0.8620
4.996	0.9944	36.72	0.9646	148.90	0.9024	297.82	0.8554
9.789	0.9892	57.11	0.9496	177.35	0.8915	322.32	0.8493
14.657	0.9843	76.10	0.9377	196.69	0.8847	347.78	0.8434
19.708	0.9794	96.84	0.9262	221.92	0.8765	363.76	0.8400
24.238	0.9752	117.32	0.9162	246.23	0.8693		
			$T = 298.14$ K				
2.547	0.9969	30.25	0.9679	138.10	0.9022	272.10	0.8563
4.996	0.9939	38.54	0.9608	158.68	0.8936	297.72	0.8495
9.813	0.9884	58.50	0.9456	176.74	0.8865	321.93	0.8434
14.844	0.9829	78.44	0.9327	197.91	0.8789	336.92	0.8399
19.517	0.9781	97.95	0.9217	222.57	0.8708	351.82	0.8366
23.689	0.9740	117.25	0.9118	248.80	0.8628		

Table 2. Coefficients of Eqs 10 and 11 for the Secant Bulk Modulus *k* for Octane

T/K	a_0/MPa	a_1	$-a_2$/GPa^{-1}	a_3/GPa^{-2}	$\langle \delta k/k \rangle$/%
278.15	921.41	5.262	5.5242	5.303	0.008
288.15	858.74	5.094	4.7403	3.908	0.006
298.15	794.38	5.107	5.3254	5.086	0.008

T/K	B/MPa	C	$\langle \delta k/k \rangle$/%
278.15	87.06	0.2157	0.022
288.15	80.49	0.2154	0.027
298.15	74.46	0.2155	0.023

Consequently for this work, new pVT measurements have been made using a bellows volumometer to supplement those available in the literature for this system in the range of states required. Temperatures in the volumometer bath were maintained constant to ±0.005 K and had an accuracy of ±0.01 K. Pressure gauges were calibrated against a dead-weight tester to ±0.05%. Details of the methods used have been described previously (Easteal and Woolf, 1985; Malhotra and Woolf, 1993; Kipkemboi and Woolf, 1995).

Results

***pVT* Data.** The pVT results for octane are given in Table 1. At each composition, the volume ratio

$$k \equiv V(p)/V(0.1\ \mathrm{MPa}) \qquad (9)$$

was evaluated over the range of experimental pressures at each temperature. The volume ratios were expressed as the secant bulk modulus k and fitted to the isothermal Hayward equation

$$k = p/(1 - k) = a_0 + a_1 p + a_2 p^2 + a_3 p^3 \qquad (10)$$

and the normal form of the Tait equation

$$1 - k = C \log[(B + p)/(B + 0.1)] \qquad (11)$$

where B and p are in MPa. The coefficients a_i and B and C are given in Table 2 for each experimental isotherm.

Table 3. Coefficients for Eqs 14 and 15

i	a_{0i}	a_{1i}	b_i
0	$-0.849\,242 \times 10^{3}$	$4.833\,12 \times 10^{5}$	$1.590\,700 \times 10^{2}$
1	$-1.359\,10$	$2.152\,46 \times 10^{3}$	$1.733\,007 \times 10^{-1}$
2	$3.245\,90 \times 10^{-1}$	$-1.278\,53 \times 10^{1}$	$1.911\,519 \times 10^{-4}$
3	$-9.544\,37 \times 10^{-5}$	$3.420\,63 \times 10^{-2}$	$1.272\,161 \times 10^{-6}$
4	$8.299\,67 \times 10^{-8}$	$-2.880\,04 \times 10^{-5}$	
	stand devn	14 MPa	0.03 cm^3/mol

Table 4. Viscosity of Toluene at 298 and 323 K

p/MPa	V/cm^3 mol^{-1}	η/mPa s	p/MPa	V/cm^3 mol^{-1}	η/mPa s
		298.15 K			
0.10	106.86	0.5542[a]	198.93	96.03	1.831
12.56	105.69	0.612	249.07	94.48	2.352
23.53	104.77	0.664	298.88	93.14	2.994
49.27	102.91	0.790	348.54	91.97	3.794
98.60	100.10	1.066	367.25	91.56	4.148
148.93	97.87	1.410			
		323.15 K			
0.10	109.86	0.4216[a]	198.59	97.51	1.309
12.71	108.42	0.463	248.39	95.79	1.636
24.12	107.28	0.506	297.39	94.34	2.021
48.63	105.22	0.596	347.09	93.05	2.489
99.17	101.98	0.800	373.40	92.43	2.776
148.45	99.54	1.031			

[a] Atmospheric pressure value from Nieto de Castro (1997).

These new pVT data were combined with the literature data (Bridgman, 1931; Eduljee et al., 1951; Brazier and Freeman, 1969; Dymond et al., 1982) used in our earlier diffusion study, and, as before, they were fitted to the Hayward equation of state where the linear secant modulus

$$\kappa = V_\sigma (p - p_\sigma)/(V_\sigma - V) \tag{12}$$

is expressed as a polynomial in the pressure, p

$$\kappa = \sum_{i=0}^{4} \alpha_i p_i \tag{13}$$

with temperature-dependent coefficients

$$a_i = a_{0i} + a_{1i}/T \tag{14}$$

V_σ is the molar volume at atmospheric pressure. These V_σ values were fitted to a polynomial in the temperature

$$V_\sigma = \sum_{j=0}^{3} \beta_j T^j \tag{15}$$

The 273 K isotherm of Bridgman (1931), previously excluded from the equation of state, now fits well with the new results, including as they do 278 and 288 K isotherms, and was therefore incorporated in the full data set. The coefficients a_{ij} and b_k are given in Table 3.

Viscosity Data. The viscosity results for toluene and octane are summarized in Tables 4 and 5.

Table 5. Viscosity of Octane from 283 K to 353 K

p/ MPa	V/cm^3 mol^{-1}	η/ mPa s	p/ MPa	V/cm^3 mol^{-1}	η/ mPa s	p/ MPa	V/cm^3 mol^{-1}	η/ Pa s
				283.15 K				
0.10	160.82	0.6146[a]	98.50	149.27	1.455	298.60	138.10	5.228
11.96	158.78	0.692	148.10	145.70	2.056	322.05	137.22	5.989
25.49	156.78	0.791	198.60	142.71	2.855	364.50	135.79	7.631
48.46	153.95	0.985	248.00	140.24	3.872	366.0	135.74	7.672
73.50	151.42	1.206	273.00	139.14	4.911			
				298.14 K				
0.10	163.54	0.5160[a]	98.83	150.77	1.183	298.75	139.06	3.893
12.66	161.11	0.587	148.51	146.98	1.640	349.00	137.16	5.069
22.94	159.39	0.655	199.24	143.85	2.230	363.73	136.66	5.468
49.14	155.80	0.814	248.69	141.28	2.959	364.80	136.62	5.494
				323.15 K				
0.1	168.37	0.3875	98.95	153.37	0.871	297.63	140.83	2.549
12.86	165.36	0.445	148.52	149.24	1.182	347.00	138.80	3.208
24.22	163.10	0.496	198.94	145.90	1.561	365.77	138.09	3.490
49.11	159.10	0.613	248.86	143.15	2.015			
				347.52 K				
0.10	173.54	0.3072[a]	100.85	155.84	0.702	293.83	142.90	1.902
12.37	169.90	0.355	151.37	151.36	0.939	325.39	141.95	2.121
26.69	166.62	0.406	199.45	148.03	1.206	350.36	140.38	2.361
51.44	162.10	0.499	250.58	145.07	1.534	373.37	139.45	2.603
76.73	158.56	0.597	273.20	143.90	1.701			
				353.15 K				
0.10	174.81	0.2921[a]	148.84	152.12	0.878	297.79	143.18	1.763
12.40	171.08	0.338	198.13	148.64	1.127	347.27	140.95	2.162
48.68	163.35	0.466	247.77	145.72	1.419	369.66	140.01	2.363
98.79	156.69	0.658						

[a] Atmospheric pressure value from Dymond and Øye (1994).

Table 6. Reference Sources of Viscosity Data for Toluene

authors	method	accuracy/%	T range/ K	max p/MPa
Hammond et al., 1958	Ubbelohde capillary	0.2	293−354	0.1
Byers and Williams, 1987	Ubbelohde capillary	0.3	298−368	0.1
Gonçalves et al., 1987	Ubbelohde capillary	0.3	298−348	0.1
Kaiser et al., 1991	Ubbelohde capillary	0.3	218−378	0.1
Dymond and Robertson, 1985	capillary	0.2	288−393	0.1
Bridgman, 1926	falling body		303−348	1178
Kashiwagi and Makita, 1982	torsion. oscill. crystal	±1	298−348	112
Assael et al., 1991	vibrating wire	±0.5	303−323	71
Dymond et al., 1991	falling body	±4	298−373	500
Krall et al., 1992	oscillating disk	±0.5	298−424	30
Oliveira and Wakeham, 1992	vibrating wire	±0.5	303−348	52
dos Santos and de Castro, 1993, 1997	torsion. oscill. crystal	0.5	298−373	200
Dymond et al., 1995	falling body	±3−5	299−323	435

Discussion

Toluene. The two isotherms (298.15 K and 323.15 K) for toluene were determined as a check on accuracy. Toluene is a strong candidate as a reference standard for high-pressure viscometers due to its broad liquid range and ease of purification. Table 6 lists recent data sources for this system, some obtained as part of a study of this material by members of the IUPAC Subcommittee on Transport Properties. The data have been fitted to eqs 1 and 3, using a weighted method of nonlinear least squares regression (Harris, 1982; Harris et al., 1993). For consistency, the molar volumes required for this correlation were obtained from the equation of state used previously (Harris, 1993; Harris et al., 1993); these values differed from those used by the several reference sources by no more than ±0.1% and were generally much closer than this.

The combined data sets cover a large range of molar volume; Figure 1 shows the Dymond reduced viscosity η^* as a function of V_r for several sets, namely those of this work, Dymond et al. (1995), Kashiwagi and Makita (1982), and Kaiser et al. (1991). The first two sets reach the region where the viscosity increases rapidly with increasing density due to the high-pressures employed, and the last set, measured along the saturation line, also extends into this region as the measurements include values at temperatures as low as 218 K.

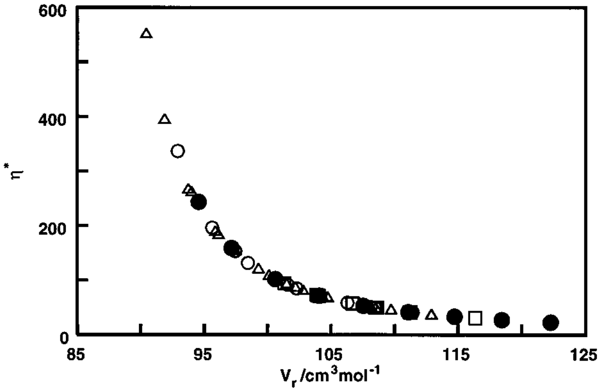

Figure 1. Dymond reduced viscosities η^* for toluene as a function of V_r: (○) this work, (△) Dymond et al. (1995), (□) Kashiwagi and Makita (1987), (●) Kaiser et al. (1991).

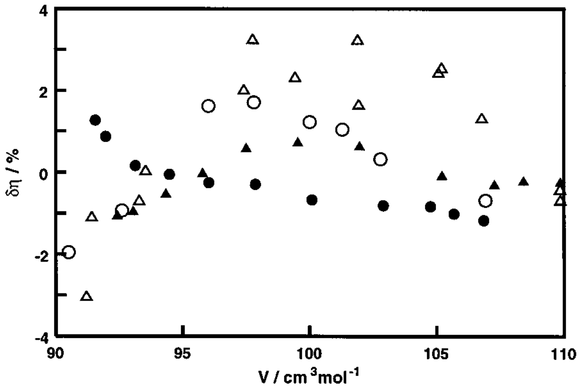

Figure 2. Residuals for the fit of eqs 1 and 3 to the viscosity of toluene as a function of molar volume: (●) 298 K, (▲) 323 K, this work; (○) 298 K, (△) 323 K, Dymond et al. (1995).

The data in the fit are weighted by the variance estimated by the authors in each case. Allowance is also made for errors in T and V, but these have negligible effect relative to those for the viscosity. Because most of the data lie in the region above 100 cm^3/mol, the residuals for data below this region are dependent to a certain extent on which data sets are combined.

The viscosities reported here have been compared with the literature values in two ways, first with the two data sets obtained by the method used here, that is with a falling-body viscometer, and second with all the data sets combined together (giving the V_r used in Figure 1). Table 7 lists the coefficients obtained from the various fits. A good fit was obtained by combination of our data with the falling-body results of Dymond et al. (1995); the standard deviation was 1.5% with the worst deviations being 1.2% for our data set and 3.2% for the other, which had an estimated precision and accuracy of 2 and 4% respectively. A deviation graph is shown as Figure 2. When the earlier falling-body data set of Dymond et al. (1991), which extends over a much larger temperature range, was added, the standard deviation increased to 2.1%, with the worst deviations being 1.6% for our data set, 3.5% for the 1996 Dymond set, and 5.7% for the 1991 Dymond set. The maximum deviation for the latter was therefore less than found previously (Harris et al., 1993), −12%, and this is now clearly seen to be due to the particular choice of data sets for comparison made at that time. Our present calculations show that the three sets of data obtained with falling-body viscometers are consistent with one another within their respective experimental errors.

The second comparison is of all the data sets taken together, with the omission of the falling-body data sets of Bridgman (1926), which diverge from the more recently obtained results. This resulted in residuals tending somewhat greater than experimental error for those data sets that extend into the region below 100 cm^3/mol, but the fit is generally very good above this value. (The difference in

Table 7. Coefficients for Eqs 1, 2, and 3 for Toluene[a]

					D^*	$(1/\eta^*)$
	$(1/\eta^*)$	$(1/\eta^*)$	$(1/\eta^*)$	$(1/\eta^*)$	(simultaneous fit)	
ζ_1	−0.453 915	−0.454 029	−0.480 423	−0.466 233	−3.007 80	0.451 830
$10^2\ \zeta_2$/mol cm^{-3}	0.231 119	0.260 829	0.275 341	0.269 573	1.762 92	0.260 566
$10^{-2}\ \zeta_3$/cm^3 mol^{-1}	−0.492 166	−0.436 216	−0.437 505	−0.432 787	−0.426 974	−0.434 525
$10^3\ \xi_1$/K^{-1}	−8.662 95	−0.867 336	−0.615 797	−0.576 297	−0.656 246	
$10^5\ \xi_2$/K^{-2}	10.678 2	0.393 520	0.141 091	0.106 122	−0.118 484	
T range/K	298−323	298−373	218−426	218−426	218−426	
stand devn/%	1.5	2.1	1.8	0.7	2.5	2.3
max devn/%	3.2	5.7	15.2	3.4	6.8	−10
data sets	this work + Dymond et al., 1995	this work + Dymond et al., 1995 and Dymond et al., 1991	all except Bridgman, 1926	all except falling-body data and Oliveira and Wakeham, 1992	Harris et al., 1993	see text

[a] $T_{\mathrm{ref}} = 273.15$ K in each case.

Table 8. Coefficients for Eqs 1, 2, and 3 for Octane[2]

					D^*	$(1/\eta^*)$
	$(1/\eta^*)$	$(1/\eta^*)$	$(1/\eta^*)$	$(1/\eta^*)$	(simultaneous fit)	
ζ_1	−0.379 296	−0.395 031	−0.379 413	0.392 240	−2.751 42	−0.378 812
$10^2\ \zeta_2$/mol cm^{-3}	0.144 104	0.149 532	0.144 040	0.148 675	1.066 64	0.144 773
$10^{-2}\ \zeta_3$/cm^3 mol^{-1}	−0.659 582	−0.662 205	−0.660 128	−0.661 262	−0.645 927	−0.655 416
$10^3\ \xi_1$/K^{-1}	−0.769 789	−0.714 723	−0.728 591	−0.681 074	−0.670 773	
$10^5\ \xi_2$/K^{-2}	0.256 964	0.232 924	0.186 898	0.186 475	0.246 007	
T range/K	283−353	283−353	283−373	283−373	248−348	283−353
stand devn/%	1.7	1.9	2.3	2.4	3.1	3.1
max devn/%	3.4	6.9	−7.1	−10.6	−7.2	7.4
data sets	this work	this work + Oliveira and Wakeham, 1992	this work + Dymond et al., 1981	this work + Oliveira and Wakeham, 1992	Harris et al., 1993	this work

[a] $T_{\mathrm{ref}} = 273.15$ K in each case.

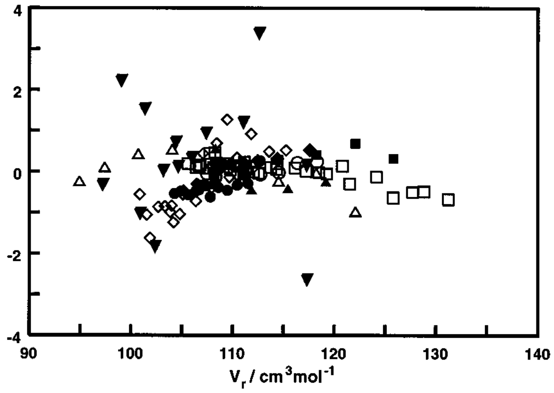

Figure 3. Residuals for the fit of eqs 1 and 3 to the viscosity of toluene as a function of reference molar volume, V_r: (●) Assael et al. (1991), (▲) Byers and Williams (1987), (■) Dymond and Robertson (1985), (◆) Gonçalves et al.. (1987), (▼) Vieira dos Santos and Nieto de Castro (1993, 1997), (○) Hammond et al. (1958), (△) Kaiser et al. (1991), (□) Krall et al. (1992), (◇) Kashiwagi and Makita (1982).

values for the parameter ξ_1, which governs the lateral shifts needed to combine isotherms, between the fit for our data combined with those of Dymond et al. (1995) and the values for the other combinations listed in Table 7 is solely due to the short temperature range for this data set.)

Another fit was made with all the falling-body viscometer points omitted. The data set of Oliveira and Wakeham (1992) was then seen to include some points with large deviations of up to −6.5% at 303 K: omission of this set produced a better fit with a standard deviation of only 0.7% and a maximum error of 3.4%. Coefficients are given in Table 7 and residuals are shown in Figure 3. This seems to be the best correlation up to about 200 MPa. Inclusion of the falling-body viscometer sets, however, again worsened the fit, with large residuals at high densities. It may be that the correlation equation is not suitable at such high densities where $(d\eta/d\rho)$ is large (Figure 1) or, given the fair fit for the falling-body viscometer data sets taken alone, that there is a yet unknown systematic error for this type of viscometer at high viscosities.

We have also combined our self-diffusion data (Harris et al., 1993) with the full set of viscosities using eqs 1−3, fitted simultaneously. The new coefficients are again given in Table 7. Due to the contribution of diffusion isotherms with points below 100 cm^3/mol, the worst viscosity residuals are improved somewhat, at the expense of a greater standard deviation overall.

Octane. Again the results have been fitted to eqs 1 and 3: the coefficients are given in Table 8. Figure 4 shows a plot of the residuals for each isotherm as a function of molar volume. There are systematic deviations at high pressures (low molar volumes), but the scatter is only of the order of ±1%, except for the three lowest and two highest pressures on the 283 K isotherm. Figure 5 shows the same residuals plotted against the viscosity. The sinusoidal pattern suggests that either the correlation is not a satisfactory representation of $\eta(T,V)$ for this system over such a range of volume and temperature or that the method of calibration (at atmospheric pressure with liquids having a range of viscosities) has introduced some systematic error. The joint fit with the diffusion coefficient (Table 8) leads to a similar conclusion. However, if one is willing to accept a tolerance of ±3%, then these fine details can be neglected.

Figure 6 shows deviations of the falling-body viscometer results of Dymond et al. (1981) from our smoothed results. They estimated their accuracy as ±2%. The difference between their results and ours is generally within the combined errors, except at high pressures where the deviations apparently become quite large. Again this could be due to the form of eq 1 if it is in fact unsatisfactory.

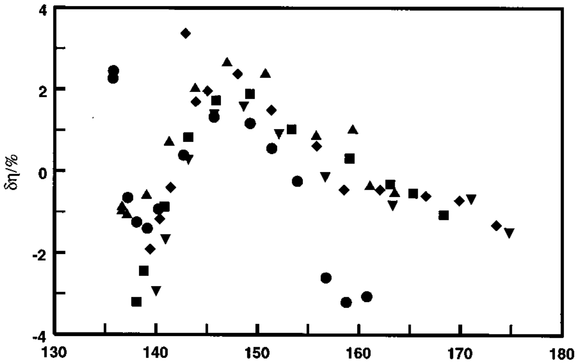

Figure 4. Residuals for the fit of eqs 1 and 3 to the viscosity of octane as a function of molar volume, this work: (●) 283 K, (▲) 298 K, (■) 323 K, (◆) 347.5 K, (▼) 353 K.

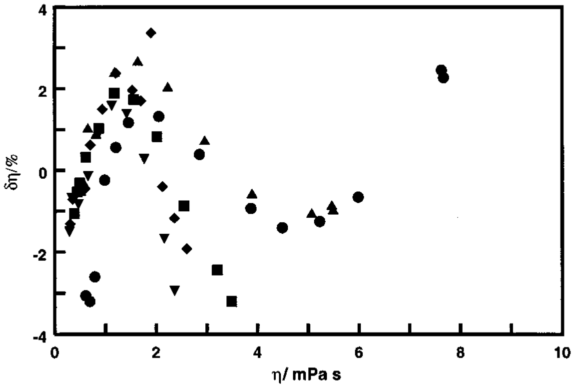

Figure 5. Residuals for the fit of eqs 1 and 3 to the viscosity of octane as a function of viscosity, this work: symbols as in Figure 3.

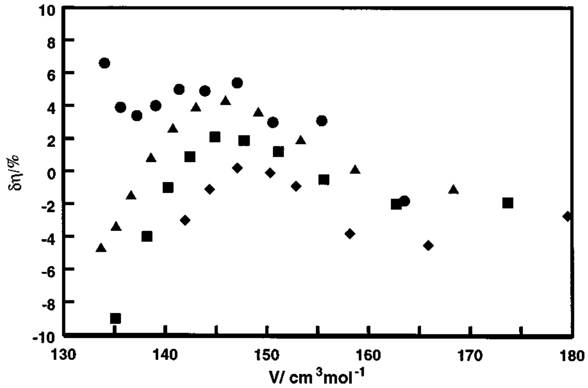

Figure 6. Differences between the viscosity of octane measured by Dymond et al. (1981) and the results of this work fitted to eqs 1 and 3: (●) 298 K, (▲) 323 K, (■) 348 K, (◆) 373 K.

Figures 7 and 8 are similar plots for the torsionally oscillating crystal viscometer results of Kashiwagi and Makita (1982), which have an accuracy of ±1% and of the vibrating wire viscometer results of Oliveira and Wakeham (1992), which have an accuracy of ±0.5%, respectively. Agreement is satisfactory for both, once it is realized that the residuals for the latter set follow those shown for our data in Figure 4.

So is the problem of the nonrandom residuals in Figure 4 due to the functional form adopted for the fitting function? Figure 9 shows residuals for a fit of the Kashi-

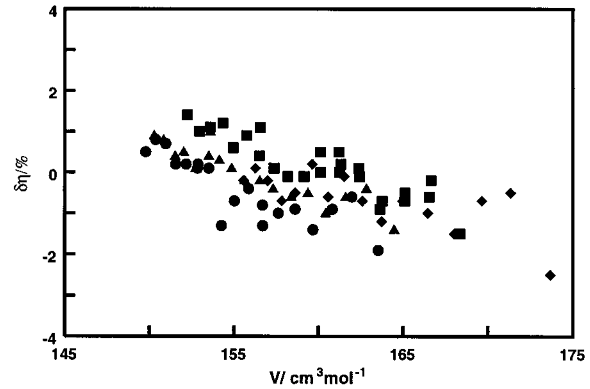

Figure 7. Differences between the viscosity of octane measured by Kashiwagi and Makita (1982) and the results of this work fitted to eqs 1 and 3: (●) 298 K, (▲) 303 K, (■) 323 K, (◆) 348 K.

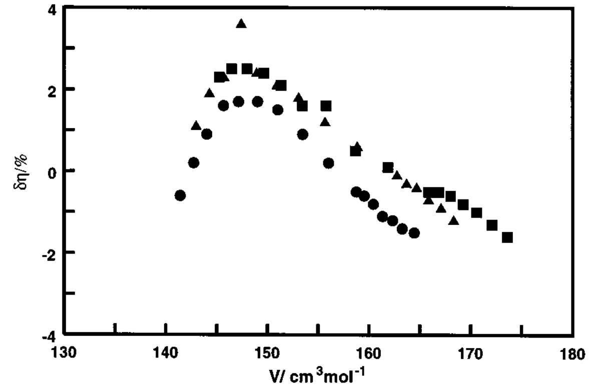

Figure 8. Differences between the viscosity of octane measured by Oliveira and Wakeham (1992) and the results of this work fitted to eqs 1 and 3: (●) 303 K, (▲) 323 K, (■) 348 K.

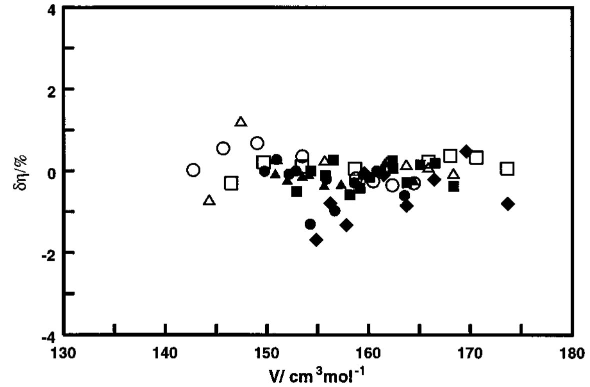

Figure 9. Residuals for the fit of eqs 1 and 3 to the viscosity of octane measured by Kashiwagi and Makita (1982) [(●) 298 K, (▲) 303 K, (■) 323 K, (◆) 348 K] and by Oliveira and Wakeham [(○) 303 K, (△) 323 K, (□) 348 K].

wagi−Makita and Oliveira−Wakeham data sets alone, which extend to 250 MPa. The fit is seen to be quite good, suggesting that eq 1 is indeed a reasonable fitting function. This has also been our experience for other systems, including hexane and hexadecane. It is probable therefore that improvement of the calibration method of our viscometer for high viscosities at high pressures may be necessary to reduce the uncertainty of the data below ±3%.

Conclusions

Measurements of the viscosity of toluene have been made at 298 K and 323 K at pressures up to 400 MPa with a falling-slug viscometer. They have been shown to be consistent with falling-body viscometer measurements made by Dymond et al. (1995) within the combined experimental errors.

Measurements have also been made of the viscosity of octane between 283 K and 348 K at pressures up to 375 MPa. Good agreement has been found with the torsionally oscillating crystal viscometer results of Kashiwagi and Makita (1982) and the vibrating wire viscometer results of Oliveira and Wakeham (1992), but there is poorer agreement with the falling-body data of Dymond et al. (1981) at high densities.

A correlation (eqs 1 and 3) for the viscosity of toluene has been produced using the best available data in the literature valid at pressures to 200 MPa. While the form of the correlation equations are such that they fit individual data sets and some combinations quite well, they fail to fit all the available data when combined into a single set. One is then faced with the difficulty of which data set(s) to exclude from the correlation. These sets have been obtained by different techniques based on different methods of calibration, and the more precise do not extend to the higher densities obtainable with the falling-body viscometers. Direct comparison is also biased by the larger number of points available at the lower densities. If the correlation is to be improved, measurements below 273 K at high densities where $(d\eta/d\rho)$ is large could be quite valuable.

It may be that the correlation equation is not suitable at very high densities where $(d\eta/d\rho)$ is large or that there is a yet unknown systematic error for this type of viscometer at high viscosities. However, the evidence suggests that eq 1 is a satisfactory function given that it can be used to correlate data sets obtained with the same or similar types of viscometer.

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