Temperature and Pressure Dependence of the Viscosity of Diisodecyl Phthalate at Temperatures between (0 and 100) °C and at Pressures to 1 GPa

Kenneth R. Harris*

School of Physical, Environmental and Mathematical Sciences, University College, University of New South Wales, Australian Defence Force Academy, Canberra, ACT 2600, Australia

Scott Bair

Center for High-Pressure Rheology, George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0405

There is an industrial requirement for a suitable reference material for viscosity measurements in the moderate to high viscosity region. Diisodecyl phthalate (DIDP) has been put forward as a candidate for this purpose. The field of elastohydrodynamics has a similar need for a reference lubricant that would allow the comparison of calculated contact behavior with experimental measurements. We report measurements of the viscosity of DIDP at atmospheric pressure between (0 and 100) °C and at high pressures to 1 GPa between (20 and 100) °C using three different falling body viscometers and samples from two different manufacturers. Densities obtained with a vibrating-tube densimeter are reported between (0 and 90) °C at atmospheric pressure.

Introduction

There is an industrial requirement for a suitable reference material for viscosity measurements in the moderate to high viscosity region [(10 to 1000) mPa·s]. Diisodecyl phthalate (DIDP) has been put forward as a candidate for this purpose[1−4] as it is chemically stable over a wide temperature range, has a low vapor pressure, and is a relatively inexpensive material. It is also useful to have high-pressure measurements for such a reference material to allow the calibration of instruments used under pressure in the oil extraction industry[5−7] and in the lubricants industry[8,9] and in addition to have high-pressure properties for a reference liquid with pressure−viscosity behavior similar to those of liquid lubricants used in high-pressure contacts. The measurements reported here are a contribution to a project of the International Association for Transport Properties,[4] members of which are making determinations of the viscosity of DIDP using viscometers of different types and operating principles.

Analysis of DIDP samples by GC−MS and ^{13}C NMR in our laboratory (see Figures 1 and 2) showed that they were actually mixtures of phthalate esters of a wide range of isomers of isodecyl alcohol. Correspondence with a number of manufacturers revealed that it is very likely that all commercial sources of DIDP available in bulk quantities are such isomeric mixtures. This may limit the applicability of DIDP as a reference material for viscometry as material from different sources, though nominally of high purity as a phthalate ester, will have different isomeric distributions, and the effect on the physical properties is unknown. We have examined three different grades of DIDP in three different high-pressure falling body viscometers in an attempt to answer this question, if only partially.

Experimental Section

Two DIDP samples were both obtained from Merck Australia. One (sample A) was DIDP "for synthesis" grade, Lot No. S14886; the second (sample B) was DIDP "GR for analysis" grade, Lot No. K22132622. The manufacturer gives purities of 99 % by acidimetry and 99.8 % by gas chromatographic analysis for these two lots, respectively. Both samples were dried for several weeks with 3 Å molecular sieves and filtered through a (40 to 60) μm filter prior to use in the Canberra instrument. Figure 1 shows ^{13}C NMR spectra obtained at 100.571 MHz with a Varian "Unity plus" 400 MHz spectrometer. For a pure substance, the resonances should be sharp distinguishable peaks (see, for example, Figure 2—2-ethylhexyl benzoate—and ref 10). The spectra obtained show sharp peaks for the phthalate carbons but a broad distribution for the alkyl carbons, indicating that the diisodecanol used in the manufacture of the ester was actually a mixture of isomers. This conclusion is reinforced by GC−MS analysis (using a Shimadzu GC17A gas chromatograph fitted with a J. W. Scientific DB5-MS 30 m × 0.25 mm column and employing a Shimadzu QP5000 mass spectroscopic detector), where a broad peak was obtained, which the detector partially resolved as a mixture of phthalate esters of C-10 alcohols.

The third sample (sample C) was obtained from ABCR GmbH, Karlsruhe, Germany. This sample had a density at 20 °C of 0.9676 g·cm^{-3}, a refractive index (n_D^{20}) of 1.4849, and an acid value of 0.06. The manufacturer confirmed that this was also an isomeric mixture,[11] and the NMR spectrum (Figure 1c) is very similar to that of the Merck samples.

Sample B was used in both the Canberra and Atlanta viscometers; samples A and C were used in the Canberra and Atlanta instruments, respectively. The molar mass was taken to be 446.662 g·mol^{-1} .

---

* Corresponding author. Email: k.harris@adfa.edu.au.

10.1021/je060382+ CCC: $37.00

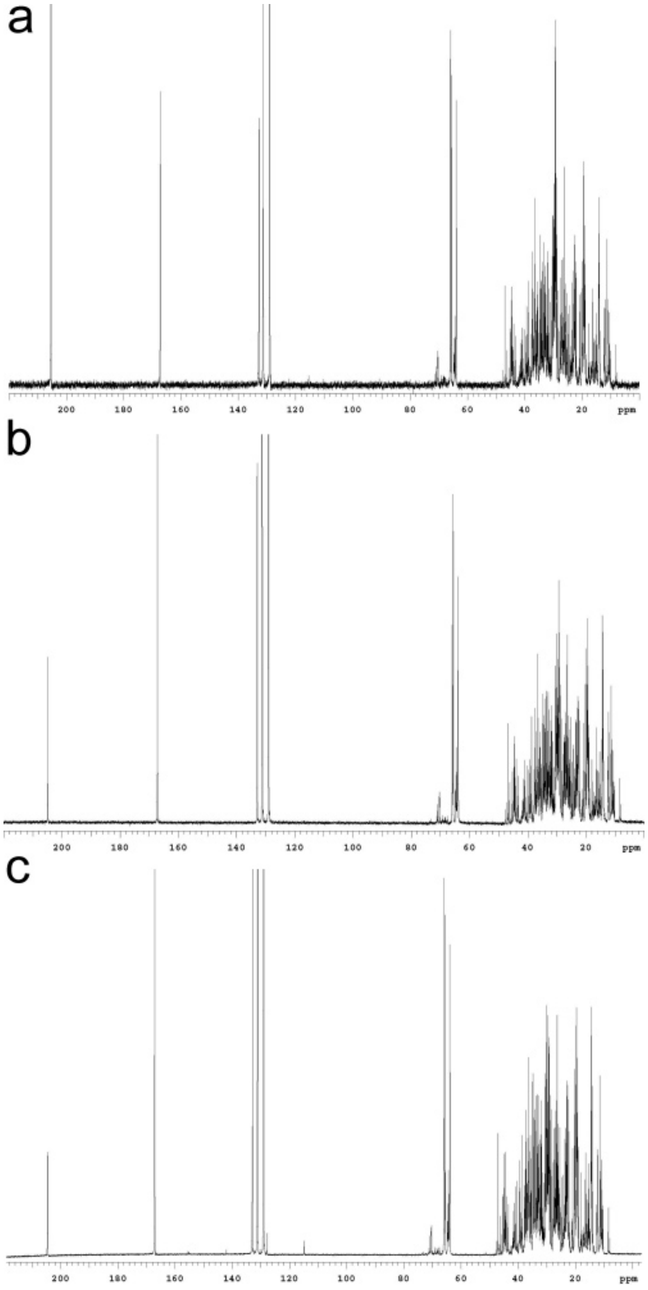

Figure 1. ^{13}C NMR spectra obtained at 100.571 MHz: (a) sample A, Merck 99 %; (b) sample B, Merck 99.8 %; (c) sample C, from ABCR GmbH. The resonances at 30 and 206 ppm are those from the solvent and deuterium-lock compound, $(CD_3)_2CO$.

Table 1. Parameters for Hayward Equation of State

	DIDP	EHB
α_{00}/MPa	−423.823	−659.430
$\alpha_{01} \times 10^{-3}$/(MPa·K)	602.491	649.426
α_{10}	0.283486	2.03369
α_{11}/K	1506.47	495.237
$\delta\rho$/%[a]	0.05	0.14

[a] Standard uncertainty of fit to the density.

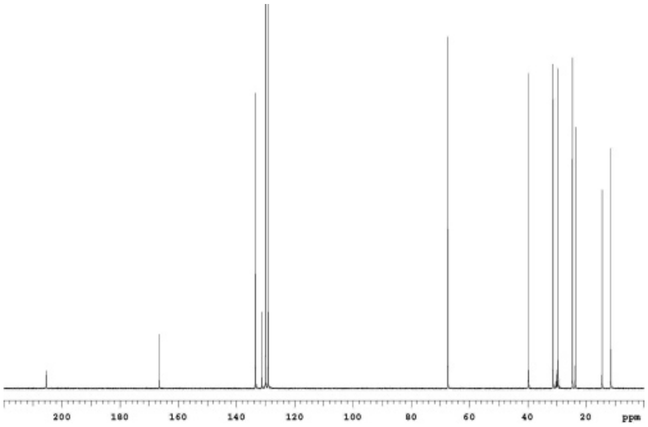

Figure 2. Same as in Figure 1, but for the ester 2-ethylhexyl benzoate. Note the sharp resonances.

Table 2. Density ρ of Samples A and B from θ = (0 to 90) °C

θ/°C	ρ/g·cm^{-3}	θ/°C	ρ/g·cm^{-3}
	Sample A (Merck, 99 %)		
0.00	0.98073	40.00	0.95220
10.00	0.97348	50.00	0.94512
20.00	0.96637	60.00	0.93805
25.00	0.96283	70.00	0.93099
30.00	0.95931	80.00	0.92395
30.00	0.95931	90.00	0.91691
30.00	0.95929		
	Sample B (Merck, 99.8 %)		
0.00	0.98075	40.00	0.95221
5.00	0.97712	50.00	0.94513
10.00	0.97349	60.00	0.93807
15.00	0.96989	70.00	0.93101
20.00	0.96638	80.00	0.92398
20.00	0.96637	80.00	0.92397
25.00	0.96284	90.00	0.91694
30.00	0.95930		

The Canberra falling body viscometer employed has been described previously.[12−15] This work employed sinkers of nominal diameters of (6.3 and 6.0) mm with calibrations covering the viscosity range (0.3 to 2875) mPa·s.[12−15] Platinum resistance thermometers calibrated between (−65 and 100) °C on ITS-90 to a tolerance of ± 8 mK were employed. The viscometer oil-bath temperature was controlled to within ± 0.01 K. The primary pressure gauge (400 MPa Heise CM) was calibrated against a deadweight tester, and pressures have an overall uncertainty of ± 0.2 MPa. The expanded uncertainty in the viscosity is estimated at ± 2 %.

Calculation of the viscosity η from fall times t requires knowledge of the density as a function of temperature T and pressure p. The working equation for the Canberra viscometer[13] is

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

where A is the calibration constant, α is the coefficient of thermal expansion, and β is the bulk compressibility of the sinker and tube material, so there is a buoyancy factor dependent on the ratio of the density of the fluid ρ to that of the sinker ρ_s. This varies slightly with temperature and pressure. For 316 stainless steel sinkers and DIDP, (ρ/ρ_s) lies between 0.125 and 0.155, so an error of ± (12 to 15) % in ρ lies within the reproducibility of our instrument, ± 1 %.

Recently Marsh measured pVT data for DIDP between (25 and 150) °C at pressures between (10 and 70) MPa.[16] These can be represented by the Hayward-type equation:[14]

$$K = (\alpha_{00} + \alpha_{10}/T) + (\alpha_{01} + \alpha_{11}/T)\,p \qquad (2)$$

where K is the secant bulk modulus [$K \equiv V_0(p - p_0)/(V_0 - V)$, where V is the specific volume at pressure p and the subscript 0 denotes the value at atmospheric pressure or on the saturation

Table 3. Viscosity η of Samples A and B from θ = (0 to 80) °C and at p = 0.1 MPa (Canberra Viscometer)

sinker diameter mm	θ °C	t s	V $cm^3 \cdot mol^{-1}$	ρ^a $g \cdot cm^{-3}$	η mPa·s	Re^b
Sample A (Merck, ~99 %)						
6.0	0.00	1792.6	455.46	0.98068	627.6	0.006
6.0	5.00	1123.5	457.13	0.97711	393.5	0.015
6.0	10.00	728.3	458.80	0.97354	255.2	0.036
6.0	15.00	487.6	460.49	0.96997	170.9	0.081
6.0	20.00	349.6	462.19	0.96641	122.6	0.16
6.0	25.00	250.1	463.90	0.96285	87.7	0.30
6.3	25.00	2783.5	463.90	0.96285	84.1	0.071
6.0	30.00	184.1	465.62	0.95929	64.6	0.56
6.3	30.00	2111.9	465.62	0.95929	63.8	0.12
6.0	35.00	139.4	467.35	0.95574	48.9	0.97
6.3	35.00	1574.3	467.35	0.95574	47.6	0.22
6.3	40.00	1208.3	469.09	0.95219	36.6	0.37
6.3	50.00	761.1	472.60	0.94511	23.0	0.93
6.3	60.00	511.3	476.17	0.93804	15.5	2.0
6.3	70.00	361.2	479.77	0.93099	11.0	4.0
6.3	80.00	267.6	483.43	0.92395	8.12	7.3
Sample B (Merck, 99.8 %)						
6.0	0.00	1897.8	455.46	0.98068	664.5	0.005
6.0	0.00	1897.8	455.46	0.98068	664.5	0.005
6.0	5.00	1172.9	457.13	0.97710	410.8	0.014
6.0	5.00	1172.0	457.13	0.97710	410.5	0.014
6.0	10.00	761.4	458.81	0.97353	266.8	0.033
6.0	10.00	761.6	458.81	0.97353	266.8	0.033
6.0	15.00	509.5	460.50	0.96996	178.6	0.074
6.0	15.00	509.5	460.50	0.96996	178.6	0.074
6.0	20.00	352.5	462.19	0.96640	123.6	0.15
6.0	20.00	352.7	462.19	0.96640	123.7	0.15
6.0	20.00	352.3	462.19	0.96640	123.5	0.15
6.0	20.00	349.2	462.19	0.96640	122.5	0.16
6.0	25.00	252.0	463.90	0.96284	88.4	0.30
6.0	25.00	252.1	463.90	0.96284	88.4	0.30
6.0	30.00	185.6	465.62	0.95928	65.1	0.55
6.0	30.00	185.1	465.62	0.95928	65.0	0.55
6.0	35.00	139.8	467.35	0.95573	49.1	0.96
6.0	35.00	138.4	467.35	0.95573	48.6	0.98
6.0	40.00	107.2	469.09	0.95219	37.6	1.6
6.0	40.00	106.7	469.09	0.95219	37.5	1.6
6.0	40.00	106.5	469.09	0.95219	37.4	1.7
6.0	50.00	67.3	472.60	0.94511	23.7	4.1
6.0	50.00	67.4	472.60	0.94511	23.7	4.1
6.3	50.00	784.1	472.60	0.94511	23.7	0.90
6.0	60.00	45.1	476.16	0.93805	15.9	9.06
6.0	60.00	45.0	476.16	0.93805	15.8	9.12
6.0	60.00	45.0	476.16	0.93805	15.8	9.14
6.3	60.00	526.9	476.16	0.93805	16.0	1.98
6.3	60.00	526.6	476.16	0.93805	16.0	1.98
6.0	65.00	37.7	477.96	0.93452	13.3	13.0
6.0	65.00	37.6	477.96	0.93452	13.2	13.0
6.0	65.00	37.6	477.96	0.93452	13.2	13.0
6.0	65.00	37.1	477.96	0.93452	13.0	13.4
6.3	65.00	440.3	477.96	0.93452	13.3	2.8
6.3	65.00	439.8	477.96	0.93452	13.3	2.8
6.0	70.00	31.6	479.77	0.93100	11.1	18.4
6.0	70.00	31.7	479.77	0.93100	11.2	18.2
6.3	70.00	371.5	479.77	0.93100	11.3	3.9
6.3	75.00	317.5	481.58	0.92749	9.63	5.4
6.3	75.00	318.2	481.58	0.92749	9.65	5.4
6.3	80.00	275.2	483.41	0.92398	8.35	7.1
6.3	80.00	275.3	483.41	0.92398	8.35	7.1

[a] Calculated from eq 3a for sample A and from eq 3b for sample B. [b] Reynolds number for annular flow: $Re = 2r_1^2\rho v/((r_2 - r_1)\eta)$ where v is the terminal velocity of the sinker and r_1 and r_2 are the radii of the sinker and tube, respectively.

Table 4. Viscosity η of Sample B (Merck, 99.8 %) from θ = (20 to 75) °C and at p = (0.5 to 400) MPa (Canberra Viscometer)

sinker diameter mm	θ °C	p MPa	t s	V $cm^3 \cdot mol^{-1}$	ρ $g \cdot cm^{-3}$	η mPa·s	Re^a
6.0	20.00	19.4	578.1	457.06	0.97725	202.4	0.06
6.0	20.00	39.7	958.5	452.27	0.98760	335.0	0.02
6.0	20.00	59.5	1531.5	448.14	0.99671	534.5	0.008
6.0	20.00	103.6	4124.9	440.38	1.01426	1435.6	0.001
6.0	20.00	118.2	5697.6	438.17	1.01939	1981.5	0.001
6.0	20.00	118.9	5848.5	438.07	1.01962	2033.8	0.00
6.0	20.00	159.6	13597.0	432.66	1.03235	4719.2	0.0001
6.0	25.00	25.4	472.8	457.12	0.97712	165.5	0.09
6.0	25.00	50.7	859.5	451.32	0.98967	300.2	0.03
6.0	25.00	75.5	1505.6	446.40	1.00058	525.0	0.01
6.0	25.00	100.6	2598.4	442.05	1.01042	904.7	0.00
6.0	40.00	0.7	109.0	468.90	0.95257	38.3	1.6
6.0	40.00	25.8	188.3	461.71	0.96740	66.0	0.54
6.0	40.00	50.6	315.4	455.62	0.98035	110.3	0.20
6.0	40.00	75.5	518.7	450.33	0.99186	181.0	0.07
6.0	40.00	100.3	836.9	445.72	1.00211	291.6	0.03
6.0	40.00	125.1	1331.3	441.66	1.01132	463.2	0.01
6.0	40.00	150.4	2108.4	437.97	1.01984	732.6	0.00
6.0	40.00	175.8	3295.1	434.69	1.02754	1143.6	0.00
6.0	40.00	197.6	4845.0	432.13	1.03363	1680.0	0.00
6.0	40.00	227.9	7714.2	428.93	1.04133	2671.7	0.0003
6.0	40.00	252.0	11364	426.64	1.04693	3932.3	0.0002
6.0	65.00	0.5	37.9	477.83	0.93477	13.3	12.8
6.0	65.00	30.5	64.7	468.30	0.95380	22.7	4.5
6.0	65.00	60.7	108.2	460.36	0.97025	37.8	1.6
6.0	65.00	90.6	174.6	453.76	0.98437	60.9	0.64
6.3	65.00	99.5	2358.9	451.99	0.98821	70.90	0.10
6.0	65.00	120.5	276.3	448.13	0.99672	96.3	0.26
6.0	65.00	150.1	430.0	443.32	1.00755	149.6	0.11
6.0	65.00	180.4	660.1	439.01	1.01742	229.2	0.05
6.0	65.00	200.6	887.1	436.44	1.02342	307.8	0.03
6.0	65.00	250.7	1775.9	430.91	1.03655	614.9	0.01
6.0	65.00	275.6	2475.8	428.53	1.04231	856.5	0.003
6.0	65.00	301.0	3482.0	426.31	1.04774	1203.7	0.002
6.0	65.00	321.8	4547.5	424.62	1.05191	1571.0	0.001
6.0	65.00	352.7	6898.3	422.33	1.05763	2381.0	0.0004
6.0	65.00	370.5	8691.8	421.10	1.06070	2998.7	0.0003
6.0	65.00	394.4	11617.0	419.56	1.06461	4005.5	0.0002
6.3	75.00	11.1	386.7	477.67	0.93509	11.7	3.7
6.3	75.00	26.5	500.3	472.67	0.94497	15.1	2.2
6.3	75.00	52.6	758.4	465.26	0.96002	22.9	0.98
6.0	75.00	78.9	96.6	458.86	0.97341	33.7	2.07
6.3	75.00	81.0	1163.9	458.40	0.97439	35.0	0.42
6.0	75.00	105.7	142.4	453.24	0.98549	49.67	0.96
6.3	75.00	124.2	2171.0	449.78	0.99306	65.18	0.12
6.0	75.00	125.7	189.4	449.51	0.99367	66.0	0.55
6.0	75.00	149.8	264.3	445.48	1.00265	92.0	0.29
6.0	75.00	175.7	375.0	441.64	1.01138	130.3	0.14
6.3	75.00	202.3	6238.2	438.10	1.01954	186.52	0.02
6.0	75.00	225.4	721.0	435.33	1.02603	250.0	0.04
6.0	75.00	274.7	1350.5	430.18	1.03830	467.3	0.01
6.0	75.00	275.7	1364.8	430.10	1.03852	472.3	0.01
6.0	75.00	324.9	2508.8	425.81	1.04896	866.8	0.003
6.0	75.00	372.5	4467.8	422.28	1.05774	1541.5	0.001

[a] Reynolds number for annular flow: $Re = 2r_1^2\rho v/((r_2 - r_1)\eta)$ where v is the terminal velocity of the sinker and r_1 and r_2 are the radii of the sinker and tube, respectively.

line]. The parameters are given in Table 1. We have also found that the pVT data for the ester 2-ethylhexyl benzoate[17] can be adequately represented from (−20 to 100) °C at pressures to 450 MPa by the same linear form. This suggests that a linear dependence of K on pressure is likely to be a sufficient approximation for estimation of the densities required for the viscometer buoyancy term for DIDP to similar pressures. This has been done by combination of eq 2 with our own atmospheric pressure densities. However, it should be noted that data for the diester bis(2-ethylhexyl)phthalate from the ASME Pressure−Viscosity Report[18] indicates that this form is overly stiff at pressures above 400 MPa. For n-alkanes and substituted benzenes, for example, higher terms to the fourth order are required in eq 2 for pressures of the order of (200 to 400) MPa.[19,20] The pressure for eq 2 is unbounded for $\rho = \rho_0(a_{01} + a_{11}/T)/(a_{01} + a_{11}/T - 1)$, an experimentally accessible density

Table 5. Viscosity η of Samples B and C from $\theta = (40 \text{ to } 100)$ °C and at $p = (0.1 \text{ to } 1000)$ MPa (Atlanta Viscometers)

Sample B (Merck, 99.8 %)

θ / °C	p / MPa	η / Pa·s	θ / °C	p / MPa	η / Pa·s
Alpha Viscometer					
40.0	0.1	0.0376	65.0	200	0.291
40.0	25	0.0654	65.0	300	1.103
40.0	50	0.1094	100.0	0.1	0.00467
40.0	100	0.290	100.0	25	0.00673
40.0	200	1.665	100.0	50	0.00966
65.0	0.1	0.0132	100.0	100	0.0180
65.0	25	0.0202	100.0	200	0.0566
65.0	50	0.0307	100.0	300	0.163
65.0	100	0.0677	100.0	400	0.442
MHP Viscometer					
40.0	200	1.58	65.0	600	45.5
40.0	252	3.75	65.0	700	160
40.0	300	8.11	65.0	800	517
40.0	400	36.3	65.0	900	1720
40.0	500	168	65.0	1000	7420
40.0	600	782	100.0	400	0.463
40.0	700	3820	100.0	500	1.18
40.0	800	23600	100.0	600	2.97
65.0	300	1.17	100.0	700	7.19
65.0	394	3.89	100.0	800	17.5
65.0	400	4.28	100.0	900	41.9
65.0	500	14.2	100.0	1000	107

Sample C (ABCR)

θ / °C	p / MPa	η / Pa·s	θ / °C	p / MPa	η / Pa·s
Alpha Viscometer					
40.0	0.1	0.0368	65.0	300	1.07
40.0	25	0.0639	100.0	0.1	0.0047
40.0	50	0.107	100.0	25	0.00686
40.0	100	0.273	100.0	50	0.00977
65.0	0.1	0.01308	100.0	100	0.0185
65.0	50	0.0311	100.0	200	0.0578
65.0	100	0.0694	100.0	300	0.166
65.0	200	0.286	100.0	400	0.437
MHP Viscometer					
40.0	100	0.271	65.0	600	43.5
40.0	200	1.53	65.0	700	146
40.0	300	7.27	65.0	800	452
40.0	400	33.7	65.0	900	1556
40.0	500	158	65.0	1000	6141
40.0	600	694	100.0	300	0.165
40.0	700	3410	100.0	400	0.453
40.0	800	19800	100.0	500	1.152
65.0	200	0.299	100.0	600	2.83
65.0	300	1.131	100.0	700	6.91
65.0	400	4.09	100.0	800	16.7
65.0	500	13.1	100.0	900	40.9
			100.0	1000	101.9

for many materials. Our adoption of the linear form in this particular case is entirely pragmatic, given the short pressure range of the available *pVT* data and the small effect of the uncertainty in the density on the buoyancy term for the viscometer.

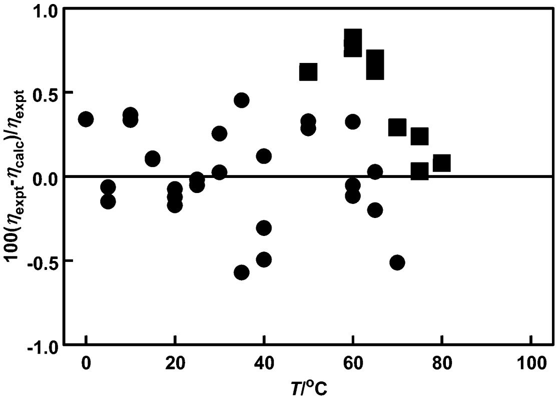

Figure 3. Residuals for the fit of sample B viscosity results at atmospheric pressure to the Barlow−Lamb equation (eq 4): ●, 6.0 mm sinker; ■, 6.3 mm sinker.

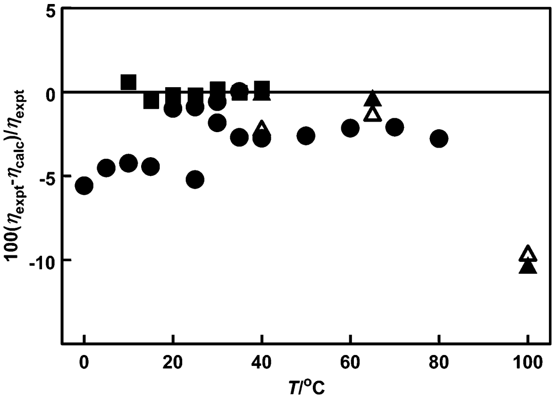

Figure 4. Comparison between the viscosities of different grades of DIDP with that of sample B (eq 4), all at atmospheric pressure: ■, ref 2, sample B; ▲, this work, Atlanta alpha viscometer, Sample B; ●, this work, Canberra viscometer, sample A; △, this work, Atlanta alpha viscometer, sample C.

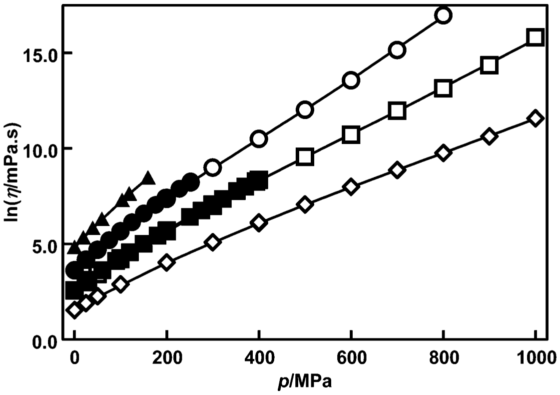

Figure 5. High-pressure isotherms for sample B (Merck, 99.8 %). The (25 and 75) °C isotherms have been omitted for clarity. Filled symbols, Canberra viscometer; open symbols, Atlanta viscometers. ▲ and △, 20 °C; ● and ○, 40 °C; ■ and □, 65 °C; ◇, 100 °C.

The Atlanta instruments have also been described elsewhere.[21,22] Two falling body viscometers were employed here. The "alpha" viscometer[21] has a pressure capability of 450 MPa, which is appropriate for the measurement of the pressure−viscosity coefficient,[8] α*, that is useful for the calculation of the thickness of the lubricant films in operating machine components. The "MHP" viscometer[22] has a pressure capability of 1.0 GPa, which is appropriate for the measurement of the viscosity that exists in the load supporting region of lubricated contacts. The viscosity at these high pressures is the property that has the strongest influence on the friction in a concentrated contact.

The alpha viscometer utilizes a guided "solid" steel sinker with density of 7.8 g·cm^{-3}. The estimated uncertainties are ± 1 MPa for pressure, ± 1 K for temperature, and ± 3 % for viscosity. The MPH viscometer employs a guided hollow sinker fabricated from a tantalum tube surrounded by a thin steel shell for inductive magnetic detection. The average density of this sinker is 13.3 g·cm^{-3}. The estimated uncertainties are ± 2 MPa for pressure, ± 1 K for temperature, and ± 4 % for viscosity. The increase in density of the sample liquid at high pressure was estimated from a universal equation of state. There is no

Table 6. Coefficients of Best Fit for Equations 4 and 5

	sample A, Canberra data		sample B, Canberra data		sample B, all data	
			Barlow−Lamb, eq 4			
ln (A/mPa·s)	−0.31500	± 0.0015	−0.31669	± 0.0027	−0.32959	± 0.0072
$B \times 10^{-10}$ /K^4	3.7687	± 0.012	3.7925	± 0.0024	± 3.8026	± 0.0065
standard uncertainty of fit	1.5 %		0.5 %		0.6 %	
			VFT, eq 5			
ln (A'/mPa·s)	−3.0871	± 0.12	− 2.8720	± 0.041	−2.9351	± 0.042
B'/K	902.05	± 30	848.47	± 10	863.28	± 11
T_0/K	178.578	± 2.0	182.717	± 0.73	181.729	± 0.77
D[a]	5.05		4.64		4.75	
standard uncertainty of fit	1.5 %		0.8 %		0.8 %	

[a] Angell strength factor (B'/ T_0).

provision for refrigeration so that only temperatures above ambient can be controlled.

Densities at atmospheric pressure for samples A and B were determined with an Anton-Paar DMA5000 vibrating-tube densimeter with an expanded uncertainty of 0.000 05 g·cm^{-3}. The in-built viscosity correction for this instrument has been checked using reference materials with a viscosity as high as 16.2 Pa·s.[14,15]

Results and Discussion

The density (ρ) results at atmospheric pressure are presented in Table 2 and can be represented by the polynomials:

$$\rho(\text{sample A}, 0 \le \theta/°\text{C} \le 80)/\text{g·cm}^{-3} = 0.980683 - 7.15300 \times 10^{-4}\,(\theta/°\text{C}) + 7.64592 \times 10^{-8}\,(\theta/°\text{C})^2 \quad (3a)$$

$$\rho(\text{sample B}, 0 \le \theta/°\text{C} \le 90)/\text{g·cm}^{-3} = 0.980677 - 7.15697 \times 10^{-4}\,(\theta/°\text{C}) + 8.65649 \times 10^{-8}\,(\theta/°\text{C})^2 \quad (3b)$$

both with a standard uncertainty of fit of ± 0.000 03 g·cm^{-3}. The densities of the two samples were essentially identical within experimental error, despite differences apparent in the isomeric distribution (Figure 1). For sample B, there is excellent agreement with the results of Caetano et al.[2] (average deviation 0.003 %, maximum deviation 0.009 %, our results being the lower), who examined a sample from the same manufacturer and batch between (10 and 40) °C.

The viscosities are presented in Tables 3 and 4 (Canberra) and in Table 5 (Atlanta). Very good agreement was obtained between the results for the two sinkers employed in the Canberra viscometer (Figure 3).

The atmospheric pressure results (Table 3) were fitted to the Barlow−Lamb equation:[23]

$$\eta = A \exp(B/T^4) \quad (4)$$

(found to be superior, in this particular case, to the Litovitz equation previously employed with ionic liquids[14,15]) and the Vogel−Fulcher−Tammann (VFT) equation:[24]

$$\eta = A' \exp(B'/(T - T_0)) \quad (5)$$

with coefficients being given in Table 6. The Angell strength parameter D ($\equiv B'/T_0$) is small for "fragile" liquids, which lose short-range order above the glass transition with increasing temperature, and large for "strong" liquids, which retain short-range order under these circumstances, with the viscosity tending toward Andrade (or Arrhenius) temperature dependence.

For the atmospheric pressure data, Figure 4 shows the deviations of our results for samples A and C, the Atlanta sample B, and those of ref 2 (which replace the original set of ref 1) from the fit of eq 4 to the Canberra sample B results. For sample B, the results of Caetano et al.[2] are in excellent agreement with the Canberra data: the Atlanta results agree very well at (40 and 65) °C but are low at 100 °C (the VFT equation gives a smaller residual for this point, at the expense of the 80 °C data). Sample A (Merck synthesis grade, 99 %) is generally of lower viscosity (average (−2.7 ± 1.7) %), with greatest differences appearing at lower temperatures. Sample C (ABCR GmbH) also gives lower viscosities.

Table 7. Fit of ln(η(T,p)) to Polynomials in the Pressure, p: ln(η/mPa·s) = $a_0 + a_1p + a_2p^2 + a_3p^3$

θ / °C	$p_{\max}$ / GPa	a_0	$10^2\,a_1$ / MPa^{-1}	$10^6\,a_2$ / MPa^{-2}	$10^9\,a_3$ / MPa^{-3}	s[a]
			Sample B, Atlanta Viscometers			
40	0.8	3.65693	2.10740	−14.0244	10.6121	2.3
65	1	4.32532	1.70594	−8.60191	4.74399	3.0
100	1	5.32911	1.34145	−6.27885	2.86558	2.1
			Sample B, Canberra Viscometer			
20	0.15	4.81382	2.56738	−17.9286		0.7
25	0.1	4.48007	2.51640	−20.2039		0.2
40	0.25	3.62567	2.19755	−15.5139	6.09086	0.7
65	0.4	2.58265	1.79995	−14.0857	13.3546	0.8
75	0.38	2.27196	1.67896	−13.5469	13.5252	0.7
			Sample C, Atlanta Viscometers			
40	0.8	3.26447	2.06649	−13.0288	9.69785	2.5
65	1	4.31194	1.69257	−8.56353	4.65659	2.8
100	1	5.31373	1.34631	−6.68304	3.17109	2.2

[a] Standard percentage uncertainty of the fit to η.

Figure 5 shows the high pressure isotherms for ln η. Those at lower temperature show the inflection typical of many liquids,[25] and all except the two shortest [(20 and 25) °C] are best represented as cubic polynomials in the pressure (Table 7). The pressure derivative function, $\alpha_p \equiv 1/[\sqrt{(\partial \ln \eta/\partial p)_T}]$,[26] has maxima at approximately (450, 600, and 750) MPa at (40, 65, and 100) °C respectively.

To fit the data sets as a whole as a function of temperature and pressure, we have used a high-pressure form of the VFT equation,[14] modified to accommodate the inflection in ln η:

$$\eta = \exp(a + bp + cp^2 + dp^3 + (e + fp + gp^2 + hp^3)/(T - T_0)) \quad (6)$$

(the coefficients are given in Table 8 and the residuals for the high pressure isotherms are shown in Figure 6a,b) and the Roelands equation,[27] often used in lubricant rheology:

$$\eta = \eta_R \exp\left\{\left(\ln\frac{\eta_R}{\eta_p}\right)\left[-1 + \left(1 - \frac{p}{p_p}\right)^z \left(\frac{T_R - T_\infty}{T - T_\infty}\right)^s\right]\right\} \quad (7)$$

where η_R, z, and s are coefficients of best fit. T_R is chosen as a reference isotherm within the data set (40 °C). The pole viscosity

Table 8. Coefficients of Best Fit for Equation 6

	sample B, Canberra viscometer	sample B, all data	sample B, Atlanta viscometers	sample C, Atlanta viscometers
a	−2.9758 ± 0.054	−2.9225 ± 0.083	−2.7175 ± 0.24	−9.6364 ± 0.23
$b \times 10^3$/MPa^{-1}	−1.0997 ± 0.32	−2.0531 ± 0.38	0.4356 ± 1.44	1.8975 ± 0.87
$c \times 10^6$/MPa^{-2}	−0.6203 ± 1.5	3.9406 ± 1.4	−0.1150 ± 3.6	−5.2288 ± 0.71
$d \times 10^9$ /MPa^{-3}		−7.1921 ± 1.3	−4.1266 ± 2.6	
e/K	875.319 ± 13.7	863.82 ± 21.2	778.07 ± 64.1	789.2 ± 65.2
f/(K·MPa^{-1})	3.0406 ± 0.052	3.0615 ± 0.070	2.3920 ± 0.25	2.1719 ± 0.20
$g \times 10^3$ /(K·MPa^{-2})	−2.3411 ± 0.21	−2.2078 ± 0.22	−1.1817 ± 0.52	−0.3969 ± 0.12
$h \times 10^6$ /(K·MPa^{-3})	2.4454 ± 0.20	2.0690 ± 0.21	1.2896 ± 0.37	0.6529 ± 0.061
T_0/K	180.76 ± 0.97	181.51 ± 1.5	191.70 ± 5.6	190.17 ± 5.9
standard uncertainty of fit/%	1.3	4.7	3.2	3.2

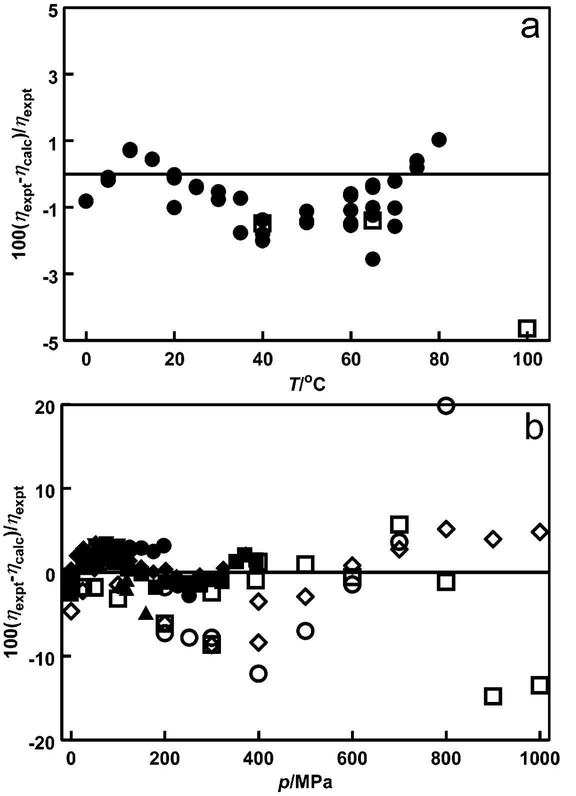

Figure 6. (a) Residuals for the fit of atmospheric pressure sample B viscosity results to the modified VFT equation (eq 6): ●, Canberra viscometer; ■, Atlanta alpha viscometer. (b) Residuals for the fit of the high-pressure sample B viscosity results to the modified VFT equation (eq 6). Canberra viscometer: ▲, 20 °C; ▼, 25 °C; ●, 40 °C; ■, 65 °C; ◆, 75 °C. Atlanta viscometers: ○, 40 °C; □, 65 °C; ◇, 75 °C.

Table 9. Coefficients of Best Fit for the Roelands Equation (eq 7) for Sample B[a]

	Canberra viscometer	Atlanta viscometers	combined data
η_R/Pa·s	0.0391	0.0388	0.0392
z	0.657	0.649	0.655
s	1.367	1.359	1.369
stndard uncertainty of fit/%	1.8	2.6	2.6

[a] Pressure limits: $T \leq 40$ °C, $p \leq 250$ MPa; $65 \leq T/$ °C ≤ 40, $p \leq 300$ MPa; $T = 100$ °C, $p \leq 400$ MPa.

(η_p), pole pressure (p_p), and divergence temperature (T_∞) are set at "universal" values of 63.1 μPa·s, −196 MPa, and −135 °C, respectively.[27] Neither equation is satisfactory at the highest pressures, and the Roelands fit is best applied below the isotherm inflection pressures.[27] Coefficients are given in Table 9.

The difference between the viscosity of samples B and C increases remarkably with pressure at low temperature reaching to nearly 20 % (see Table 5). This improved discrimination with increasing pressure is apparently not unusual among isomers.[28]

Conclusions

We have compared the viscosity of DIDP of several grades from different sources using three falling body viscometers. At atmospheric pressure, our results agree well with those of Caetano et al.[2] for Merck "GR for analysis" grade (99.8 %), but we find significant differences between this grade and Merck "for synthesis" grade (99 %) and the ABCR product. We find essentially no difference between the densities of the two Merck grades, so the viscosity appears to be the property more sensitive to differences in purity and/or composition. The question of the effect of differences in the distribution of isomers in DIDP samples remains open, although it appears from the results of this work that it is more likely that changes to the isomeric distribution do change the viscosity. Nevertheless, DIDP may still be a potential moderate to high-viscosity calibrant for industrial viscometers, provided that one grade from one source is agreed on for this purpose.

The viscosity of DIDP has a pressure dependence similar to those of mineral oils that are used for the blending of lubricants such as gear oils, making this material a useful reference for laboratories comparing calculations with experimental measurements of lubricant performance. However we note that a number of highly viscous fluids (e.g., squalane[29] as well as other esters such as 2-ethylhexyl benzoate and bis(2-ethylhexyl) phthalate, that are available as single isomers) may also be suitable candidate materials for use as high-viscosity calibrants. Some measurements, including *pVT* data, are already in the literature (2-ethylhexyl benzoate[17] and 2-ethylhexyl cyclohexanecarboxylate[30]). We intend further high-pressure measurements on a number of these substances.

Acknowledgment

We thank Prof. João Fareleira (Instituto Superior Técnico, Lisbon, Portugal) for suggesting these measurements. Prof. Ken Marsh and Dr. Mohamed Kandil (University of Canterbury, Christchurch, NZ) kindly made their *pVT* data available to us prior to publication. We are grateful to Dr. Lawrie Woolf for assistance with the density measurements and to Dr. Barry Gray for the ^{13}C NMR spectra determination and the GC−MS analyses (UNSW@ADFA).

Literature Cited

(1) Caetano, F. J. P.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P.; Wakeham, W. A. Viscosity of diisodecyl phthalate: a potential standard of moderate viscosity. *Int. J. Thermophys.* **2004**, *25*, 1311−1322.

(2) Caetano, F. J. P.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P.; Wakeham, W. A. New measurements of the viscosity of diisodecyl phthalate using a vibrating wire technique. *J. Chem. Eng. Data* **2005**, *50*, 1875−1878.

(3) Caetano, F. J. P.; Fareleira, J. M. N. A.; Fernandes, A. C.; Oliveira, C. M. B. P.; Serro, A. P.; Simões de Almeida, I. M.; Wakeham, W. A. Diisodecylphthalate (DIDP)—a potential standard of moderate viscosity: surface tension measurements and water content effect on viscosity. *Fluid Phase Equilib.* **2006**, *245*, 1−5.

(4) Caetano, F. J. P.; Fareleira, J. M. N. A.; Fröba, A. P.; Harris, K. R.; Leipertz, A.; Oliveira, C. M. B. P.; Wakeham, W. A. An industrial reference fluid for moderately high viscosity. *Int. J. Thermophys*. Manuscript in preparation.

(5) Lundstrom, R.; Goodwin, A. R. H.; Hsu, K.; Frels, M.; Caudwell, D. R.; Trusler, J. P. M.; Marsh, K. N. Measurement of the viscosity and density of two reference fluids, with nominal viscosities at $T = 298$ K and $p = 0.1$ MPa of (16 and 29) mPa·s, at temperatures between (298 and 393) K and pressures below 55 MPa. *J. Chem. Eng. Data* **2005**, *50*, 1377−1388; errata, 1787.

(6) Sopkow, T.; Goodwin, A. R. H.; Hsu, K. Vibrating wire viscometer with nominal wire diameter of 0.15 mm: measurement of the viscosity of two certified reference fluids, with nominal viscosities at $T = 298$ K and $p = 0.1$ MPa of (16 and 29) mPa·s, at temperatures between (298 and 353) K and pressures below 55 MPa. *J. Chem. Eng. Data* **2005**, *50*, 1732−1735.

(7) Kandil, M.; Harris, K. R.; Goodwin, A. R. H.; Hsu, K.; Marsh, K. N. Measurement of the viscosity and density of a reference fluid, with nominal viscosity at $T = 298$ K and $p = 0.1$ MPa of 29 mPa·s, at temperatures between (273 and 423) K and pressures below 275 MPa. *J. Chem. Eng. Data* **2006**, *51*, xxxx−xxxx.

(8) Glovnea, R. P.; Olver, A. V.; Spikes, H. A. Experimental investigation of the effect of speed and load on film thickness in elastohydrodynamic contact. *Tribol. Trans.* **2005**, *48*, 328−335.

(9) Bair, S.; Liu, Y.; Wang, Q. J. The pressure−viscosity coefficient for newtonian EHL film thickness with general piezoviscous response. *J. Tribol.* **2006**, *123*, 624−631.

(10) Kim, Y. J.; Jonas, J. High pressure ^{13}C NMR study of the motional dynamics of liquid bis(2-ethylhexyl) phthalate. *J. Phys. Chem.* **1995,** *99*, 6777−6788.

(11) Dr I. Oksengendler, ABCR GmbH & Co KG, Karlsruhe, Germany, Private communication.

(12) 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.

(13) Harris, K. R. Temperature and pressure dependence of the viscosity of toluene. *J. Chem. Eng. Data* **2000**, *45*, 893−897.

(14) Harris, K. R.; Woolf, L. A.; Kanakubo, M. Temperature and pressure dependence of the viscosity of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. *J. Chem. Eng. Data* **2005**, *50*, 1777−1782.

(15) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and pressure dependence of the viscosity of the ionic liquids 1-octyl-3-methylimidazolium hexafluorophosphate and 1-octyl-3-methylimidazolium tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1161−1167.

(16) Marsh, K. N. University of Canterbury, Christchurch, New Zealand, private communication.

(17) Walker, N. A.; Lamb, D. M.; Adamy, S. T.; Jonas, J.; Dare-Edwards, M. P. Self-diffusion in the compressed, highly viscous liquid 2-ethylhexyl benzoate. *J. Phys. Chem.* **1988**, *92*, 3675−3679.

(18) Kleinschmidt, R. V; Bradbury, D; Mark, M. *Viscosity and Density of over Forty Lubricating Fluids of Known Composition at Pressures to 150,000 psi and Temperatures to 425 F*; American Society of Mechanical Engineers: New York, 1953.

(19) 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.

(20) Harris, K. R;, Alexander, J. J.; Goscinska, T.; Malhotra, R.; Woolf, L. A.; Dymond, J. H. Temperature and density dependence of the self-diffusion coefficients of liquid *n*-octane and toluene. *Mol. Phys.* **1993**, *78*, 235−248.

(21) Bair, S.; Qureshi, F. Accurate measurements of pressure−viscosity behavior in lubricants. *Tribol. Trans.* **2002**, *45*, 390−396.

(22) Bair, S. A routine high-pressure viscometer for accurate measurements to 1 GPa. *Tribol. Trans.* **2004**, *47*, 356−360.

(23) Barlow, A. J.; Lamb, J. The visco-elastic behaviour of lubricating oils under cyclic shearing stress. *Proc. R. Soc. London A* **1959**, *253*, 52−69.

(24) (a) Vogel, H. Das Temperaturabhängigkeitgesetz der Viskosität von Flüssigkeiten (The temperature dependence of the viscosity of liquids). *Physik. Z.* **1921**, *22,* 645−646. (b) Fulcher, G. S. Analysis of recent measurements of the viscosity of glasses. *J. Am. Ceram. Soc.* **1925**, *8*, 339−355. (c) Tammann, G.; Hesse, W. Die Abhängigkeit der Viskosität von der Temperatur bei unterkühlten Flüssigkeiten (The dependence of the viscosity on temperature for super-cooled liquids). *Z. Anorg. Allg. Chem*. **1926**, *156*, 245−257.

(25) Bridgman, P. W. Viscosities to 30,000 kg/cm^2. In *P. W. Bridgman Collected Experimental Papers*; Harvard University Press: Cambridge, MA, 1964; pp 3903−3914.

(26) (a) Casalini, R.; Paluch, M.; Roland, M. R. Dynamic crossover in supercooled liquids induced by high pressure. *J. Chem. Phys.* **2003**, *118*, 5701−5703. (b) Casalini, R.; Roland, M. R. Viscosity at the dynamic crossover in *o*-terphenyl and salol under high pressure. *Phys. Rev. Lett.* **2004**, *92*, 245702-1−245702-4.

(27) Roelands, C. J. A. Correlational aspects of the viscosity−temperature−pressure relationship of lubricating oils. Thesis, Technische Hogeschool van Delft, The Netherlands, 1966.

(28) Bair, S. The high pressure rheology of some simple model hydrocarbons. *Proc. I. Mech. Eng.* **2002**, *216*, 139−149.

(29) Bair, S. Reference liquids for quantitative elastohydrodynamics: selection and rheological characterization. *Tribol. Lett.* **2006**, *22*, 197−206.

(30) Jonas, J.; Adamy, S. T.; Grandinetti, P. J.; Masuda, Y.; Morris, S. J.; Campbell, D. M.; Li, Y. High-pressure NMR study of transport and relaxation in complex liquids of 2-ethylhexyl cyclohexanecarboxylate and 2-ethyl benzoate. *J. Phys. Chem.* **1990**, *94*, 1157−1164.

Received for review August 29, 2006. Accepted September 21, 2006.

JE060382+