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Temperature and Pressure Dependence of the Viscosities of 2-Ethylhexyl Benzoate, Bis(2-ethylhexyl) Phthalate, 2,6,10,15,19,23-Hexamethyltetracosane (Squalane), and Diisodecyl Phthalate†

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The viscosities of the esters 2-ethylhexyl benzoate (EHB), bis(2-ethylhexyl) phthalate (DEHP), and the long-chain hydrocarbon 2,6,10,15,19,23-hexamethyltetracosane (squalane, $C_{30}H_{62}$) have been measured between (0 and 80) °C with a falling-body viscometer to a maximum pressures of (315, 371, and 379) MPa, respectively. The expanded uncertainty is estimated at ± 2 %. These substances are possible alternatives to diisodecyl phthalate (DIDP) as reference materials for viscometry at moderate to high pressures. In addition, further measurements for DIDP are reported in the range (0.1 to 90) MPa and (25 to 75) °C to supplement those given by Harris and Bair (*J. Chem. Eng. Data*, **2007**, *52*, 272−278). These are compared with vibrating-wire measurements reported by Al Motari et al. (*J. Chem. Eng. Data*, **2007**, *52*, 1233−1239). The data have also been fitted as a function of the quantity (TV^{γ}) using the thermodynamic scaling method of Roland et al. (*J. Chem. Phys.* **2006**, *125*, 124508-1−124508-8), yielding scaling parameters, γ, equal to 3.69, 3.65, 4.16, and 3.96 for EHB, DEHP, squalane, and DIDP, respectively.

Introduction

As is well-known, the primary standard for measurements of the viscosities of Newtonian liquids is water at 20 °C and 0.1 MPa.[1,2] This single-point ISO standard is impractical for work on materials with much higher viscosities or for the calibration of viscometers at temperatures far removed from 20 °C.[3] A common solution is to use proprietary viscosity standards available from companies such as Cannon Instruments and Paragon Scientific[4] that are traceable to the primary standard. These cover a very large range of viscosities and typically temperatures between (−55 and 100) °C. However many are mixtures whose composition may change with time (e.g., due to evaporation of more volatile components) and in consequence have a fixed shelf life before expiry of the certification of their properties. Additionally, different batch lots have slightly different viscosities at a given temperature. In many scientific and industrial applications, it is more convenient to use a single reference compound, available commercially in high purity, spanning a range of viscosities. Water is often used when measurements below 0 °C are not required, its viscosity ranging from (1.8 to 0.28) mPa·s between (0 and 100) °C, though the ISO recommended values are limited to the range (15 to 40) °C.[2] Recommended values for high pressures are also available.[5] However, water, due to its high surface tension, heat capacity, and thermal conductivity and low electrical resistivity, relative to those of most other fluids, is often an unsuitable calibrant for certain types of viscometers or where the measurements are to be carried out on a fluid with very different properties (e.g., surface tension in the case of capillary or falling-body viscometers).

In recent years, the grouping known as the International Association for Transport Properties (IATP), which continues the work of the former Subcommittee on Transport Properties of the IUPAC Commission I.2: Thermodynamics, disbanded as a consequence of the IUPAC restructure of 2000,[6] has produced sets of recommended viscosities for three reference materials: cyclopentane,[7] toluene,[8] and diisodecyl phthalate (DIDP).[9] These are based on measurements made with a variety of viscometer types and techniques (capillary, falling body, surface light scattering, and vibrating wire) in different laboratories, each specializing in a given type of measurement. The recommendations for the low viscosity materials cyclopentane

Table 1. Parameters for the Hayward Equation of State

	EHB[a]	DEHP[b]	squalane
α_{00}/MPa	−659.430	−452.852	−896.384
$\alpha_{01}\cdot 10^{-3}$/(MPa·K)	649.426	650.553	679.559
α_{10}	2.033 69	2.874 16	4.329 03
α_{11}/K	495.237	460.123	94.468 3
$\delta\rho$/%[c]	0.14	0.15	0.04

[a] 1 point at 80 °C, 100 MPa omitted. [b] 1 point at 0 °C, 315 MPa omitted. [c] Standard uncertainty of the fit to the density.

Table 2. Density ρ of EHB, DEHP, and Squalane from θ = (0 to 90) °C

	EHB	DEHP	squalane
θ/°C		ρ/g·cm^{-3}	
0.0	0.98112	0.99882	0.82158
5.0	0.97718	0.99501	
10.0	0.97325	0.99126	0.81516
15.0	0.96932		0.81195
20.0	0.96540	0.98387	0.80874
25.0	0.96149	0.98015	0.80555
30.0	0.95757	0.97642	0.80234
40.0	0.94973	0.96898	0.79593
50.0	0.94192	0.96153	0.78953
60.0	0.93411	0.95411	0.78314
70.0	0.92628	0.94668	0.77677
80.0	0.91845	0.93927	0.77042
90.0	0.91061	0.93185	0.76406

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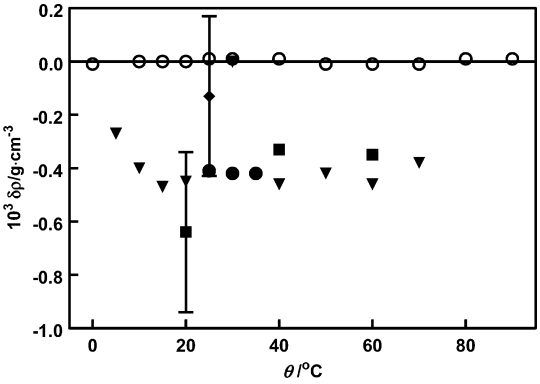

Figure 1. Residuals (experimental − calculated values) for the fit of the experimental atmospheric pressure and literature densities for squalane. ○, this work; ■, ref 36, pycnometry (one point off-scale at [0 °C, $-7.2\cdot10^{-3}$ g·cm^{-3}]); ▲, ref 37, DMA 602H vibrating tube; ▼, ref 35, DMA 512P vibrating tube, viscosity corrected; ◆, ref 38, pycnometry; ●, ref 39, DSA 5000 vibrating tube. The error bars for the vibrating-tube results are of the order of the size of the symbols.

and toluene provide values to low temperatures [(220 and 213) K, respectively]. Recommended values for high pressure extend to 250 MPa for toluene.[8]

IATP chose DIDP as a reference material for moderate viscosities (its viscosity is 123.5 mPa·s at 20 °C). It is chemically stable over a wide temperature range, has a low vapor pressure, and was a relatively inexpensive material suitable for industrial use as a secondary viscometer calibrant. However, there are two drawbacks: commercial samples are actually mixtures of phthalate esters of a wide range of isomers of isodecyl alcohol,[10,11] so it does not really meet the requirement of being a pure compound; and since IATP began the series of measurements leading to the published recommendations, the prime manufacturer has indicated that production is likely to be discontinued. In addition, while data are available extending to 1 GPa over a broad range of temperatures,[11] potential differences between batches may limit the applicability of these data for calibrating or comparing the behavior of high-pressure viscometers. This difficulty has been apparent in the work of Goodwin, Marsh, and co-workers[12−14] on the pressure dependence of the viscosity of the commercial certified reference materials, N10 and S20.

Consequently, it seems useful to have good high-pressure viscosity data for pure viscous substances that might be considered as alternatives to DIDP and the commercial mixtures. Here data are reported for two esters having the advantage of being available as pure isomers, 2-ethylhexyl benzoate (EHB) and bis(2-ethylhexyl) phthalate (DEHP), as shown by the ^{13}C NMR studies of Jonas and co-workers,[15−17] and for 2,6,10,15,19,23-hexamethyltetracosane or squalane, a hydrocarbon of similar viscosity. Like EHB[17] and DEHP,[18,19] squalane has been used in viscoelasticity and elastohydrodynamics studies of lubricants.[18−23] All three substances are also of more fundamental interest in terms of liquid-state theories as glass-formers with extended experimentally accessible viscosity ranges.[24−26]

Finally, additional data are also reported for DIDP at moderate pressures [(10 to 90) MPa] to supplement and confirm the high-pressure results published earlier by Harris and Bair, who employed three different falling-body viscometers located in two different laboratories.[11] Al Motari et al.,[27] using a moderate pressure vibrating-wire viscometer (70 MPa maximum pressure), found systematic differences between the results of their instrument and those of the falling-body instruments that appear to increase with increasing viscosity and under some temperature conditions become larger than the combined uncertainties of the data sets. The new data, together with new high-pressure vibrating-wire results of Ciotta et al.[28] for squalane, are used to examine this discrepancy.

Table 3. Viscosity of EHB (6.3 mm sinker)

θ/°C	p/MPa	t/s	V/cm^3·mol^{-1}	η/mPa·s	Re
−10.00	0.1	976.0	236.96	29.42	0.59
−10.00	0.1	975.1	236.96	29.39	0.59
−5.00	0.1	710.9	237.90	21.43	1.1
−5.00	0.1	710.2	237.90	21.41	1.1
0.00	0.1	537.7	238.84	16.22	1.9
0.00	0.1	537.5	238.84	16.21	1.9
0.00	0.7	543.6	238.76	16.39	1.9
0.00	14.2	693.1	236.94	20.88	1.2
0.00	16.1	734.0	236.70	22.11	1.0
0.00	29.7	957.2	234.98	28.80	0.62
0.00	45.5	1291	233.12	38.79	0.35
0.00	47.1	1315	232.93	39.50	0.33
0.00	60.9	1730	231.40	51.94	0.19
0.00	81.8	2615	229.24	78.37	0.086
0.00	102.0	3832	227.31	114.7	0.040
0.00	110.6	4429	226.52	132.5	0.030
0.00	149.8	9614	223.25	286.9	0.0065
10.00	0.1	333.6	240.77	10.07	5.0
10.00	0.1	333.5	240.77	10.07	5.0
20.00	0.1	223.5	242.73	6.753	11
20.00	0.1	223.6	242.73	6.756	11
25.00	0.1	184.4	243.72	5.574	16
25.00	0.1	182.9	243.72	5.529	16
25.00	0.3	188.8	243.69	5.708	15
25.00	0.9	190.9	243.59	5.771	15
25.00	26.0	278.6	239.82	8.400	7.2
25.00	50.9	401.1	236.47	12.07	3.5
25.00	75.6	572.4	233.48	17.19	1.8
25.00	100.8	820.1	230.75	24.58	0.87
25.00	125.5	1166	228.30	34.90	0.43
25.00	150.9	1671	226.02	49.92	0.21
25.00	175.1	2358	224.03	70.34	0.11
25.00	200.7	3390	222.09	101.0	0.053
25.00	225.2	4810	220.38	143.1	0.027
25.00	250.7	6933	218.74	206.0	0.013
30.00	0.1	160.3	244.72	4.847	21
30.00	0.1	160.3	244.72	4.847	21
40.00	0.1	120.3	246.74	3.641	37
40.00	0.1	120.3	246.74	3.641	37
40.00	0.1	120.4	246.74	3.644	37
40.00	0.1	120.5	246.74	3.646	37
50.00	0.1	94.39	248.78	2.859	60
50.00	0.1	94.30	248.78	2.857	60
50.00	25.9	130.8	244.33	3.952	32
50.00	50.9	176.5	240.54	5.320	18
50.00	75.8	235.7	237.16	7.088	10
50.00	100.6	312.1	234.15	9.368	5.9
50.00	125.7	411.7	231.41	12.33	3.4
50.00	150.4	540.5	228.96	16.17	2.0
50.00	174.8	694.8	226.76	20.75	1.2
50.00	175.6	714.4	226.69	21.33	1.2
50.00	200.8	940.2	224.62	28.03	0.68
50.00	225.6	1236	222.75	36.82	0.40
50.00	250.4	1621	221.02	48.19	0.23
50.00	275.2	2117	219.43	62.86	0.14
50.00	300.0	2770	217.95	82.18	0.081
50.00	300.1	2765	217.95	82.04	0.082
60.00	0.1	75.86	250.86	2.300	92
60.00	0.1	75.85	250.86	2.300	92
70.00	0.1	60.12	252.98	1.824	145
70.00	0.1	59.46	252.98	1.804	149
70.00	0.1	60.46	252.98	1.834	144
70.00	0.1	62.04	252.98	1.882	136
70.00	0.1	62.33	252.98	1.891	135
75.00	0.1	56.92	254.06	1.728	161
75.00	0.1	56.99	254.06	1.730	161
75.00	10.8	64.51	251.88	1.956	127
75.00	25.4	75.99	249.08	2.300	93
75.00	50.8	99.18	244.73	2.994	55
75.00	75.9	127.0	240.95	3.826	34
75.00	100.8	161.1	237.60	4.842	22
75.00	125.7	200.3	234.61	6.009	14
75.00	150.7	255.0	231.91	7.634	8.9
75.00	175.7	318.2	229.45	9.511	5.8
75.00	200.7	396.9	227.23	11.85	3.8
75.00	225.7	495.6	225.20	14.77	2.4
75.00	250.5	612.6	223.35	18.23	1.6
75.00	275.3	758.9	221.65	22.56	1.1
75.00	276.3	768.2	221.59	22.83	1.0
75.00	302.3	959.3	219.95	28.48	0.67
75.00	315.2	1065	219.18	31.58	0.55

Table 4. Viscosity of DEHP

θ / °C	p / MPa	t / s	V / $cm^3 \cdot mol^{-1}$	η / $mPa \cdot s$	Re
6.0 mm sinker					
0.00	0.1	1031	391.02	359.9	0.019
0.00	0.1	1030	391.02	359.7	0.019
0.00	24.1	1953	386.41	680.7	0.005
10.00	0.1	454.0	394.00	158.6	0.10
10.00	0.1	452.3	394.00	158.0	0.10
10.00	0.4	458.5	393.93	160.2	0.093
10.00	20.8	764.0	389.80	266.5	0.034
10.00	41.0	1236	386.05	430.5	0.013
10.00	60.0	1908	382.83	663.5	0.0056
10.00	80.4	2977	379.65	1034	0.0023
10.00	100.1	4513	376.81	1566	0.0010
10.00	123.4	7137	373.68	2473	0.0004
25.00	0.1	168.1	398.47	58.79	0.69
25.00	0.1	164.6	398.47	57.58	0.72
25.00	0.1	164.6	398.47	57.59	0.72
25.00	0.6	169.7	398.35	59.35	0.67
25.00	25.8	296.1	392.90	103.4	0.22
25.00	50.0	480.4	388.26	167.4	0.087
25.00	50.9	500.1	388.11	174.2	0.080
25.00	76.3	827.6	383.75	287.8	0.030
25.00	100.5	1311	380.01	455.2	0.012
25.00	126.6	2108	376.37	730.7	0.005
25.00	150.4	3185	373.34	1103	0.0021
25.00	174.3	4715	370.54	1631	0.0009
25.00	199.8	7317	367.78	2527	0.0004
30.00	0.1	126.6	399.99	44.29	1.2
30.00	0.1	126.3	399.99	44.20	1.2
30.00	0.1	124.3	399.99	43.49	1.3
30.00	0.1	124.3	399.99	43.49	1.3
37.78	0.1	82.3	402.38	28.83	2.8
37.78	0.1	82.2	402.38	28.77	2.8
37.78	0.1	82.6	402.38	28.91	2.8
37.78	0.1	82.6	402.38	28.91	2.8
37.78	0.1	82.5	402.38	28.88	2.8
37.78	47.4	210.9	392.05	73.56	0.44
37.78	75.3	345.6	386.97	120.3	0.17
37.78	99.5	532.6	383.04	185.1	0.072
37.78	148.6	1192	376.12	413.1	0.015
37.78	176.0	1786	372.76	617.9	0.007
37.78	201.8	2641	369.88	912.7	0.003
37.78	223.8	3648	367.61	1259	0.002
37.78	247.8	5203	365.29	1794	0.001
37.78	250.8	5276	365.01	1819	0.001
37.78	274.0	7416	362.94	2555	0.0004
40.00	0.1	76.0	403.06	26.60	3.3
40.00	0.1	75.9	403.06	26.58	3.3
50.00	0.1	49.0	406.18	17.17	7.9
50.00	0.1	48.5	406.18	17.01	8.1
50.00	0.7	49.2	406.01	17.26	7.8
50.00	10.6	59.3	403.52	20.76	5.4
50.00	25.7	77.9	399.96	27.26	3.2
50.00	50.7	120.9	394.61	42.19	1.3
50.00	75.6	183.0	389.88	63.74	0.59
50.00	100.6	272.3	385.64	94.67	0.27
50.00	125.6	399.5	381.80	138.7	0.13
50.00	150.6	577.7	378.34	200.2	0.06
50.00	175.6	827.0	375.16	286.3	0.030
50.00	200.3	1167	372.29	403.4	0.015
50.00	223.1	1561	369.83	539.0	0.009
50.00	252.3	2304	366.93	794.8	0.004
50.00	276.7	3062	364.69	1055.1	0.002
50.00	295.4	3935	363.07	1355.1	0.001
50.00	323.7	5676	360.76	1952.3	0.001
75.00	50.8	44.4	401.26	15.52	9.8
75.00	75.9	63.3	396.04	22.09	4.9
75.00	100.8	88.8	391.41	30.91	2.5
75.00	125.8	122.6	387.25	42.61	1.3
75.00	150.8	167.4	383.49	58.12	0.72
75.00	175.7	227.1	380.08	78.72	0.40
75.00	200.7	305.2	376.95	105.6	0.22
75.00	225.5	406.1	374.10	140.4	0.13
75.00	250.3	537.6	371.46	185.6	0.073
75.00	275.0	706.8	369.02	243.8	0.043
75.00	299.1	918.9	366.80	316.7	0.025
75.00	324.1	1199	364.64	412.7	0.015
75.00	348.1	1539	362.69	529.4	0.009
75.00	371.0	1947	360.93	669.0	0.006
6.3 mm sinker					
50.00	0.1	566.3	406.18	17.10	1.7
60.00	0.1	388.1	409.34	11.73	1.5
60.00	0.1	387.3	409.34	11.71	1.5
70.00	0.1	281.0	412.55	8.499	2.7
70.00	0.1	281.4	412.55	8.510	2.7
75.00	0.1	245.1	414.17	7.416	3.6
75.00	0.1	245.3	414.17	7.422	3.6
75.00	54.1	546.3	400.55	16.45	0.75
75.00	103.5	1072	390.95	32.17	0.20

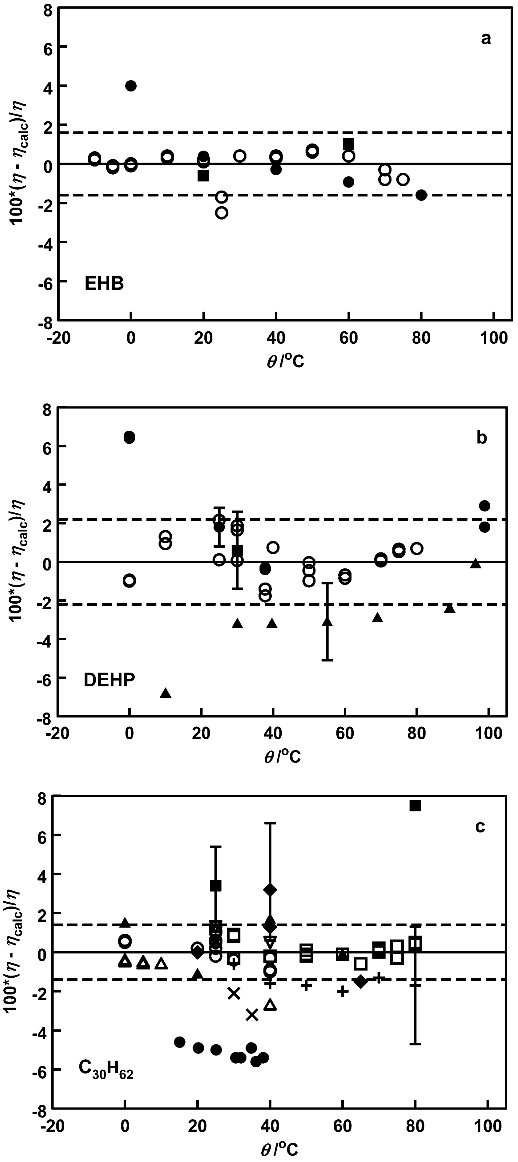

Figure 2. Residuals (experimental − calculated values) for the VFT equation fit of the atmospheric pressure viscosities. (a) EHB: ○, this work, the dashed lines represent the expanded uncertainty of the fit ($k = 2$); ●, ref 17, capillary viscometer, no uncertainty given; ■, ref 45, falling sinker viscometer, ± 3 %. (b) DEHP: ○, this work; ●, ref 33, falling sinker viscometer, standard uncertainty ± 2 %; ■, ref 46, falling sinker viscometer, ± 2 %; ▲, ref 40, capillary viscometer, ± (0.5 to 1) %. (c) Squalane: ○, 6.0 mm sinker; □, 6.3 mm sinker; △, 6.0 mm sinker, rewound coils, this work; ●, ref 21, capillary viscometer, ± 0.5 %; ■, ref 47, rolling-ball viscometer, ± 2 %;▲, ref 48, falling-body viscometer, ± 3 %; ▼, ref 37, capillary viscometer, ± 0.1 %; ◆, ref 22, 23, falling sinker viscometer, ± 3 %; +, ref 49, rolling ball viscometer, ± 3 %; ×, ref 39, capillary viscometer, ± 0.1 %; ◆, ref 50, falling-body viscometer, ± 0.4 %. An off-scale point from ref 38 (25, 9.6 %) is not shown (capillary viscometer, ± 0.9 %).

Experimental Section

EHB (CAS No. 5444-75-7), 99 %, was obtained from ABCR GmbH, Karlsruhe, Germany; the DEHP (CAS No 117-81-7) sample was obtained from Sigma-Aldrich Australia (product no. D201154, lot no. 09428JC, manufacturer's purity 99.7 % by gas-chromatographic analysis); Fluka squalane (CAS No 111-01-3) was obtained from Sigma-Aldrich Australia (product no. 85629, lot no. 1140335, manufacturer's purity > 99.0 % by gas-chromatographic analysis); the DIDP (CAS No 26761-40-0) sample was Merck "GR for Analysis" grade, lot no. K22132622, manufacturer's purity 99.5 % by gas-chromatographic analysis.

Table 5. Viscosity of Squalane

θ/°C	p/MPa	t/s	V/cm^3·mol^{-1}	η/mPa·s	Re	θ/°C	p/MPa	t/s	V/cm^3·mol^{-1}	η/mPa·s	Re
6.0 mm sinker											
0.00	0.1	323.3	514.63	116.0	0.2	40.00	0.1	41.88	531.22	15.07	8.7
0.00	0.1	323.6	514.63	116.2	0.2	40.00	0.1	42.14	531.22	15.16	8.7
0.00	0.6	339.6	514.46	121.9	0.1	40.00	0.8	42.11	530.95	15.15	8.7
0.00	10.6	445.0	511.34	159.6	0.1	40.00	10.7	51.69	526.96	18.58	5.8
0.00	20.6	580.3	508.38	208.0	0.05	40.00	20.6	63.03	523.25	22.64	4.0
0.00	30.7	747.2	505.56	267.6	0.03	40.00	30.7	76.16	519.74	27.33	2.7
0.00	41.4	973.4	502.72	348.4	0.02	40.00	40.5	91.17	516.54	32.69	1.9
0.00	50.5	1237	500.43	442.3	0.01	40.00	50.2	108.9	513.54	39.01	1.4
10.00	9.6	212.6	515.49	76.31	0.4	40.00	60.6	130.6	510.53	46.76	0.95
10.00	19.9	272.4	512.27	97.69	0.2	40.00	70.6	155.2	507.82	55.53	0.67
10.00	25.81	321.5	510.48	115.2	0.2	40.00	80.6	183.7	505.25	65.68	0.48
10.00	50.88	577.0	503.56	206.5	0.05	40.00	91.7	219.9	502.57	78.58	0.34
10.00	76.76	1009	497.33	360.6	0.02	40.00	112.4	305.0	497.97	108.9	0.18
10.00	100.40	1607	492.30	573.5	0.01	40.00	131.7	407.6	494.11	145.3	0.10
20.00	0.1	100.1	522.80	35.97	1.6	40.00	151.6	541.1	490.48	192.8	0.06
20.00	0.1	100.1	522.80	35.96	1.6	40.00	151.9	552.4	490.43	196.8	0.05
25.00	0.1	78.85	524.89	28.35	2.5	40.00	168.6	702.4	487.65	250.0	0.04
25.00	0.1	78.55	524.89	28.24	2.5	40.00	175.4	777.6	486.57	276.7	0.03
25.00	0.7	79.48	524.65	28.57	2.5	40.00	190.0	947.3	484.38	336.9	0.02
25.00	0.8	79.74	524.63	28.67	2.4	40.00	190.1	956.2	484.36	340.1	0.02
25.00	10.8	99.58	520.98	35.77	1.6	40.00	210.4	1221	481.53	433.8	0.01
25.00	20.6	123.2	517.60	44.20	1.0	65.00	40.8	37.5	525.13	13.45	11.0
25.00	26.0	137.6	515.86	49.37	0.8	65.00	60.7	50.0	518.51	17.92	6.3
25.00	30.8	152.0	514.34	54.49	0.7	65.00	80.7	67.7	512.66	24.24	3.5
25.00	40.2	183.7	511.49	65.84	0.5	65.00	100.6	89.6	507.53	32.02	2.0
25.00	50.1	223.6	508.65	80.08	0.3	65.00	120.4	116.6	503.00	41.62	1.2
25.00	50.6	226.9	508.49	81.24	0.3	65.00	140.4	150.5	498.88	53.67	0.72
25.00	60.7	274.5	505.78	98.21	0.2	65.00	160.3	193.7	495.20	69.03	0.44
25.00	70.7	332.2	503.22	118.8	0.1	65.00	175.3	231.5	492.66	82.43	0.34
25.00	75.8	364.6	502.00	130.3	0.1	65.00	199.8	312.1	488.87	111.0	0.17
25.00	80.5	398.2	500.87	142.3	0.1	65.00	226.5	423.6	485.20	150.6	0.11
25.00	100.1	565.1	496.47	201.8	0.1	75.00	60.4	36.95	521.84	13.25	11.4
25.00	125.9	885.9	491.33	315.8	0.02	75.00	70.3	42.51	518.72	15.23	8.7
25.00	150.0	1308	487.06	465.7	0.01	75.00	80.3	48.57	515.79	17.39	6.7
30.00	0.1	62.79	526.98	22.58	3.9	75.00	90.3	55.75	513.05	19.95	5.1
30.00	0.1	62.80	526.98	22.58	3.9	75.00	100.1	63.33	510.50	22.65	4.1
40.00	0.1	41.82	531.22	15.05	8.8						
6.3 mm sinker; coils rewound											
30.00	0.1	756.0	526.98	22.86	0.80	70.00	0.1	197.1	544.32	5.976	11.3
30.00	0.1	755.2	526.98	22.84	0.80	70.00	0.1	197.0	544.32	5.972	11.4
40.00	0.1	501.5	531.22	15.17	1.8	75.00	0.1	174.2	546.56	5.281	14.5
40.00	0.1	501.6	531.22	15.18	1.8	75.00	0.1	174.1	546.56	5.280	14.5
50.00	0.1	354.3	535.52	10.73	3.6	75.00	0.1	173.1	546.56	5.248	14.7
50.00	0.1	353.6	535.52	10.71	3.6	75.00	9.7	204.5	541.80	6.195	10.6
50.00	0.1	353.1	535.52	10.69	3.6	75.00	20.6	244.9	536.80	7.410	7.5
60.00	0.1	259.3	539.89	7.856	6.6	75.00	30.8	287.4	532.55	8.689	5.5
60.00	0.1	259.5	539.89	7.861	6.6	75.00	40.9	335.7	528.64	10.14	4.0
65.00	0.1	223.9	542.09	6.785	8.8	75.00	50.4	385.5	525.20	11.63	3.1
65.00	9.7	266.4	537.60	8.064	6.3	75.00	60.5	446.2	521.79	13.45	2.3
65.00	22.1	329.3	532.30	9.958	4.2	75.00	70.9	514.5	518.56	15.50	1.8
65.00	30.1	376.0	529.09	11.36	3.2	75.00	80.1	594.2	515.84	17.89	1.3
65.00	40.6	443.8	525.22	13.40	2.3	75.00	90.6	680.7	512.96	20.48	1.0
65.00	50.3	515.4	521.86	15.55	1.7	75.00	100.8	770.8	510.34	23.18	0.82
65.00	60.0	596.5	518.73	17.98	1.3	80.00	0.1	154.7	548.81	4.692	18.3
70.00	0.1	197.4	544.32	5.984	11.3	80.00	0.1	154.8	548.81	4.695	18.2
70.00	0.1	197.2	544.32	5.979	11.3						
6.0 mm sinker; coils rewound											
0.00	0.1	328.2	514.63	115.0	0.15	65.00	255.1	586.6	481.70	201.5	0.051
0.00	0.1	327.9	514.63	114.9	0.15	65.00	274.8	729.1	479.51	252.5	0.033
5.00	0.1	235.9	516.65	82.67	0.29	65.00	275.2	712.8	479.48	246.9	0.034
5.00	0.1	235.6	516.65	82.55	0.29	65.00	300.0	929.0	476.95	321.5	0.020
10.00	0.1	174.0	518.69	61.01	0.53	65.00	303.6	974.8	476.61	337.4	0.019
10.00	0.1	174.0	518.69	61.00	0.53	65.00	324.9	1203	474.64	416.3	0.012
25.00	0.1	81.1	524.89	28.45	2.4	65.00	350.6	1562	472.47	540.2	0.0073
25.00	0.1	81.0	524.89	28.42	2.4	65.00	373.0	1960	470.72	677.2	0.0048
25.00	0.1	81.5	524.89	28.61	2.4	75.00	101.5	65.47	510.16	22.85	3.8
25.00	0.1	81.4	524.89	28.56	2.4	75.00	126.3	89.16	504.42	31.07	2.1
25.00	51.6	240.4	508.24	84.03	0.29	75.00	151.7	120.7	499.30	42.01	1.2
25.00	74.7	371.2	502.25	129.5	0.12	75.00	176.5	159.6	494.93	55.49	0.67
25.00	98.8	575.8	496.76	200.7	0.051	75.00	176.7	160.3	494.90	55.74	0.66
25.00	150.1	1362	487.04	473.5	0.0093	75.00	200.5	206.4	491.18	71.69	0.40
40.00	0.1	42.16	531.22	14.81	8.83	75.00	225.5	270.3	487.70	93.81	0.23
40.00	199.8	1093	482.97	379.2	0.016	75.00	250.3	351.4	484.59	121.8	0.14
40.00	227.9	1586	479.26	549.9	0.0071	75.00	275.3	453.4	481.78	157.1	0.085
40.00	241.7	1932	477.58	669.3	0.0047	75.00	300.0	582.1	479.26	201.5	0.052
40.00	261.5	2494	475.33	863.8	0.0028	75.00	319.7	706.1	477.41	244.4	0.035
40.00	279.8	3077	473.40	1065	0.0019	75.00	339.6	855.2	475.68	295.8	0.024
40.00	300.5	4032	471.35	1395	0.0011	75.00	359.0	1030	474.09	356.2	0.017
65.00	246.0	532.4	482.77	184.6	0.062	75.00	378.6	1240	472.60	428.5	0.012

(This was sample B of ref 11 and the same lot used for the IATP recommendations.[9]) All samples were dried for several weeks with 3A molecular sieves and filtered through a (40 to 60) μm filter prior to use. ^{13}C NMR spectra obtained at 100.571 MHz with a Varian "Unity plus" 400 MHz spectrometer confirmed the isomeric purity of EHB, DEHP, and squalane. The molar masses of these three substances were taken to be (234.334, 390.556, and 422.813) g·mol^{-1}, respectively.

The falling-body viscometer employed has been described previously.[29−31] This work employed self-centering cylindrical sinkers with hemispherical faces of nominal diameters of (6.3 and 6.0) mm with calibrations obtained with Cannon Instruments viscosity standards covering the range (0.3 to 2875) mPa·s.[30,31] During the measurements on squalane, it was necessary to rewind the detection coils on the viscometer tube, as the insulation on these had deteriorated after many temperature and

Table 6. Viscosity of DIDP

θ	p	t	V	η	
°C	MPa	s	$cm^3\cdot mol^{-1}$	$mPa\cdot s$	Re
			6.0 mm sinker		
0.00	0.10	1787	455.46	625.8	0.0061
0.00	9.9	2416	453.04	845.1	0.0033
25.00	0.1	249.1	463.90	87.37	0.31
25.00	0.1	249.2	463.90	87.41	0.31
25.00	9.6	315.8	461.22	110.7	0.19
25.00	20.6	414.2	458.34	145.0	0.11
25.00	20.7	415.6	458.30	145.5	0.11
25.00	30.1	521.5	455.98	182.5	0.071
25.00	30.3	523.2	455.93	183.0	0.071
25.00	40.7	669.8	453.52	234.2	0.043
25.00	50.2	828.3	451.43	289.4	0.029
25.00	59.2	1020	449.57	356.2	0.019
25.00	71.6	1334	447.14	465.4	0.011
25.00	82.0	1690	445.23	589.0	0.0070
25.00	83.3	1746	444.99	608.4	0.0065
40.00	0.1	107.4	469.09	37.71	1.6
40.00	10.9	134.8	465.83	47.29	1.0
40.00	21.2	168.2	462.93	58.95	0.67
40.00	30.6	204.3	460.45	71.54	0.46
40.00	40.9	254.3	457.89	88.99	0.30
40.00	51.6	312.1	455.40	109.1	0.20
40.00	62.4	391.4	453.01	136.7	0.13
40.00	71.3	460.6	451.16	160.8	0.093
40.00	80.3	551.3	449.38	192.4	0.065
40.00	89.8	672.2	447.60	234.4	0.044
65.00	0.10	37.36	477.96	13.14	13
65.00	9.70	44.67	474.69	15.70	10
65.00	19.40	53.56	471.60	18.81	7.0
65.00	31.77	66.37	467.92	23.27	4.6
65.00	41.11	77.58	465.33	27.18	3.4
65.00	51.10	91.94	462.72	32.19	2.4
65.00	60.51	107.8	460.40	37.73	1.8
65.00	70.71	126.0	458.02	44.06	1.3
65.00	80.97	149.6	455.76	52.27	0.94
75.00	30.23	45.48	471.55	15.96	9.0
75.00	40.81	53.93	468.47	18.91	6.5
75.00	50.71	62.95	465.76	22.05	4.8
75.00	61.22	73.97	463.06	25.89	3.5
75.00	72.33	87.35	460.38	30.55	2.5
75.00	85.77	106.6	457.35	37.23	1.7
			6.3 mm sinker		
65.00	0.1	441.1	477.96	13.37	2.8
65.00	0.1	441.3	477.96	13.38	2.8
65.00	0.1	440.9	477.96	13.36	2.8
65.00	10.7	537.9	474.35	16.28	1.9
65.00	20.5	640.7	471.26	19.38	1.4
65.00	31.0	770.7	468.15	23.29	0.94
65.00	40.1	902.1	465.62	27.24	0.69
65.00	50.3	1075	462.92	32.42	0.49
65.00	60.4	1271	460.42	38.31	0.35
65.00	70.7	1503	458.03	45.25	0.25
65.00	80.2	1745	455.93	52.53	0.19
75.00	0.10	320.1	481.58	9.710	5.3
75.00	9.8	378.5	478.14	11.47	3.8
75.00	20.6	453.1	474.53	13.71	2.7
75.00	31.3	540.4	471.24	16.34	1.9
75.00	50.6	733.8	465.81	22.15	1.0
75.00	69.8	987.8	460.98	29.77	0.58

pressure cycles. New calibrations were then carried out. A platinum resistance thermometer calibrated between (−65 and 100) °C on ITS-90 to a tolerance of ± 8 mK was 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 dead weight tester, and pressures have an overall uncertainty of ± 0.2 MPa. The fall times are the average of at least three replicates. The combination of the uncertainties in replicate measurements (± 1 %) determined from up to ten measurements at randomly selected state points, the calibration (± 1 %), and the calibrant viscosities in quadrature yields an expanded uncertainty of ± 2 %.

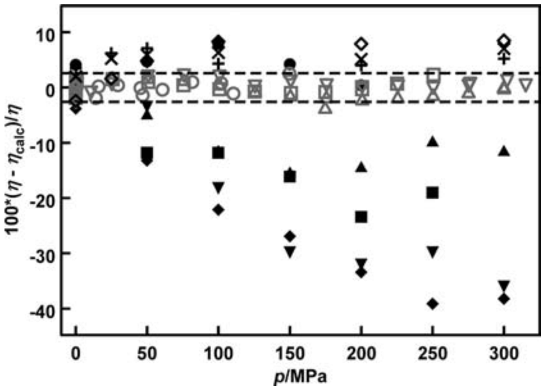

Figure 3. Residuals (experimental − calculated values) for the MVFT equation fit of the high-pressure viscosities for EHB. This work, expanded uncertainty of the fit ± 2.6 % (dashed lines, $k = 2$): ○, 0 °C; □, 25 °C; Δ, 50 °C; ▽, 75 °C. Ref 17, falling sinker viscometer, standard deviation ± 10 %: ●, 0 °C; ■, 20 °C; ▲, 40 °C; ▼, 60 °C; ◆ 80 °C. Ref 45, falling sinker viscometer, standard deviation ± 3 %: +, 20 °C; ×, 60 °C; ◇, 100 °C.

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 viscometer[29,30] is

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

(where A is the calibration constant; α is the coefficient of thermal expansion; θ is the Celsius temperature; and β is the bulk compressibility of the sinker and tube material; $\theta_{ref} = 25$ °C and $p_{ref} = 0.1$ MPa), 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 the liquids examined in this work, (ρ/ρ_s) is of the order of 0.11 to 0.15, so an error of ± (5 to 7) % in ρ lies within the reproducibility of our instrument, ± 1 %.

pVT data required for estimation of the fluid densities at the measured state points were derived from several sources. For EHB, the results of Walker et al.,[17] obtained between (−20 and 100) °C at pressures to 450 MPa, were employed. These can be represented by the Hayward-type equation[11,31]

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

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 the saturation line]. The parameters are given in Table 1. The required density was then calculated from $K(T, p)$ and atmospheric pressure densities determined with an Anton-Paar DMA5000 vibrating-tube densimeter. This has a measurement uncertainty of 0.000 05 $g\cdot cm^{-3}$. The in-built viscosity correction for this instrument has been checked using reference materials with a viscosity as high as 16.2 Pa·s.[31,32]

For DEHP, data between (counterfitting −20 and 100) °C at pressures to 372 MPa from the ASME Pressure-Viscosity Report[33] and for squalane from the results of Kuss and Taslimi[34] obtained between (25 and 80) °C at pressures to 196 MPa and of Fandiño et al.[35] obtained between (5 and 80) °C at pressures

Table 7. Coefficients of Best Fit for Equations 4 and 5

	coefficients and standard uncertainties		
	EHB	DEHP	squalane
VFT, eq 4			
ln (A/mPa·s)	− 2.2978 ± 0.038	−2.9769 ± 0.062	−2.9227 ± 0.040
B/K	487.25 ± 8.9	846.1 ± 16	854.1 ± 11
T_0/K	177.32 ± 1.0	177.78 ± 1.2	161.88 ± 0.9
D^a	2.75	4.76	5.28
standard uncertainty of fit/%	0.8	1.1	0.7
eq 5			
ln (A'/mPa·s)	− 0.7922 ± 0.0065	− 0.3769 ± 0.0089	− 0.6525 ± 0.047
$B'\cdot 10^{-10}/\mathrm{K}^n$	1.9964 ± 0.0049	3.4992 ± 0.0079	0.1635 ± 0.041^b
n	4 (4.00 ± 0.07)^c	4 (3.98 ± 0.05)^b	3.481 ± 0.046
standard uncertainty of fit/%	1.1	1.3	1.2

[a] Angell strength factor (B'/T_0). [b] units: K^n. [c] Bracketed value: exponent if allowed to float.

Table 8. Fit of ln($\eta(T, p)$) to Polynomials in the Pressure, p: ln(η) = $\Sigma\, a_{i-1}p^i$

T/°C	$p_{\max}$/MPa	a_0	10^2a_1/MPa^{-1}	10^5a_2/MPa^{-2}	10^8a_3/MPa^{-3}	s^a
EHB						
0	150	2.78297	1.91497	0.0145764		1.0
25	250	1.73073	1.47737	−0.185358		1.2
50	300	1.06222	1.17802	−0.215821		0.3
75	315	0.55166	1.10305	−0.993257	1.33488	0.6
DEHP						
10	123	5.06416	2.54573	−2.57752		0.3
25	200	4.06086	2.27700	−2.64450	3.43974	1.1
37.78^b	274	3.36052	2.06734	−2.27005	2.55066	0.8
50	324	2.83504	1.88146	−1.91149	1.90231	0.7
75	371	2.00275	1.52607	−1.19198	0.949465	0.3
Squalane						
0	51	4.75579	2.92442	−5.90386		1.6
10	100	4.10117	2.56463	−3.17525		1.1
25	150	3.34340	2.21565	−2.82855	3.57214	0.8
40	300	2.71057	2.01419	−2.56338	2.92030	0.8
65	373	1.92665	1.70379	−1.89479	1.67301	0.9
75	379	1.66571	1.65887	−2.21802	2.40389	1.2
DIDP^c						
25	101	4.47522	2.47363	−1.66975		0.9
40	252	3.62435	2.16082	−1.24389		1.0
65	394	2.58253	1.80416	−1.43887	1.38709	1.1
75	373	2.27435	1.67981	−1.37438	1.39667	0.6

[a] Standard percentage uncertainty of the fit to η. [b] 100 °F. [c] Including data from ref 11.

to 45 MPa have been similarly fitted to eq 2 and combined with new atmospheric pressure measurements.

Results and Discussion

The density results at atmospheric pressure are presented in Table 2 and can be represented by the following polynomials

$$\rho(\mathrm{EHB})/\mathrm{g{\cdot}cm^{-3}} = 0.981\,078 \;-\; 7.829\,73 \cdot 10^{-4}(\theta/^{\circ}\mathrm{C}) \tag{3a}$$

$$\rho(\mathrm{DEHP})/\mathrm{g{\cdot}cm^{-3}} = 0.998\,739 \;-\; 7.43568 \cdot 10^{-4}(\theta/^{\circ}\mathrm{C}) \tag{3b}$$

$$\rho(\mathrm{squalane})/\mathrm{g{\cdot}cm^{-3}} = 0.821592 \;-\; 6.435\,36 \cdot 10^{-4}(\theta/^{\circ}\mathrm{C}) + 4.770\,60 \cdot 10^{-8}(\theta/^{\circ}\mathrm{C})^2 \tag{3c}$$

where θ is the Celsius temperature, with standard uncertainties of (± 2, ± 1, and ± 1)·10^{-5} g·cm^{-3}, respectively. For EHB, the results agree with those of Walker et al.,[17] determined with an Anton-Paar DMA45 vibrating-tube densimeter, with an average deviation of (−0.0003) g·cm^{-3}, comparable with the precision of this instrument. For DEHP, data from ref 33 lie approximately 0.1 % higher in the interval (0 to 99) °C for a sample with 97 % purity. For squalane, there are more extensive literature data:[35−39] deviations from the results of this work are shown in Figure 1. Generally, the results of this work lie approximately 0.0004 g·cm^{-3} higher than the literature values.

The viscosities are presented in Tables 3 to 6. Satisfactory agreement was obtained between the results for the two sinkers employed.

The transport properties of glass-forming liquids show varied dependences on temperature,[40−42] depending, in part, on the temperature range examined. The atmospheric pressure results were fitted to the Vogel−Fulcher−Tammann (VFT) equation

$$\eta = A\exp(B/(T - T_0)) \tag{4}$$

The data were also fitted to the generalized Andrade equation[43]

$$\eta = A'\exp(B'/T^n) \tag{5}$$

with $n = 4$ (Barlow−Lamb equation[44]) for EHB and DEHP and the fitted value 3.49 for squalane. The unusual fractional value for squalane may indicate a gradual, transitional, behavior between a low-temperature dependence of one kind and a high-temperature dependence of another due to changes in the number of rotational degrees of freedom with temperature: sharp discontinuities are known for diisobutyl phthalate and other compounds.[40,41] The coefficients for these fits are given in Table 7.

Figure 2 compares the atmospheric pressure literature viscosity data with the present results, using the VFT fits. For EHB, there is satisfactory agreement with the results of Walker et al.,[17] obtained with a glass capillary viscometer, in the range of temperature overlap other than at 0 °C, and with those of Bair.[45] There is also satisfactory agreement with the literature[33,40,46] for DEHP. For squalane,[21−23,37−39,47−50] there is also good agreement with rolling-ball[47,49] and falling-body results,[22,23,48,50] except for a point of Krahn and Luft[47] at 80 °C. Capillary viscometer data[21,37−39] tend to be lower by more than the stated uncertainties, possibly due to the large differences between the viscosities and surface tensions of the calibrants and squalane; the single point of Tripathi[38] at 25 °C is far too high.

As in the previous work on DIDP,[11] isotherms for the high-pressure results were fitted to polynomials in the pressure and the

Table 9. Coefficients of Best Fit for Equations 6 and 7

	coefficients and standard uncertainties			
	EHB	DEHP	squalane	DIDP
		MVFT, eq 6		
a	-2.0984 ± 0.036	-3.2021 ± 0.054	-2.6400 ± 0.036	-2.8386 ± 0.041
$b \cdot 10^4/\mathrm{MPa}^{-1}$	-10.91 ± 2.6	-1.55 ± 3.3	12.21 ± 2.3	-6.68 ± 2.5
$c \cdot 10^6/(\mathrm{MPa}^{-2})$	-4.27 ± 1.0	0.157 ± 1.3	-4.135 ± 0.94	-2.49 ± 1.2
d/K	442.04 ± 8.1	904.7 ± 14	772.35 ± 9.7	841.1 ± 10
$e/(\mathrm{K} \cdot \mathrm{MPa}^{-1})$	1.851 ± 0.44	2.7973 ± 0.054	2.7207 ± 0.038	2.9540 ± 0.039
$f \cdot 10^4\ /(\mathrm{K} \cdot \mathrm{MPa}^{-2})$	1.902 ± 1.4	-26.60 ± 1.6	-29.82 ± 1.3	-25.78 ± 2.4
$g \cdot 10^6/(\mathrm{K} \cdot \mathrm{MPa}^{-3})$		2.631 ± 0.29	3.869 ± 0.18	5.25 ± 1.1
$h \cdot 10^9/(\mathrm{K} \cdot \mathrm{MPa}^{-4})$				-4.10 ± 1.5
T_0/K	182.59 ± 1.0	173.54 ± 1.0	168.871 ± 0.82	183.138 ± 0.75
standard uncertainty of fit/%	1.3	1.3	1.1	1.8
		eq 7		
a'	-0.78600 ± 0.0059	-0.3687 ± 0.012	-0.6443 ± 0.032	-0.4054 ± 0.034
$b' \cdot 10^3/\mathrm{MPa}^{-1}$	4.893 ± 0.15	8.168 ± 0.29	7.957 ± 0.16	7.815 ± 0.17
$c'' \cdot 10^6/\ \mathrm{MPa}^{-2}$	-5.594 ± 0.65	-7.20 ± 1.2	-8.406 ± 0.63	-6.742 ± 0.77
$d' \cdot 10^{-10}/\mathrm{K}^n$	1.98973 ± 0.0044	3.4916 ± 0.011	0.1746 ± 0.029	2.267 ± 0.41
$e' \cdot 10^{-7}\ /(\mathrm{K}^n \cdot \mathrm{MPa}^{-1})$	8.158 ± 0.12	11.115 ± 0.25	0.632 ± 0.11	7.82 ± 1.5
$f' \cdot 10^{-3}/(\mathrm{K}^n \cdot \mathrm{MPa}^{-2})$	5.43 ± 8.1	-112.6 ± 12	-8.81 ± 1.5	-63.2 ± 13
$g' \cdot 10^{-1}/(\mathrm{K}^n \cdot \mathrm{MPa}^{-3})$	8.48 ± 2.5	20.37 ± 3.6	1.512 ± 0.27	11.49 ± 2.4
n	4	4	3.493 ± 0.031	3.907 ± 0.033
standard uncertainty of fit/%	1.2	2.2	1.2	1.3

molar volume to assess the quality of the data. Coefficients for the pressure fits are given in Table 8. The data sets were then fitted to modified VFT and modified Andrade equations, as appropriate

$$\eta = \exp(a + bp + cp^2 + (d + ep + fp^2 + gp^3 + hp^4)/(T - T_0)) \quad (6)$$

$$\eta = \exp(a' + b'p + c'p^2 + (d' + e'p + f'p^2 + g'p^3)/T^n) \quad (7)$$

with the fitting parameters being given in Table 9. For squalane, as for DIDP,[11] the fit to these functions over the full temperature range is not as good as one might be led to expect from the polynomial fits for individual isotherms. Examination of the Stickel parameter,[43] $\phi_T = \{[1/(\partial \ln \eta/\partial(1/T)]_p\}^{1/2}$, at 0.1 MPa, shows it to be nonlinear in $(1/T)$ (as can be confirmed by differentiating eq 5). As ϕ_T is a constant for Andrade temperature dependence and linear in $(1/T)$ for VFT temperature dependence,[51] this implies that the MVFT type of fitting equation, while found to be adequate here for the purposes of correlation and data comparison, may not be the best form for these substances.

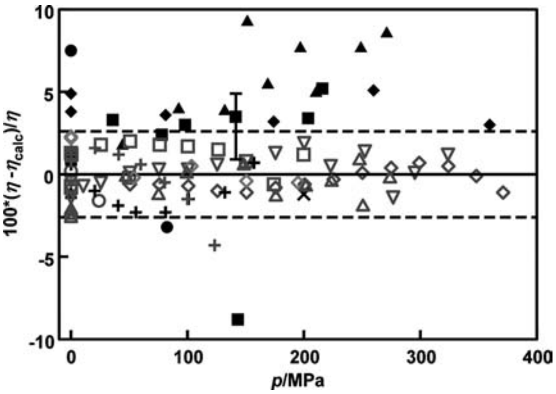

Figure 4. Residuals (experimental − calculated values) for the MVFT equation fit of the high-pressure viscosities for DEHP. This work, expanded uncertainty of the fit ± 2.6 % (dashed lines, $k = 2$): 6.0 mm sinker, ○, 0 °C; ○, 10 °C; □, 25 °C; △, 37.78 °C; ▽, 50 °C; ◇, 75 °C; 6.3 mm sinker, ◇, 75 °C. ASME tables, ref 33, falling sinker viscometer, standard deviation ± 2 %: ●, 0 °C; ■, 25 °C; ▲, 37.78 °C; ▼, 99 °C. Ref 46, falling sinker viscometer, standard deviation ± 3 %: +, 30 °C. Ref 52, falling sinker viscometer, standard deviation ± 3 %: ×, 30 °C.

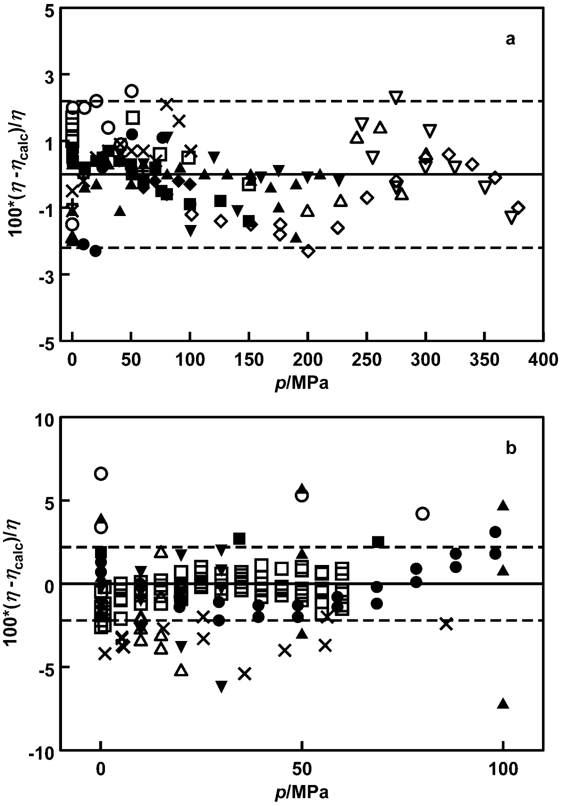

Figure 5. Residuals (experimental − calculated values) for the fit to the MVFT equation of the high-pressure viscosities for squalane. (a) This work, expanded uncertainty of the fit ± 2.2 % (dashed lines, $k = 2$): 6.0 mm sinker, ○, 0 °C; ●, 10 °C; ■, 25 °C; ▲, 40 °C; ▼, 50 °C; ◆, 75 °C. 6.3 mm sinker, rewound coils: +, 65 °C; ×, 75 °C. 6.0 mm sinker, rewound coils: □, 25 °C; △, 40 °C; ▽, 50 °C; ◇, 75 °C. (b) Literature values: rolling ball, ○, ref 47, (25, 80) °C, ± 2 %; □, ref 49, (30 to 80) °C, ± 3 %; △, ref 54, (20 to 80) °C, ± 3 %; falling sinker, ●, ref 50, (25, 40) °C, ± 0.4 %; ■, ref 22, 40 °C, ± 3 %; ▲, ref 23, (20, 40, 65) °C, ± 3 %; ▼, ref 48, (0 to 60) °C, ± 3 %; vibrating wire, ×, ref 28, (30, 75)°C, ± 1 %. For clarity of presentation, only values for pressures below 110 MPa are shown.

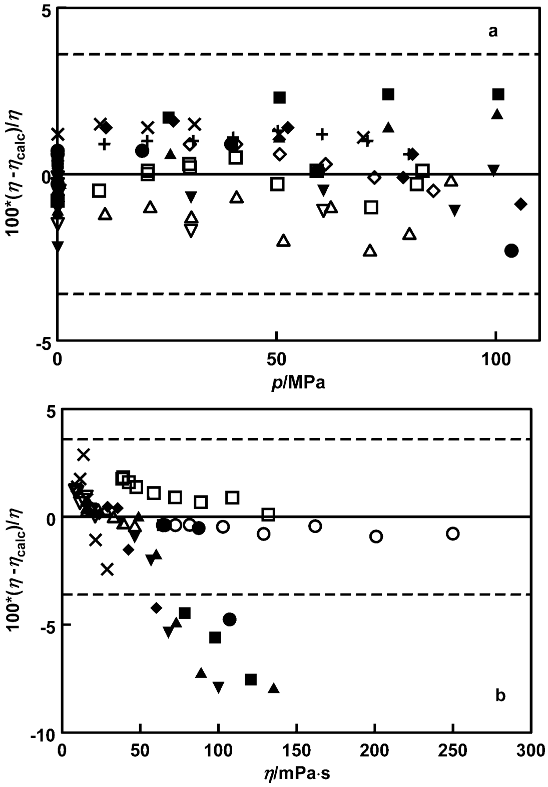

Figure 6. (a) Residuals (experimental − calculated values) for the fit to the MVFT equation of the high-pressure viscosities for DIDP. (a) This work, expanded uncertainty of the fit ± 3.6 % (dashed lines, $k = 2$): ref 11, ●, 20 °C; ■, 25 °C; ▲, 40 °C; ▼, 50 °C; ◆, 75 °C. New measurements, [(0 to 100) MPa]; 6.0 mm sinker, □, 25 °C; △, 40 °C; ▽, 50 °C; ◇, 75 °C; 6.3 mm sinker, +, 65 °C; ×, 75 °C; (b) Literature values: ref 58, rolling ball, (0.1 to 60) MPa, ± 4 %; ○, 30 °C; □, 40 °C; △, 60 °C; ▽, 60 °C; vibrating wire, ref 27, (2 to 2.5) %; ●, 25 °C, (0.1 to 10) MPa; ■, 30 °C, (0.1 to 30) MPa; ▲, 35 °C, (0.1 to 50) MPa; ▼, 40 °C, (0.1 to 50) MPa; ◆, 50 °C, (0.1 to 70) MPa; ×, 75 °C, (0.1 to 70) MPa.

Figure 3 compares the high-pressure data for EHB with the results of Walker et al.[17] and of Bair[45] as deviations from the MVFT fit, eq 6. Walker et al. used a falling-body viscometer where the terminal velocity of the sinker was determined with a linear variable differential transformer (LVDT). The accuracy of this instrument is given as ± 10 %, but the deviations from the results of this work within the ranges of overlapping pressures and temperatures generally exceed this value at high pressures, except at 0 °C. On the other hand, the LVDT falling-body viscometer results of Bair, which have an expanded uncertainty of ± 3 %, though slightly higher, are in better agreement with those of this work, even at 100 °C.

Figure 4 compares the high-pressure MVFT1 fit for DEHP with literature results.[33,46,52] The ASME tabulation[33] yields values that deviate from this correlation with increasing pressure, and the scatter is larger than the ± 2 % uncertainty (cited elsewhere[44]). The results of Irving and Barlow,[46] and of Bair,[52] obtained at 30 °C, agree well with those of this work. The results of Mclachlan,[53] also obtained at 30 °C, apply to higher pressures and viscosities.

Figure 5 compares the high-pressure MVFT1 fit for squalane with literature results.[22,23,28,47−50,54] There is good agreement with the falling-body results of Kuss and Golly,[50] the moderate pressure falling-body[48] and rolling-ball results[54] of Kumagai and co-workers, and the rolling-ball measurements of Pensado et al.[49] Our results are in fair agreement with the very high-pressure falling-body results of Bair[22,23] in the region of overlap, though there are some outliers. The falling-body results of Krahn and Luft[47] are in poorer agreement, being up to 15 % higher at 80 °C.

Of particular interest are the high-pressure vibrating-wire results of Ciotta et al.[28] At the temperatures at which their data set overlaps this work, (30 and 75) °C, the data partly cover the range of viscosities where the falling-body[11] and vibrating-wire[27] data sets for DIDP diverge. The Ciotta data set is an average of 3 % below the MVFT1 correlation, which is within the combined expanded uncertainties [(2.2 and 2.3) %]. In this case, the vibrating-wire results seem consistent with those derived from the mechanical techniques. The deviations also show no viscosity dependence in the range (5 to 66) mPa·s. It should be noted that the two vibrating-wire instruments differ in their design and therefore have slightly different working equations.[55]

Scaling concepts are a useful way of examining, classifying, and applying the density dependence of liquids, particularly glass-formers and highly viscous liquids.[56,57] The transport properties of dense liquids are primarily governed by the repulsive component of intermolecular forces. Scaling assumes an intermolecular potential varying to the power 3γ

$$U \sim (1/r)^{3\gamma} \tag{8}$$

with the parameter γ being a material specific, thermodynamic state independent quantity that can be used to scale structural relaxation times and the viscosity

$$\eta(T, V) = f(TV^{\gamma}) \tag{9}$$

From the examination of the properties of a large number of real and model liquids,[56,57] γ has been found to be related to the Angel fragility concept and to be sensitive to the asymmetry and complexity of intermolecular interactions in ionic liquids, polymer melts, and liquids of highly asymmetric molecules such as esters. Typical values[57] are: n-alkanes, 6 to 13, increasing with decreasing carbon number; ionic liquids, 2 to 4; alcohols, 1.5 to 3.5; and complex esters, 3 to 6.

The function f is not known. To evaluate γ, it is sufficient to fit the viscosity data as ln η to simple polynomials in (TV^{γ}), choosing γ such that the isotherms fall on a common curve with minimized residuals. The fits are not perfect, tending to be poorer for higher viscosities, but given the simplicity of the approach and that there is only one disposable parameter, the quality and utility of the model are quite good. From the results for EHB, DEHP, and squalane, one obtains γ values of (3.69 ± 0.02), (3.65 ± 0.03), and (4.16 ± 0.04), respectively. The values for the two viscous esters fall within the range of typical values, and Roland et al.[56] have previously reported a value of 4.2 for squalane.

DIDP. As remarked in the Introduction, Al Motari et al.,[27] using a moderate pressure vibrating-wire viscometer (70 MPa maximum pressure), found systematic differences between the results of their instrument and our earlier work on DIDP.[11] These differences increase with increasing viscosity and under some temperature conditions become larger than the combined uncertainties of the data sets. We have repeated our determinations between (0 and 75) °C, with measurements at approximately 10 MPa intervals between (0.1 and 100) MPa at (25, 40, 65 and 75) °C to more closely match the data reported by Al Motari and co-workers[27] (Table 6). As shown in Figure 6, the difference remains at the highest viscosities, above atmospheric pressure. Very recent data from the Fernández group,[58] also shown in Figure 6, are consistent with our results. Our two sets of experiments employed two sinkers, calibrated between (51 and 2966) mPa•s (6.0 mm diameter) and (0.5 and 202) mPa•s (6.3 mm diameter). As for EHB, DEHP, squalane, and various viscous ionic liquids, there is good agreement between the results obtained with the two sinkers. It has been shown previously, using additional sinkers, that Scott's theoretical linear relationship[59] between the fourth power of the sinker-tube clearance and the calibration constant is obeyed for this viscometer.[31] Al Motari et al.[27] have suggested that the differences may be due to incomplete theoretical descriptions of one, or possibly even both, types of viscometer. This aspect of the problem is currently under investigation, but at present the falling-body results for viscous fluids seem entirely consistent with one another for at least three fluids (DIDP, DEHP, and squalane). Further, the vibrating-wire results of Trusler's group for squalane are also consistent with the other measurements for this substance.

Finally, a fit of the data as a function of (TV^{γ}) yields a scaling parameter, γ, of (3.96 ± 0.03) for DIDP.

Conclusions

The viscosities of the highly viscous fluids 2-ethylhexyl benzoate, bis(2-ethylhexyl) phthalate, and 2,6,10,15,19,23-hexamethyltetracosane (squalane) have been measured at high pressure using a falling-body viscometer over a range of temperatures. These have an expanded uncertainty of ± 2 %. Ancillary data for the densities have been obtained at atmospheric pressure between (0 and 90) °C using a vibrating-tube densimeter and are viscosity corrected. Empirical correlations are provided for the viscosities in terms of temperature and pressure. These complement those previously measured for the reference material diisodecyl phthalate and have the advantage that they are for isomerically pure materials. New values of the viscosity of diisodecyl phthalate have been measured between (25 and 75) °C to approximately 90 MPa. These are consistent with the earlier results of Harris and Bair[11] and the rolling-ball results of Paredes et al.,[58] but the vibrating-wire results of Al Motari et al.[27] show deviations that systematically increase with increasing viscosity. This contrasts with squalane where the vibrating-wire results of Ciotta et al.,[28] though slightly offset from the correlation of this work, are consistent with the results from mechanical viscometers within the experimental uncertainties and the deviations show no viscosity dependence. The viscosity data have also been fitted as a function of temperature and volume to the thermodynamic scaling model of Roland et. al,[56] yielding scaling parameters of 3.69, 3.65, 4.16, and 3.96 for EHB, DEHP, squalane, and DIDP, respectively.

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Note Added in Proof: The European Chemical Agency has recently (20 Oct 2008) listed DEHP as a "Substance of Very High Concern (SVHC)", classifying it as toxic to (human) reproduction. Consequently, this substance may not meet OH & S criteria in some countries or organizations for use as a reference or calibration material. See http://echa.europa.eu/chem_data/candidate_list_table_en.asp.

Literature Cited

(1) Swindells, J. F.; Coe, J. R.; Godfrey, J. B. Absolute viscosity of water at 20 °C. *J. Res. NBS* **1952**, *48*, 1–31.
(2) ISO/TR 3666: 1998(E) Viscosity of water.
(3) Nieto de Castro, C. A.; Santos, F. J. V.; Fareleira, J. M. N. A.; Wakeham, W. A. Metrology of viscosity: have we learned enough? *J. Chem. Eng. Data* **2009**, *54*, 171–178.
(4) Cannon Instrument Company, 2139 High Tech Road, State College, PA 16803, USA; Paragon Scientific Limited, 2 Kelvin Park, Dock Road, Birkenhead, Wirral CH41 1LT, UK.
(5) International Association for the Properties of Water and Steam, *Release on the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance*, available at http://www.iapws.org (accessed September 2008).
(6) IATP: http://transp.eng.auth.gr/.
(7) Assael, M. J.; Bauer, H.; Dalaouti, N. K.; Harris, K. R. Reference correlation for the viscosity of liquid cyclopentane from 220 to 310 K at pressures to 25 MPa. *Int. J. Thermophys.* **2004**, *25*, 13–20.
(8) Assael, M. J.; Avelino, H. M. T.; Dalaouti, N. K.; Fareleira, J. M. N. A.; Harris, K. R. Reference correlation for the viscosity of liquid toluene from 213 to 373 K at pressures to 250 MPa. *Int. J. Thermophys.* **2001**, *22*, 789–799.
(9) Caetano, F. J. P.; Fareleira, J. M. N. A.; Fröba, A. P.; Harris, K. R.; Leipertz, A.; Oliveira, C. M. B. P.; Trusler, J. P. M.; Wakeham, W. A. An industrial reference fluid for moderately high viscosity. *J. Chem. Eng. Data* **2008**, *53*, 2003–2011.
(10) 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.
(11) Harris, K. R.; Bair, S. Temperature and pressure dependence of the viscosity of diisodecyl phthalate at temperatures between (0 and 100) °C and at pressures to 1 GPa. *J. Chem. Eng. Data* **2007**, *52*, 272–278.
(12) 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.
(13) Lundstrum, 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; correction, 1787.
(14) 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 a nominal viscosity at $T = 298$ K and $p = 0.1$ MPa of 290 mPa•s, at temperatures between (273 and 423 K) and pressures below 275 MPa. *J. Chem. Eng. Data* **2006**, *51*, 2185–2196.
(15) Walker, N. A.; Lamb, D. M.; Jonas, J.; Dare-Edwards, M. P. The use of spin-echo Bessel analysis and rotating-frame relaxation techniques to measure self-diffusion over an extended viscosity range. *J. Magn. Reson.* **1987**, *74*, 580–583.
(16) 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.
(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) Barlow, A. J.; Harrison, G.; Irving, J. B.; Kim, M. G.; Lamb, J.; Pursley, W. C. The effect of pressure on the viscoelastic properties of liquids. *Proc. R. Soc., London A* **1972**, *327*, 403–412.
(19) Bair, S.; Winer, W. O. A quantitative test of the Einstein-Debye relation using the shear dependence of the viscosity for low molecular weight liquids. *Tribol. Lett.* **2007**, *26*, 223–228.
(20) Barlow, A. J.; Erginsav, A.; Lamb, J. Viscous relaxation of supercooled liquids II. *Proc. R. Soc. London A* **1967**, *298*, 481–494.
(21) Barlow, A. J.; Erginsav, A. Viscoelastic retardation of supercooled liquids. *Proc. R. Soc. London A.* **1972**, *327*, 175–190.
(22) Bair, S. The high pressure rheology of some simple model hydrocarbons. *Proc. Inst. Mech. Eng., Part J: J. Eng. Tribol.* **2002**, *216*, 139–149.
(23) Bair, S. Reference liquids for quantitative elastrohydrodynamics: selection and rheological characterization. *Tribol. Lett.* **2006**, *22*, 197–206.

(24) Paluch, M.; Ziolo, J.; Rzoska, S. J.; Habdas, P. The influence of pressure on dielectric relaxation for phthalate derivatives in the supercooled state. *J. Phys.: Condens. Matter* **1997**, *9*, 5485–5494.

(25) Pensado, A. S.; Padua, A. A. H.; Comuñas, M. J. P.; Fernández, J. Relationship between viscosity coefficients and volumetric properties using a scaling concept for molecular and ionic liquids. *J. Phys. Chem. B* **2008**, *112*, 5563–5574.

(26) Bair, S.; Cassalini, R. A scaling parameter and function for the accurate correlation of viscosity with temperature and pressure across eight orders of magnitude. *J. Tribol.* **2008**, *130*, 041802-1–041802-7.

(27) Al Motari, M. M.; Kandil, M. E.; Marsh, K. N.; Goodwin, A. R. H. Density and viscosity of diisodecyl phthalate $C_6H_4(COOC_{10}H_{21})_2$, with nominal viscosity at $T = 298$ K and $p = 0.1$ MPa of 87 mPa·s, at temperatures from (298.15 to 423.15) K and pressures up to 70 MPa. *J. Chem. Eng. Data* **2007**, *52*, 1233–1239.

(28) Ciotta, F.; Maitland, G.; Smietana, M.; Trusler, J. P. M.; Vesovic, V. Viscosity and density of carbon dioxide + 2,6,10,15,19,23-hexamethyltetracosane (squalane). *J. Chem. Eng. Data*, **2009**,*54*, DOI: 10.1021/je800894y.

(29) 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.

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

(31) 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.

(32) 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.

(33) 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.

(34) Kuss, E.; Taslimi, M. p, V, T-Messungen an zwanzig organischen Flüssigkeiten. *Chem. Ing. Tech.* **1970**, *17*, 1073–1120.

(35) Fandiño, O.; Pensado, A. S.; Comuñas, M. J. P.; Fernández, J. Compressed liquid densities of squalane and pentaerythritol tetra(2-ethylhexanoate). *J. Chem. Eng. Data* **2005**, *50*, 939–946; correction, **2006**, *51*, 2274.

(36) Kumagai, A.; Takahashi, S. Viscosity and density of liquid mixtures of n-alkanes with squalane. *Int. J. Thermophys.* **1995**, *16*, 773–779.

(37) Fermeglia, M.; Torriano, G. Density, viscosity, and refractive index for binary systems of *n*-C16 and four nonlinear alkanes at 298.15 K. *J. Chem. Eng. Data* **1999**, *44*, 965–969.

(38) Tripathi, N. Densities, viscosities and refractive indices of mixtures of hexane with cyclohexane, decane, hexadecane, and squalane at 298.15 K. *Int. J. Thermophys.* **2005**, *26*, 693–703.

(39) Dubey, G. P.; Sharmas, M. Excess volumes, densities, speeds of sound, and viscosities for the binary systems of 1-octanol with hexadecane and squalane at (298.15, 303.15 and 308.15) K. *Int. J. Thermophys.* **2008**, *29*, 1361–1375.

(40) Barlow, A. J.; Lamb, J.; Matheson, A. J. Viscous behaviour of supercooled fluids. *Proc. R. Soc. London A* **1966**, *292*, 322–342.

(41) Tyrrell, H. J. V.; Watkiss, P. J. Diffusion in viscous solvents Part 3.-Interdiffusion coefficients for planar and spherical solutes in 2-methylpentane 2,4-diol and their relationship to diffusion coefficients derived from luminescence measurements. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1417–1432.

(42) Casalini, R.; Bair, S. The inflection point in the pressure dependence of viscosity under high pressure: a comprehensive study of the temperature and pressure dependence of the viscosity of propylene carbonate. *J. Chem. Phys.* **2008**, *128*, 084511-1–084511-7.

(43) Stickel, F.; Fischer, E. W.; Richert, R. Dynamics of glass-forming liquids. I. Temperature-derivative analysis of dielectric relaxation data. *J. Chem. Phys.* **1995**, *102*, 6251–6257.

(44) 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.

(45) Bair, S. *High Pressure Rheology For Quantitative Elastohydrodynamics*; Tribology and Interface Engineering Series, 54; Elsevier: Amsterdam, 2007; p 97.

(46) Irving, J. B.; Barlow, A. J. An automatic high pressure viscometer. *J. Phys. E: Sci. Instrum.* **1971**, *4*, 232–236.

(47) Krahn, U. G.; Luft, G. Viscosity of several liquid hydrocarbons in the temperature range 298−453 K at pressures up to 200 MPa. *J. Chem. Eng. Data* **1994**, *39*, 670–672.

(48) Kumagai, A.; Tomida, D.; Yokoyama, C. Measurements of the liquid viscosities of *n*-butane, *n*-hexane, and *n*-octane with squalane to 30 MPa. *Int. J. Thermophys.* **2006**, *27*, 376–393.

(49) Pensado, A. S.; Comuñas, M. J. P.; Lugo, L.; Fernández, J. High pressure characterization of dynamic viscosity and derived properties for squalane and two Pentaerythritol ester lubricants: pentaerythritol tetra-2-ethylhexanoate and pentaerythritol tetranonanoate. *Ind. Eng. Chem. Res.* **2006**, *45*, 2394–2404.

(50) Kuss, E.; Golly, H. Viscosity-pressure relation of gas-liquid solutions. *Ber. Bunsen-ges. Phys. Chem.* **1972**, *76*, 131–138.

(51) Bair, S.; Roland, C. M.; Casalini, R. Fragility and the dynamic crossover in lubricants. *Proc. Inst. Mech. Eng., Part J: J. Eng. Tribol.* **2007**, *221*, 801–810.

(52) Bair, S. Georgia Institute of Technology, private communication.

(53) Mclachlan, R. A new high pressure viscometer for viscosity range 10 to 10^6 Pa·s. *J. Phys. E: Sci. Instrum.* **1976**, *9*, 391–392.

(54) Tomida, D.; Kumagai, A.; Yokoyama, C. Viscosity measurements and correlation of the squalane + CO_2 mixture. *Int. J. Thermophys.* **2007**, *28*, 133–145.

(55) Goodwin, A. R. H., private communication.

(56) Roland, C. M.; Bair, S.; Casalini, R. Thermodynamic scaling of the viscosity of van der Waals, H-bonded, and ionic liquids. *J. Chem. Phys.* **2006**, *125*, 124508-1–124508-8.

(57) Pensado, A. S.; Pádua, A. A. H.; Comuñas, M. J. P.; Fernández, J. Relationship between viscosity coefficients and volumetric properties using a scaling concept for molecular and ionic liquids. *J. Phys. Chem. B* **2008**, *112*, 5563–5574.

(58) Paredes, X.; Fandiño, O.; Comuñas, M. J. P.; Pensado, A. S.; Fernández, J. Study of the effects of pressure on the viscosity and density of diisodecyl phthalate. *J. Chem. Thermodyn.* **2009**, in press, doi: 10.1016/j.jct.2009.04.002.

(59) Scott, R. The Viscosity of Argon. Thesis, Imperial College of Science and Technology, University of London, UK., 1959.

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