Temperature and Volume Dependence of the Viscosity of Water and Heavy Water at Low Temperatures

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New measurements have been made for the viscosity (η) of light and heavy water between the temperatures of 255.65 K and 298.15 K at pressures up to approximately 375 MPa with a falling-body viscometer. A revised correlation function is used to represent the results as a function of temperature and molar volume (V) with a standard deviation of ±0.2% for both H_2O and D_2O. The overall uncertainty is estimated at ±1%. Comparison of the two sets of data shows that they are consistent with the correlation $\eta(D_2O,T,V) = 1.0544\eta(H_2O,T - 6.498\ K,V)$ where 1.0544 is the square root of ratio the molar masses and 6.498 K is the thermal offset proposed by Robinson and co-workers.

Introduction

Recently Harris[1] examined the difference between the viscosity and self-diffusion coefficients of water and heavy water at high pressures in terms of the scaling relationship suggested by Robinson and co-workers,[2] the so-called thermal-offset effect. Within experimental precision, the viscosity of heavy water at a given temperature and pressure was found to equal that of ordinary water at a temperature 6.498 K lower and the same pressure, corrected for the difference in molar mass

$$\eta(D_2O,T/K,p) = 1.0544\eta(H_2O,(T - 6.498)/K,p) \quad (1)$$

An analogous relation holds for the self-diffusion coefficient

$$D(D_2O,T/K,p) = D(H_2O,(T - 6.498)/K,p)/1.0544 \quad (2)$$

The quantity 1.0544 is the square root of the molar mass ratio of the two isotopomeric forms of water. While the self-diffusion data conformed to eq 2 down to temperatures of −30 °C and up to pressures of 400 MPa, the low-temperature viscosity data (−15 °C to 10 °C) of Jonas and co-workers [3,4] showed considerable scatter in the correlation, whereas the higher-temperature data (2 °C to 25 °C) of Harlow [5] conformed well.

At the time of publication of the correlating paper,[1] we were unaware of the low-temperature results of Först and co-workers[6] for ordinary water which extend to −13 °C, but unfortunately these diverge by as much as 6% from those of DeFries and Jonas at high pressures. Agayev[7,8] has also made viscosity measurements on both isotopomers to −10 °C, but to much lower pressures than the other groups. Table 1 summarizes the available high-pressure measurements, including two other sets of high-pressure data for ordinary water that overlap the range of state points reported here.[9,10] It is desirable to be able to test the viscosity correlation at least as well as has been done for self-diffusion, and this is best accomplished if data are available for the two isotopomers measured with the same instrument and under the same range of conditions. This was the impetus for this work.

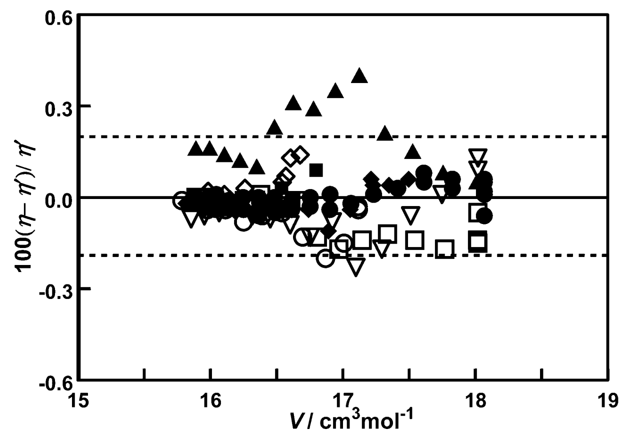

Figure 1. Residuals (experimental − calculated values) for the fit of the experimental high-pressure viscosities for H_2O to eq 4 as a function of molar volume, V. The dashed lines represent the expanded uncertainty of the fit, or 95% confidence limits, that is, the standard uncertainty multiplied by 2. ◇, −17.5 °C; ■, −15 °C; ○, −10 °C; ◆, − 5 °C; ▽, 0 °C; ▲, 5 °C; □, 10 °C; ●, 25 °C.

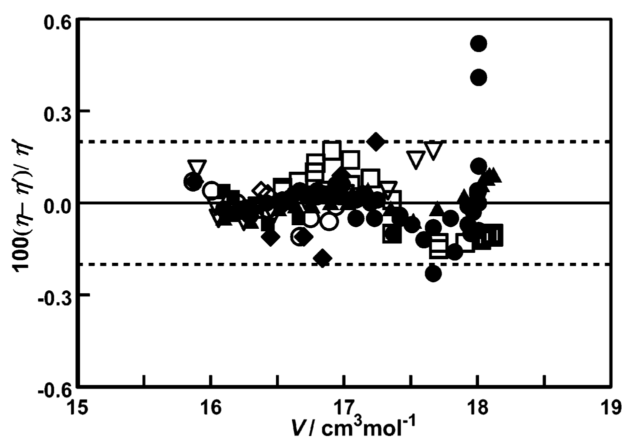

Figure 2. Residuals (experimental − calculated values) for the fit of the experimental high-pressure viscosities for D_2O to eq 4 as a function of molar volume, V. ◇, −17.5 °C; ■, −15 °C; ○, −10 °C; ◆, − 5 °C; ▽, 0 °C; ▲, 5 °C; □, 10 °C; ●, 25 °C.

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10.1021/je049918m CCC: $27.50
Published on Web 05/15/2004

Table 1. High-Pressure Viscosity Data for H_2O and D_2O

substance	temperature range/°C	pressure range /MPa	uncertainty	ref and technique
H_2O	2.2 to 100	0.1−990	1.4%	Harlow, 1967;[5] centered falling body
D_2O	10 to 100	0.1−990	1.4%	Harlow, 1967;[3] centered falling body
H_2O	2 to 30	0.1−138	±1.5%	Stanley and Batten, 1969;[9] rolling ball
H_2O	−15 to 10	0.1−600	±2%	DeFries and Jonas, 1977;[3] rolling ball
D_2O	−15 to 10	0.1−700	±2%	DeFries and Jonas, 1977;[4] rolling ball
H_2O	−10 to 375	0.1−200	±1.5%	Agayev, 1980;[7] capillary
D_2O	4	0.1−196	±1.5%	Agayev, 1980;[7] capillary
H_2O	10 to 75	0.1−120	±2%	Tanaka et al., 1987;[10] centered falling body
D_2O	−9 to 0	0.1−216	±1.2%	Agayev, 1989[8]
H_2O	−13 to 20	0.1−700	±0.5%	Först et al., 2000;[6] rolling ball

Table 2. Viscosity of Ordinary Water from 298 K to 255 K

T/K	t/s	p/MPa	V/(cm^3/mol)	ρ/(g/cm^3)	η/(mPa·s)	Re^a	T/K	t/s	p/MPa	V/(cm^3/mol)	ρ/(g/cm^3)	η/(mPa·s)	Re^a
298.15	29.64	0.1	18.068	0.99706	0.892	374	273.15	59.77	0.1	18.020	0.99974	1.799	92
298.15	29.64	0.1	18.068	0.99706	0.892	374	273.15	59.88	0.1	18.020	0.99974	1.802	92
298.15	29.68	0.1	18.068	0.99706	0.893	373	273.15	57.33	30.7	17.748	1.01507	1.722	102
298.15	29.68	0.1	18.068	0.99706	0.893	373	273.15	55.99	60.4	17.512	1.02876	1.678	109
298.15	29.68	0.1	18.068	0.99706	0.893	373	273.15	55.26	90.7	17.295	1.04165	1.653	113
298.15	29.58	31.0	17.828	1.01053	0.888	382	273.15	55.05	120.6	17.099	1.05359	1.644	116
298.15	29.64	61.0	17.613	1.02284	0.888	386	273.15	55.31	150.3	16.921	1.06469	1.649	116
298.15	29.80	90.9	17.416	1.03443	0.891	387	273.15	55.75	180.0	16.755	1.07521	1.659	115
298.15	30.06	120.7	17.233	1.04538	0.898	384	273.15	56.46	209.6	16.602	1.08513	1.678	114
298.15	30.42	150.6	17.064	1.05578	0.907	380	273.15	57.43	240.3	16.453	1.09496	1.704	111
298.15	30.87	180.6	16.905	1.06566	0.919	373	273.15	58.54	270.4	16.316	1.10412	1.735	108
298.15	31.36	210.6	16.758	1.07504	0.933	365	273.15	59.84	300.4	16.188	1.11287	1.771	104
298.15	31.92	240.6	16.620	1.08394	0.948	356	273.15	61.24	330.3	16.067	1.12126	1.810	100
298.15	32.53	270.1	16.494	1.09225	0.965	345	273.15	62.72	359.5	15.955	1.12916	1.852	96
298.15	33.18	299.7	16.374	1.10023	0.983	335	273.15	64.19	386.7	15.855	1.13626	1.893	93
298.15	33.86	329.2	16.261	1.10785	1.002	324	268.15	65.70	61.1	17.496	1.02966	1.969	79
298.15	34.58	358.5	16.155	1.11515	1.022	313	268.15	64.88	80.8	17.349	1.03839	1.942	82
298.15	35.30	384.3	16.065	1.12139	1.042	302	268.15	64.45	98.0	17.228	1.04572	1.927	84
283.15	43.65	0.1	18.020	0.99974	1.313	173	268.15	64.42	100.2	17.213	1.04661	1.926	84
283.15	43.56	0.1	18.020	0.99974	1.310	174	268.15	64.11	124.2	17.056	1.05626	1.914	85
283.15	43.54	0.1	18.020	0.99975	1.310	174	268.15	64.17	151.1	16.892	1.06652	1.913	86
283.15	43.54	0.5	18.017	0.99991	1.310	174	268.15	64.65	177.5	16.742	1.07608	1.924	86
283.15	42.65	30.7	17.769	1.01388	1.280	184	268.15	65.61	213.3	16.554	1.08830	1.949	84
283.15	42.19	60.7	17.544	1.02684	1.264	191	268.15	66.81	245.4	16.398	1.09863	1.982	82
283.15	42.03	90.7	17.337	1.03910	1.257	195	268.15	69.18	295.3	16.176	1.11372	2.047	78
283.15	42.09	120.8	17.147	1.05062	1.257	197	268.15	72.40	350.8	15.953	1.12930	2.138	72
283.15	42.38	150.8	16.973	1.06143	1.263	197	268.15	74.26	376.7	15.856	1.13620	2.190	69
283.15	42.84	180.8	16.812	1.07156	1.275	195	268.15	75.01	387.9	15.815	1.13910	2.212	68
283.15	43.49	210.2	16.668	1.08086	1.293	191	263.15	75.59	112.0	17.117	1.05246	2.258	61
283.15	44.26	240.6	16.529	1.08989	1.314	186	263.15	75.58	112.1	17.116	1.05251	2.258	61
283.15	45.11	270.7	16.402	1.09833	1.337	181	263.15	75.29	128.6	17.008	1.05921	2.247	62
283.15	46.00	300.2	16.286	1.10620	1.362	175	263.15	75.28	150.8	16.870	1.06787	2.244	63
283.15	46.98	330.0	16.176	1.11372	1.390	169	263.15	75.83	180.7	16.698	1.07890	2.256	63
283.15	48.06	359.2	16.073	1.12083	1.420	163	263.15	76.76	209.9	16.542	1.08905	2.281	62
283.15	49.12	385.2	15.986	1.12694	1.450	157	263.15	78.03	240.1	16.392	1.09902	2.315	60
278.15	50.78	0.1	18.015	0.99999	1.528	128	263.15	79.56	270.5	16.251	1.10855	2.357	59
278.15	50.77	0.1	18.015	0.99999	1.528	128	263.15	81.65	302.0	16.114	1.11799	2.415	56
278.15	50.76	0.6	18.011	1.00024	1.527	128	263.15	83.99	335.4	15.978	1.12749	2.481	54
278.15	49.33	30.7	17.758	1.01452	1.481	138	263.15	88.37	386.4	15.785	1.14126	2.605	49
278.15	48.53	60.7	17.527	1.02785	1.454	144	258.15	89.90	159.3	16.797	1.07251	2.678	44
278.15	48.16	90.5	17.318	1.04029	1.440	149	258.15	90.47	188.4	16.630	1.08333	2.690	44
278.15	48.18	120.3	17.126	1.05196	1.439	151	258.15	91.14	205.2	16.538	1.08930	2.708	44
278.15	48.44	150.8	16.946	1.06310	1.444	151	258.15	91.22	209.2	16.517	1.09068	2.710	44
278.15	48.93	180.7	16.785	1.07327	1.456	149	258.15	92.85	239.8	16.363	1.10098	2.754	43
278.15	49.67	210.7	16.638	1.08279	1.476	147	258.15	95.73	282.6	16.164	1.11450	2.834	41
278.15	50.47	240.4	16.504	1.09160	1.498	143	258.15	98.00	309.0	16.051	1.12237	2.898	39
278.15	51.32	270.4	16.378	1.09997	1.522	140	258.15	99.30	323.5	15.991	1.12657	2.934	38
278.15	52.51	300.6	16.261	1.10789	1.555	135	258.15	100.12	333.2	15.952	1.12933	2.957	38
278.15	53.77	330.3	16.153	1.11530	1.591	129	258.15	102.29	354.1	15.871	1.13512	3.019	36
278.15	55.18	360.0	16.051	1.12238	1.631	124	258.15	102.79	361.0	15.844	1.13701	3.033	36
278.15	56.64	389.0	15.956	1.12903	1.672	118	255.65	98.97	177.5	16.678	1.08018	2.945	37
							255.65	99.38	190.3	16.606	1.08489	2.955	37
							255.65	99.56	196.7	16.571	1.08719	2.959	37
							255.65	99.74	201.8	16.542	1.08904	2.964	37
							255.65	101.20	231.8	16.387	1.09937	3.003	36
							255.65	103.11	257.8	16.261	1.10789	3.056	35
							255.65	105.97	292.3	16.105	1.11860	3.135	33
							255.65	108.86	321.1	15.984	1.12710	3.217	32

[a] Reynolds number for annular flow: $\mathrm{Re} = 2r_1^2\rho v/((r_2 - r_1)\eta)$, where v is the terminal velocity of the sinker and r_1 and r_2 are the radii of the sinker and tube, respectively.[9]

A high-pressure falling-body viscometer has been used to determine the viscosity of both light and heavy water from 25 °C to our lowest operational temperature of −17.5 °C and our highest operational pressure of 400 MPa, while staying within the liquid phase bounded by the ice I and ice III melting lines.

Experimental Section

Ordinary water, deionized with a reverse-osmosis system, was further purified with a MilliQ ion exchange system (Waters-Millipore Ltd). The resistivity was 18 MΩ·cm. The heavy water (99.9 atom % D, resistivity of 11 MΩ·

Table 3. Viscosity of Heavy Water from 298 K to 255 K

T/K	t/s	p/MPa	V/(cm^3/ mol)	ρ/(g/cm^3)	η/(mPa·s)	Re	T/K	t/s	p/MPa	V/(cm^3/ mol)	ρ/(g/cm^3)	η/(mPa·s)	Re
298.15	37.08	0.1	18.0054	1.11230	1.095	272	278.15	67.14	0.1	18.1177	1.10540	1.987	82
298.15	37.34	0.1	18.0054	1.11230	1.103	268	278.15	66.85	3.1	18.0926	1.10694	1.977	83
298.15	37.10	0.1	18.0054	1.11230	1.096	272	278.15	66.56	5.6	18.0707	1.10828	1.968	84
298.15	37.14	0.1	18.0054	1.11230	1.097	271	278.15	66.32	8.1	18.0491	1.10961	1.961	85
298.15	37.28	0.1	18.0054	1.11230	1.101	269	278.15	66.03	10.8	18.0261	1.11102	1.952	86
298.15	37.04	0.1	18.0054	1.11230	1.094	272	278.15	64.74	25.9	17.9000	1.11885	1.911	90
298.15	37.00	5.6	17.9670	1.11467	1.092	274	278.15	63.18	50.8	17.7030	1.13130	1.862	95
298.15	36.94	8.0	17.9502	1.11572	1.090	275	278.15	62.18	75.6	17.5192	1.14317	1.829	100
298.15	36.97	10.3	17.9345	1.11670	1.091	275	278.15	61.67	100.7	17.3457	1.15461	1.811	103
298.15	36.93	10.7	17.9319	1.11686	1.090	275	278.15	61.50	125.6	17.1837	1.16549	1.803	104
298.15	36.77	25.7	17.8297	1.12326	1.084	280	278.15	61.57	150.5	17.0322	1.17585	1.802	105
298.15	36.71	50.7	17.6675	1.13357	1.081	284	278.15	61.90	174.5	16.8953	1.18538	1.809	105
298.15	36.66	50.7	17.6675	1.13358	1.079	284	278.15	62.44	199.1	16.7624	1.19478	1.822	104
298.15	36.73	75.6	17.5132	1.14356	1.080	286	278.15	63.17	224.1	16.6359	1.20387	1.841	103
298.15	36.81	90.6	17.4243	1.14939	1.081	287	278.15	64.08	249.6	16.5141	1.21274	1.865	101
298.15	36.85	100.6	17.3664	1.15323	1.081	287	278.15	66.19	299.7	16.2957	1.22900	1.922	96
298.15	37.09	125.6	17.2268	1.16257	1.087	286	278.15	68.79	349.1	16.1024	1.24376	1.993	90
298.15	37.16	130.6	17.1999	1.16439	1.089	286	273.15	74.52	52.0	17.6726	1.13324	2.196	69
298.15	37.39	150.6	17.0938	1.17162	1.094	284	273.15	73.36	69.6	17.5413	1.14173	2.159	72
298.15	37.75	170.5	16.9926	1.17860	1.104	281	273.15	72.07	99.7	17.3309	1.15559	2.116	75
298.15	37.81	175.6	16.9673	1.18035	1.105	280	273.15	72.07	99.7	17.3309	1.15559	2.116	75
298.15	38.28	200.6	16.8468	1.18880	1.117	276	273.15	71.59	130.4	17.1314	1.16905	2.098	77
298.15	38.47	210.2	16.8019	1.19197	1.122	274	273.15	71.61	150.6	17.0083	1.17750	2.096	78
298.15	38.81	225.5	16.7320	1.19695	1.131	270	273.15	71.97	177.3	16.8550	1.18822	2.103	78
298.15	39.37	249.7	16.6260	1.20459	1.146	265	273.15	72.62	204.3	16.7091	1.19859	2.119	77
298.15	40.66	299.6	16.4208	1.21963	1.181	252	273.15	73.25	223.0	16.6138	1.20547	2.135	77
298.15	41.53	331.9	16.2978	1.22884	1.205	244	273.15	74.42	252.9	16.4697	1.21602	2.165	75
298.15	42.10	349.0	16.2357	1.23354	1.221	238	273.15	75.82	279.5	16.3497	1.22494	2.203	73
298.15	37.10	0.1	18.0054	1.11230	1.096	271	273.15	76.99	302.9	16.2500	1.23245	2.234	71
298.15	37.10	0.2	18.0050	1.11232	1.095	272	273.15	80.03	350.5	16.0632	1.24679	2.318	67
298.15	37.10	0.2	18.0045	1.11235	1.095	272	273.15	80.68	357.5	16.0374	1.24879	2.336	66
298.15	36.79	30.7	17.7964	1.12536	1.084	280	273.15	84.22	395.2	15.9044	1.25923	2.435	61
298.15	36.69	60.7	17.6046	1.13762	1.079	285	268.15	84.98	109.7	17.2360	1.16195	2.494	54
298.15	36.81	90.7	17.4241	1.14941	1.081	287	268.15	84.44	125.3	17.1364	1.16870	2.475	55
298.15	37.06	120.7	17.2539	1.16075	1.086	286	268.15	84.33	150.9	16.9800	1.17947	2.468	56
298.15	37.42	150.6	17.0937	1.17162	1.095	284	268.15	84.33	174.7	16.8426	1.18909	2.464	57
298.15	37.93	180.6	16.9427	1.18207	1.108	279	268.15	85.04	201.2	16.6980	1.19939	2.481	56
298.15	38.49	210.6	16.8001	1.19210	1.123	274	268.15	87.14	251.4	16.4471	1.21768	2.535	55
298.15	39.16	240.6	16.6653	1.20174	1.141	267	268.15	89.59	289.2	16.2761	1.23048	2.601	52
298.15	39.87	270.5	16.5382	1.21098	1.160	260	268.15	92.27	325.5	16.1253	1.24199	2.675	50
298.15	40.68	300.3	16.4183	1.21983	1.182	252	268.15	98.60	390.6	15.8843	1.26083	2.850	45
298.15	41.53	330.1	16.3046	1.22833	1.205	244	263.15	100.46	153.2	16.9364	1.18250	2.939	40
298.15	42.43	359.8	16.1971	1.23648	1.230	235	263.15	100.43	160.8	16.8922	1.18560	2.937	40
298.15	43.43	389.4	16.0954	1.24429	1.257	226	263.15	100.84	185.3	16.7550	1.19531	2.944	40
283.15	56.68	0.1	18.1213	1.10519	1.677	115	263.15	101.22	200.8	16.6713	1.20131	2.953	40
283.15	56.66	0.2	18.1206	1.10523	1.676	115	263.15	103.81	249.5	16.4257	1.21927	3.020	39
283.15	56.68	0.2	18.1205	1.10523	1.677	115	263.15	107.71	299.6	16.1992	1.23632	3.125	36
283.15	56.47	3.0	18.0959	1.10674	1.670	116	263.15	112.62	347.1	16.0065	1.25121	3.260	34
283.15	56.31	5.6	18.0742	1.10806	1.665	117	263.15	116.98	383.4	15.8733	1.26171	3.381	32
283.15	56.15	8.1	18.0528	1.10938	1.660	118	258.15	122.22	196.9	16.6621	1.20198	3.566	27
283.15	55.98	10.8	18.0305	1.11075	1.655	119	258.15	123.12	215.3	16.5656	1.20897	3.588	27
283.15	55.17	25.8	17.9068	1.11842	1.629	123	258.15	124.71	242.9	16.4273	1.21916	3.629	27
283.15	54.20	50.8	17.7123	1.13070	1.597	130	258.15	127.24	271.0	16.2940	1.22913	3.697	26
283.15	54.23	50.8	17.7120	1.13073	1.598	129	258.15	130.19	298.5	16.1710	1.23848	3.777	25
283.15	53.42	100.8	17.3601	1.15364	1.569	137	258.15	132.31	315.6	16.0982	1.24408	3.835	24
283.15	53.36	100.8	17.3600	1.15365	1.567	137	255.65	135.97	212.2	16.5662	1.20893	3.963	22
283.15	53.41	125.5	17.2021	1.16424	1.566	138	255.65	136.38	220.1	16.5257	1.21189	3.973	22
283.15	53.63	150.6	17.0524	1.17446	1.570	138	255.65	137.87	239.2	16.4303	1.21893	4.012	22
283.15	53.59	150.8	17.0512	1.17454	1.569	139	255.65	138.79	249.5	16.3800	1.22268	4.036	22
283.15	54.03	175.5	16.9122	1.18420	1.579	138							
283.15	54.54	199.4	16.7862	1.19309	1.592	136							
283.15	54.52	199.7	16.7846	1.19320	1.592	136							
283.15	55.17	224.3	16.6617	1.20200	1.608	134							
283.15	55.96	249.6	16.5431	1.21062	1.629	132							
283.15	55.99	249.7	16.5428	1.21064	1.630	132							
283.15	57.76	299.2	16.3293	1.22647	1.678	126							
283.15	57.78	299.6	16.3275	1.22661	1.678	126							
283.15	59.95	348.6	16.1383	1.24099	1.737	118							
283.15	59.95	348.7	16.1377	1.24103	1.737	118							

cm) was obtained from the Aldrich Chemical Co. and used without further purification. The molar masses were taken to be (18.0153 and 20.0275) g/mol.

The high-pressure viscometer and its operation have been described elsewhere.[11,12] It was calibrated with Cannon standards.[12] Platinum-resistance thermometers newly recalibrated by the National Measurement Laboratory (CSIRO, West Lindfield, NSW) between (−65 and 100) °C on the ITS-90 to a tolerance of ±8 mK were employed. The viscometer oil-bath temperature was controlled[12] to within ±0.01 K (between −10 °C and 25 °C) and to ±0.02 K below −10 °C. The primary pressure gauge (400 MPa Heise CM) was calibrated[11] against a deadweight tester to ±0.05% and pressures have an overall uncertainty of ±0.2 MPa.

The working equation for the falling-body viscometer is[11,13,14]

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

where t is the fall time, ρ the density of the fluid, ρ_s the density of the sinker, α the coefficient of thermal expansion (1.6×10^{-5} K^{-1}), and β the bulk compressibility (2×10^{-6}

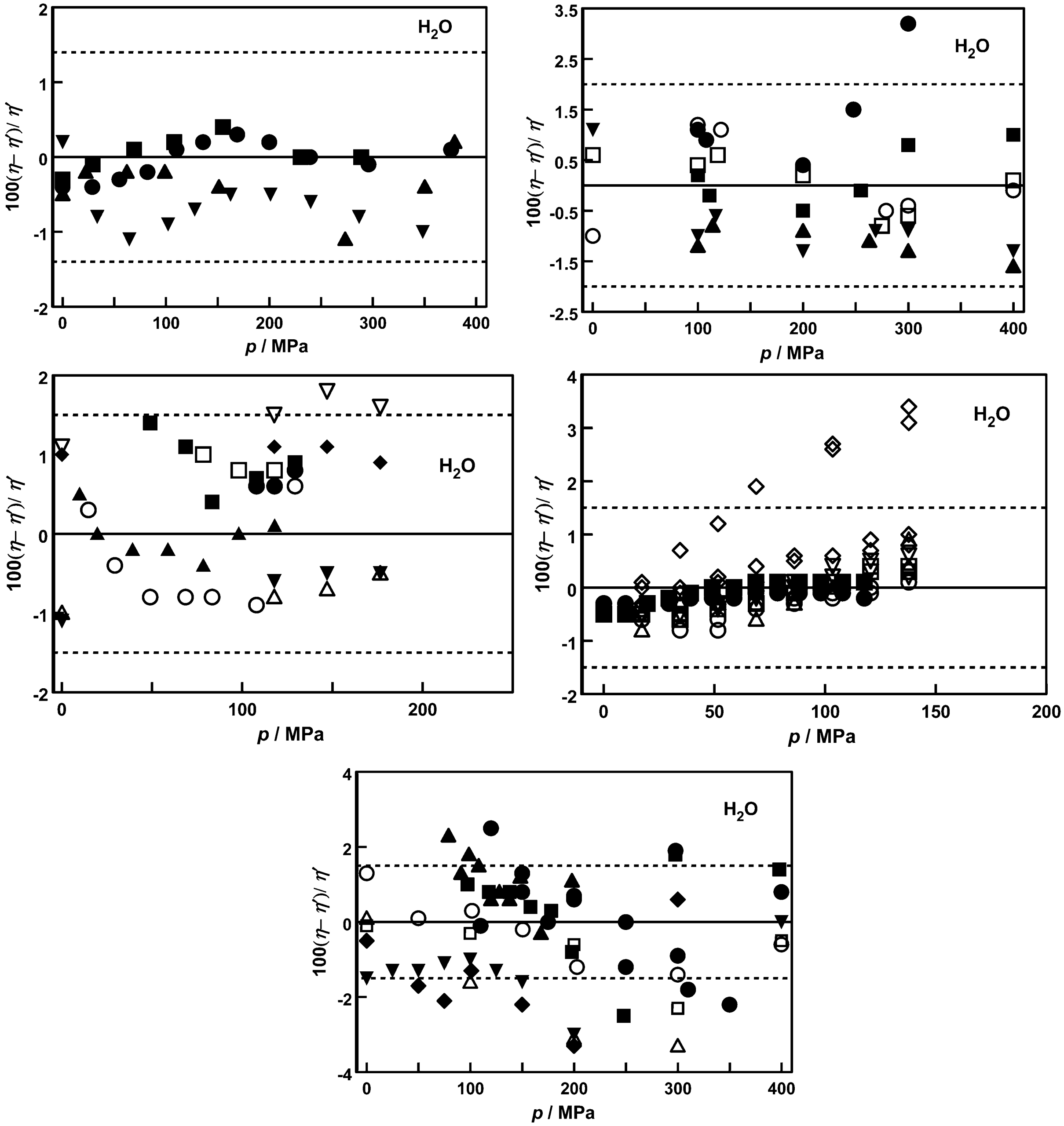

Figure 3. (a) Comparison of Harlow's data[5] for ordinary water (estimated uncertainty 1.4%) with the results of this work. The ordinate is the percentage difference between the experimental viscosity and that predicted from eq 4 using $x = p$. ▼, 2.2 °C; ●, 10 °C; ■, 20 °C; ▲, 25 °C. (b) Comparison of the DeFries and Jonas data[3] for ordinary water (estimated uncertainty ±2%) with the results of this work. ●, −15 °C; ■, −10 °C; ▲, − 5 °C; ▼, 0 °C; □, 5 °C; ○, 10 °C. (c) Comparison of Agayev's data[7] for ordinary water (estimated uncertainty ±1.5%) with the results of this work. ●, −8.9 °C; □, −6.6 °C; ■, −3.7 °C; ○, −1 °C; ▲, 0 °C; △, 2.2 °C; ▼, 10.6 °C; ▽, 18.2 °C; ◆, 19.7 °C. (d) Comparison of literature data for ordinary water with the results of this work. Tanaka et al. (estimated uncertainty ± 2%):[10] ●, 10 °C; ■, 25 °C. Stanley and Batten (estimated uncertainty ±1.5%):[9] ○, 2.2 °C; □, 6 °C; △, 10 °C; ▽, 15 °C; ◇, 20 °C. (e) Comparison of the data of Först et al.[6] for ordinary water (estimated uncertainty ±0.5%) with the results of this work (estimated uncertainty ± 1%). ●, −13 °C; ■, −8 °C; ▲, −5 °C; ◆, −2 °C; ▼, 0 °C; □, 4 °C; ○,10 °C; △, 20 °C.

Pa^{-1}) of the sinker and tube material, in this case, 316 stainless steel. A is the calibration constant, 28 707 Pa^{-1}, ±0.17%[12], obtained at temperature T_{ref} and pressure p_{ref}, valid for Re < 1000. [11] The sinker density was corrected for changes in T and p from the calibration state point, $T_{ref} = 298.15$ K and $p_{ref} = 0.1$ MPa using the relation[15]

$$\rho_s = \frac{\rho_s(T_{ref}, p_{ref})}{[1 + 3\alpha(T - T_{ref})][1 - \beta(p - p_{ref})]} \qquad (4)$$

The tube and sinker diameters are 6.5 mm and 6.3 mm, respectively. The overall uncertainty in the viscosity, based on replicate measurements and the sum of the uncertainty in the calibration (±0.2%) and that in the fit to the function of temperature and density described below (±0.3%), is estimated at ±1%.

Calculation of the viscosity from fall times requires knowledge of the density as a function of T and p. The equations of state recommended by the International Association for Water and Steam (IAWPS) were used to obtain the densities of H_2O[17] and D_2O[16] at the experimental state points. These equations are recommended for temperatures above the normal freezing points and for pressures to 100 MPa, though they can be employed outside these limits.

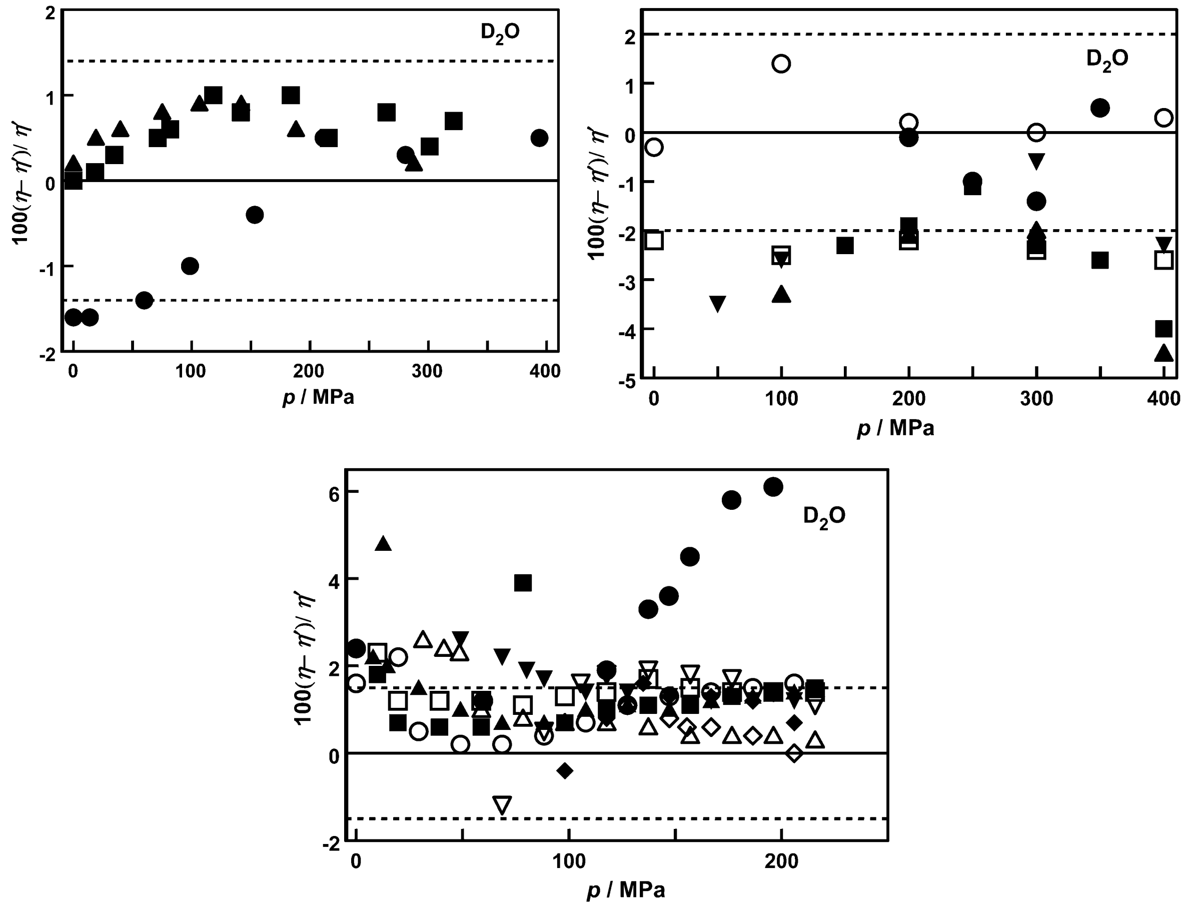

Figure 4. (a) Comparison of Harlow's data[5] for heavy water (estimated uncertainty ±1.4%) with the results of this work. ●, 10 °C; ■, 20 °C; ▲, 25 °C. (b) Comparison of the DeFries and Jonas data[4] for heavy water (estimated uncertainty ±2%) with the results of this work. ●, −15 °C; ■, −10 °C; ▲, −5 °C; ▼, 0 °C; □, 5 °C; ○, 10 °C. (c) Comparison of Agayev's data[7,8] for heavy water (estimated uncertainty ±1.5%) with the results of this work. ◇, −9.9 °C; ◆, −7.5 °C; ▽, −4.9 °C; ▼, −2.5 °C; △, 0 °C; ▲, 2.9 °C; ○, 3.8 °C; ●, 4 °C; ■, 7 °C; □, 10 °C.

Below the normal freezing point of water we have used the recent *pVT* measurements of Asada et al.[18] for H_2O as the IAWPS correlation is largely based on the older density data of Bridgman[19] at subzero temperatures. The Asada data, when differentiated to yield compressibilities and thermal expansivities, are in excellent agreement with experimental measurements for these quantities.

For heavy water, the IAWPS density values at (300 to 400) MPa and below 0 °C are significantly different (1 to 2%) from those based on the data of Bridgman[19] used by DeFries and Jonas.[4] The Bridgman densities were also used for the viscosity correlation of Aleksandrov and Mateev.[20] It is of interest that while the IAWPS density data for heavy water can be correlated with those for light water using the Robinson approach to some (25 to 30) MPa above the limit of the IAWPS equation of state (100 MPa) at temperatures below about 40 °C,[1] those of Bridgman show large deviations. Clearly new high-pressure density measurements for heavy water below the normal freezing point would be extremely useful. In the tables, we report the densities we have used in order for the viscosities to be recalculated should that be found necessary in the future.

Results and Discussion

The results are presented in Tables 2 and 3.

The viscosities were fitted as functions of temperature and pressure and temperature and molar volume to the empirical equation first used by Woolf[21]

$$\eta = \exp(a_1 + a_2 x + a_3 x/T + a_4 x^2 + a_5 x^2/T + a_6 x^3 + a_7/T + a_8/T^2) \quad (4)$$

where here x is either pressure, p, or molar volume, V (Woolf used pressure and density). The coefficients for the fits are given in Tables 4 and 5. The fit of $\eta(T,V)$ is better than that of $\eta(T,p)$ in each case. The residual plots for the former are shown as Figures 1 and 2.

Parts a−e of Figure 3 show a comparison of the literature data for water with our results, based on fitting the data as a function of pressure. There is excellent agreement with the data sets of Harlow,[5] Tanaka and co-workers,[10] Stanley and Batten[9] (except for one of the two isotherms reported for 20 °C), and Agayev.[7] There is also generally good agreement with the data sets of DeFries and Jonas[3] and of Först and co-workers,[6] though with some outliers, and we note that the latter group reported a divergence from the DeFries−Jonas data set at pressures higher than those covered in this work.

Parts a−c of Figure 4 show a comparison of the literature data for heavy water with our results. Again there is good agreement with the results of Harlow[5] and reasonable agreement with those of DeFries and Jonas[4] given the uncertainty in the densities referred to above, though there is some scatter between −5 °C and 5 °C. There is poor agreement with Agayev's 4 °C isotherm from his 1980 paper[7] but generally better agreement with his later

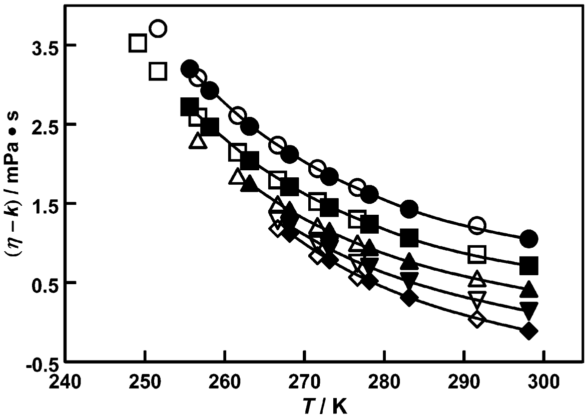

Figure 5. Comparison of isochoric viscosities of light (closed symbols) and heavy water (open symbols). The heavy water viscosities are divided by the factor 1.0544 and shifted to (T − 6.548 K). The isochores are also offset by the quantity k to avoid overlap. ●, ○, 16 cm^3/mol, $k = 0$ mPa·s; ■, □, 16.5 cm^3/mol, $k = 0.25$ mPa·s; ▲, △, 17 cm^3/mol, $k = 0.5$ mPa·s; ▼, ▽, 17.5 cm^3/mol, $k = 0.75$ mPa·s; ◆, ◇, 18 cm^3/mol, $k = 1$ mPa·s.

Table 4. Coefficients of Best Fit for Equation 4, $x = p$

	H_2O	D_2O
a_1	0.411 011	1.391 70
$a_2 \times 10^2/MPa^{-1}$	0.854 113	1.076 27
$a_3 \times 10^{-1}/(K \cdot MPa^{-1})$	−0.267 340	−0.337 597
$a_4 \times 10^4/MPa^{-2}$	−0.135 750	−0.176 949
$a_5 \times 10^2/(K \cdot MPa^{-2})$	0.525 404	0.656 687
$a_6 \times 10^8/MPa^{-3}$	−0.515 042	−0.534 170
$a_7 \times 10^{-4}/K$	−0.235 032	0.301 449
$a_8 \times 10^{-6}/K^2$	0.654 401	0.783 377
standard uncertainty/(mPa·s)	0.007	0.006
standard percentage uncertainty	0.4	0.3
maximum percentage deviation	1.1	1.2

Table 5. Coefficients of Best Fit for Equation 4, $x = V$

	H_2O	D_2O
$a_1 \times 10^{-2}$	−0.600 113	−0.349 075
$a_2 \times 10^{-1}/(mol \cdot cm^{-3})$	0.695 355	0.357 257
$a_3 \times 10^{-4}/(K \cdot mol \cdot cm^{-3})$	−0.373 675	−0.333 775
$a_4 \times 10/(mol^2 \cdot cm^{-6})$	−1.265 912	0.183 286
$a_5 \times 10^{-3}/(K \cdot mol^2 \cdot cm^{-6})$	0.116 435	0.104 781
$a_6 \times 10^2/(mol^3 \cdot cm^{-9})$	−0.400 576	−0.579 565
$a_7 \times 10^{-5}/K$	0.269 496	0.230 844
$a_8 \times 10^{-6}/K^2$	0.692 075	0.779 586
standard uncertainty/(mPa·s)	0.004	0.005
standard percentage uncertainty	0.1	0.1
maximum percentage deviation	0.4	0.4

results.[8] The higher deviations at lower pressures, where the experimental viscosity is higher than predicted from our correlation, correspond to points taken in the supercooled region, where Agayev estimated an uncertainty of 2.5%, somewhat higher than the 1.2% given for the normal liquid region.

Comparison of the light and heavy water viscosities shows they are better fitted by the volume analogue of eq 1

$$\eta(D_2O, T/K, V) = 1.0544\eta(H_2O, (T - 6.498\ K), V) \quad (5)$$

than as a function of pressure. This is shown in Figure 5; the maximum deviation is 1%. An analysis of the applicability of the Robinson conjecture to these and other data will be made in a separate article.

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Received for review February 23, 2004. Accepted April 14, 2004.

JE049918M