Measurements of the Viscosity of Alcohols in the Temperature Range 290–340 K at Pressures up to 30 MPa

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New measurements of the viscosity of methanol, ethanol, 1-propanol, and 1-butanol are presented. The measurements were performed in a vibrating-wire instrument and cover a temperature range of 290–340 K and pressures up to 30 MPa. The overall uncertainty in the reported data, confirmed by the measurement of the viscosity of water, is ± 0.5 %. The high-pressure experimental results were correlated by a Tait-like equation. It was found that the isothermal viscosity data were satisfactorily correlated by such an equation.

KEY WORDS: 1-butanol; ethanol; high pressure; methanol; 1-propanol; viscosity; water.

1. INTRODUCTION

Although the alcohols are among the most commonly encountered liquids today, their viscosity up to 30 MPa pressure has not been studied in detail. To our knowledge, very few sets of measurements of inferior accuracy have been reported.

In this paper new measurements of the viscosity of methanol, ethanol, 1-propanol, and 1-butanol are presented. At atmospheric pressure, the measurements cover a temperature range of 290–340 K, while at 298.15 and 323.15 K the measurements extend up to 30 MPa. The choice of the two temperatures along which pressure measurements were performed was dictated by the availability of accurate density measurements. The overall uncertainty of the present measurements is estimated to be better than ± 0.5 %, an estimate confirmed by the measurement of the viscosity of water over the whole aforementioned range of conditions.

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2. EXPERIMENTAL

The gross features of the vibrating-wire viscometer employed for the present measurements have already been described [1-3]. However, the special characteristics of water made the detailed construction of the instrument used earlier, inappropriate for such measurements. Consequently the construction of the vibrating-wire viscometer was modified for such measurements [4]. There are two major differences of the new construction in relation to the old one. The samarium-cobalt magnets that provide the magnetic field are plated with an impervious gold layer to guard against chemical attack and are linked by a yoke made of a magnetic stainless steel, in order to secure as high a magnetic field as possible. Moreover, except for the vibrating-wire itself and the inner weight, which are made out of tungsten, all other components and electrical leads are made out of stainless steel, spot-welded together where necessary. The latter precaution was found to be necessary to eliminate the dissimilar metals present in the earlier version of the instrument.

Following the introduction of these two modifications, it was found [4] that the reproducibility of the instrument under repeated cycling of temperature and pressure was ± 0.1 % over several weeks and was therefore approximately equal to the precision of measurements. Indeed, even if the vibrating-wire sample was exchanged with another sample from the same roll, the reproducibility remained of the same order. The instrument was further calibrated, as described in detail elsewhere [4], with respect to the viscosity of water at a pressure of 0.1 MPa and a temperature of 293.15 K for which an accurate reference value is available. With due regard to the precision of the determination of the individual quantities and the accuracy of the calibration data, it is estimated that the overall uncertainty of the present results is better than ± 0.5 % under all conditions.

3. RESULTS

3.1. Water

The sample of water employed for the present measurements was distilled and doubly deionized before use. Its electrical conductivity was checked before and after use and found in both cases to be $1.3 \,\mu\text{S} \cdot \text{cm}^{-1}$. The density of water required for the evaluation of the viscosity has been taken from the work of Sengers and Watson [5]

Table I presents the atmospheric-pressure viscosity measurements of water from 290 to 330 K. The table includes the results of the special

Temp. T (K)	Density ρ (kg · m ⁻³)	Viscosity η (μPa·s)	Kestin et al. [6] η (μPa·s)	Deviatior (%)
293.108	998.2	1003.0	1003.0	+ 0.00
297.964	997.1	894.4	893.9	+ 0.06
303.750	995.5	786.2	787.1	-0.12
307.971	994.1	722.4	721.7	+ 0.09
312.899	992.3	654.7	656.0	-0.19
317.916	990.3	599.8	598.6	+0.20
322.827	988.2	551.1	550.1	+0.18
328.076	985.7	505.5	505.0	+0.10

Table I. Viscosity of Water as a Function of Temperature at Atmospheric Pressure

correlation of critically evaluated experimental data for calibration purposes given by Kestin et al. [6] and the deviations between the two sets of results. The greatest deviation amounts to 0.2% and is therefore consistent with the mutual uncertainty of the two sets of data.

Table II contains the results of measurements of the rather weak pressure dependence of the viscosity of liquid water at two nominal temperatures, 298.15 and 313.15 K. The two isotherms have been selected in

Press. P (MPa)	Temp. <i>T</i> (K)			$\rho(T_{\rm nom}, P)$	Viscosity $\eta(T_{nom}, P)$ $(\mu Pa \cdot s)$	$\eta(T_{\rm nom}, P)$	Deviation (%)
			T _{nom} =	= 298.15 K			
0.10	297.964	997.1	894.4	997.1	890.6	890.5	+ 0.01
5.27	298.043	999.4	892.7	999.4	890.5	889.3	+0.13
10.64	298.046	1001.8	892.0	1001.8	889.9	888.3	+0.18
15.50	298.040	1003.9	890.4	1003.9	888.2	887.5	+ 0.08
21.38	298.034	1006.5	889.6	1006.5	887.3	886.6	+0.08
24.62	298.022	1007.9	888.2	1007.8	885.7	886.2	-0.06
			$T_{nom} =$	= 313.15 K			
0.10	312.899	992.3	654.7	992.2	651.6	653.2	-0.24
5.17	312.914	994.5	654.5	994.4	651.6	653.6	- 0.30
10.23	312.905	996.7	655.2	996.6	652.2	654.1	-0.29
15.50	312.881	999.0	654.5	998.9	651.3	654.7	-0.52
20.47	312.844	1001.1	656.6	1001.0	652.9	655.3	-0.36
25.53	312.789	1003.2	657.8	1003.1	653.5	656.0	-0.38
32.02	312.707	1005.9	659.1	1005.7	653.7	656.9	-0.48

Table II. Viscosity of Water as a Function of Pressure

this study since the pressure dependence of the viscosity is of opposite sign in the two cases. Corrections from the experimental temperature to the nominal temperature have been made using the IAPS representation [5] of the viscosity of water and do not amount to more than 0.4% so that the application of the correction introduces a negligible additional error. The IAPS recommendation [5] is a weighted fit of previous measurements in the range of conditions of interest here and therefore provides a convenient basis for comparison. Table II, therefore, also includes the results of the

	Temp. T	Density ρ	Viscosity η
Alcohol	(K)	$(kg \cdot m^{-3})$	$(\mu \mathbf{Pa} \cdot \mathbf{s})$
Methanol	294.998	789.9	570.2
	298.055	787.0	546.4
	302.946	782.4	510.4
	308.007	777.5	477.1
	312.982	772.7	447.1
	318.060	767.7	419.5
	323.193	762.7	394.0
Ethanol	298.170	785.0	1081
	302.975	780.9	988.1
	307.928	776.5	903.1
	313.076	772.0	824.4
	318.179	767.5	755.2
	323.061	763.1	695.5
	328.225	758.4	639.7
1-Propanol	294.589	802.1	2133
	298.171	799.3	1954
	303.115	795.3	1734
	308.129	791.3	1545
	313.052	787.3	1384
	318.072	783.2	1241
	323.110	779.0	1116
	328.094	774.8	1009
1-Butanol	293.629	808.8	2869
	298.213	805.4	2545
	303.106	801.7	2243
	308.166	797.9	1977
	313.107	794.1	1757
	318.145	790.2	1564
	323.223	786.2	1394
	328.359	782.1	1247
	333.364	778.1	1121

Table III. Viscosity of Alcohols as a Function of Temperature at Atmospheric Pressure

IAPS recommendation and the deviations between the two sets of results. Since the IAPS formulation has an uncertainty of $\pm 1.0\%$ in the range of interest, the degree of agreement shown is satisfactory.

The aforementioned discussion and the results of water confirm therefore that the overall uncertainty of the instrument is better than ± 0.5 %.

3.2. Alcohols

The sample of methanol employed was supplied by BDH Chemicals Ltd. (Aristar grade) at 99.8% nominal purity. The samples of ethanol, 1-propanol, and 1-butanol were supplied by Merck (Proanalysi grade), all at 99.5% nominal purity. The nominal purity of the alcohols was checked by chromatography. The density of the alcohols at atmospheric pressure was obtained by a recent recommendation [7] based on a critical evaluation of all previous measurements, while for higher pressures the values

Pressure P (MPa)	Temp. <i>T</i> (K)	Density $\rho(T, P)$ $(kg \cdot m^{-3})$	Viscosity $\eta(T, P)$ $(\mu Pa \cdot s)$	Density $\rho(T_{nom}, P)$ $(kg \cdot m^{-3})$	Viscosity $\eta(T_{nom}, P)$ $(\mu Pa \cdot s)$
		$T_{\text{nom}} = 2$	98.15 K		
0.10	298.055	787.0	546.4	786.9	545.9
2.94	298.162	789.7	554.1	789.7	554.2
6.38	298.176	793.0	564.2	793.0	564.3
9.22	298.193	795.6	572.5	795.6	572.7
12.36	298.171	798.4	581.3	798.4	581.4
15.30	298.129	801.0	590.1	801.0	590.0
18.34	298.174	803.6	597.7	803.6	597.8
21.38	298.248	806.0	605.4	806.1	606.0
24.42	298.144	808.5	613.9	808.5	613.9
27.05	298.168	810.6	620.8	810.6	620.9
		$T_{\rm nom} = 3$	23.15 K		
0.10	323.193	762.7	394.0	762.7	394.2
3.14	323.205	766.1	400.6	766.2	400.9
6.18	323.196	769.5	407.5	769.5	407.8
9.22	323.199	772.7	414.3	772.7	414.6
12.26	323.199	775.8	421.2	775.8	421.5
15.30	323.177	778.8	427.7	778.8	427.9
18.34	323.147	781.7	434.5	781.7	434.5
21.48	323.165	784.6	442.0	784.6	442.1
25.43	323.116	788.2	449.8	788.2	449.6

Table IV. Viscosity of Methanol as a Function of Pressure

measured by Kubota et al. [8] were used. Both sets of density values were fully compatible with an uncertainty of better than ± 0.1 %.

Table III shows the atmospheric measurements of the viscosity of alcohols as a function of temperature. The high-pressure measurements of the four alcohols are presented in Tables IV to VII. In these tables, the viscosity adjusted to the nominal temperatures of 298.15 and 323.15 K, respectively, by means of a linear correction, is also provided. Since this correction is very small, less than 0.3%, the uncertainty introduced with this assumption is negligible.

The atmospheric-pressure measurements of the viscosity, η , of the four alcohols have been correlated as a function of the absolute temperature, T, for the purpose of interpolation only, by an equation of the form

$$\eta = A e^{B/T} \tag{1}$$

Pressure P (MPa)	Temp. <i>T</i> (K)	Density $\rho(T, P)$ $(\text{kg} \cdot \text{m}^{-3})$	Viscosity $\eta(T, P)$ $(\mu Pa \cdot s)$	Density $\rho(T_{nom}, P)$ $(kg \cdot m^{-3})$	Viscosity $\eta(T_{nom}, P)$ $(\mu Pa \cdot s)$
		$T_{nom} = 2$	98.15 K		
0.10	298.170	785.0	1080	785.0	1081
3.14	298.199	787.7	1103	787.7	1103
6.18	298.190	790.2	1127	790.2	1127
9.22	298.193	792.6	1150	792.6	1151
12.36	298.184	795.0	1173	795.0	1174
15.81	298.181	797.5	1198	797.5	1199
18.24	298.193	799.3	1215	799.3	1215
20.77	298.223	801.1	1230	801.1	1232
23.91	298.226	803.3	1246	803.3	1247
24.93	298.229	804.0	1250	804.0	1251
		$T_{\rm nom} = 3$	23.15 K		
0.10	323.061	763.1	695.5	763.1	694.1
2.94	323.113	764.9	710.5	764.9	709.9
6.08	323.147	767.8	727.2	767.8	727.2
9.22	323.129	770.6	743.7	770.6	743.4
12.16	323.119	773.1	758.9	773.1	758.4
15.30	323.113	775.8	774.7	775.8	774.1
18.34	323.113	778.3	790.7	778.3	790.1
21.38	323.104	780.7	806.6	780.7	805.8
24.42	323.104	783.1	821.0	783.1	820.2
27.56	323.129	785.5	835.3	785.5	835.0

Table V. Viscosity of Ethanol as a Function of Pressure

The values of the constants are given in Table VIII. In the same table, the standard deviation of each fit is shown. It can be seen that the maximum standard deviation is ± 0.09 %.

In Fig. 1, the deviations of the present atmospheric-pressure measurements of the four alcohols, from those correlated by Eq. (1) are shown. The maximum deviation is 0.13%. In the same figure measurements of other investigators are also shown. As discussed later on, to our knowledge only Tanaka et al. [9], Isdale et al. [10], Isakova and Oshueva [11], and Papaioannou [12] have measured the viscosity of alcohols in the aforementioned pressure range. Tanaka et al. [9] measured the viscosity of methanol, ethanol, and 1-propanol using a falling-cylinder viscometer calibrated with water, with a quoted uncertainty of $\pm 2\%$. Their values agree with the present measurements to 1%, except in the case of ethanol at 323.15 K, where there is a deviation of 3.8%. However, as shown later, as the whole isotherm at this temperature agrees with the present

Pressure P (MPa)	Temp. <i>T</i> (K)	Density $\rho(T, P)$ $(kg \cdot m^{-3})$	Víscosity η(T, P) (μPa·s)	Density $\rho(T_{nom}, P)$ $(kg \cdot m^{-3})$	Viscosity $\eta(T_{nom}, P)$ $(\mu Pa \cdot s)$
		$T_{nom} = 2$	98.15 K		
0.10	298.171	799.3	1954	799.3	1954
3.14	298.184	801.6	2003	801.6	2005
6.08	298.184	803.8	2050	803.9	2052
9.22	298.176	806.2	2102	806.2	2103
12.26	298.173	808.3	2153	808.4	2154
15.30	298.162	810.5	2202	810.5	2202
18.34	298.179	812.6	2252	812.6	2253
21.38	298.184	814.6	2303	814.6	2304
24.32	298.187	816.5	2352	816.5	2354
27.46	298.179	818.5	2405	818.6	2407
		$T_{\rm nom} = 3$	23.15 K		
0.10	323.110	779.0	1116	779.0	1114
2.94	323.211	781.4	1140	781.5	1142
6.08	323.184	784.1	1171	784.2	1172
9.22	323.223	786.7	1199	786.8	1202
12.26	323.220	789.2	1228	789.3	1231
15.30	323.205	791.6	1259	791.7	1261
18.24	323.202	793.9	1288	793.9	1290
21.38	323.205	796.2	1317	796.3	1320
24.32	323.184	798.4	1346	798.4	1348
27.86	323.171	800.9	1381	800.9	1382

Table VI.	Viscosity of	1-Propanol as a	Function of	Pressure
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Pressure P (MPa)	Temp. <i>T</i> (K)	Density $\rho(T, P)$ $(kg \cdot m^{-3})$	Viscosity η(T, P) (μPa·s)	Density $\rho(T_{nom}, P)$ $(kg \cdot m^{-3})$	Viscosity $\eta(T_{nom}, P)$ $(\mu Pa \cdot s)$
		$T_{nom} = 2$	98.15 K		
0.10	298.213	805.4	2545	805.4	2547
3.14	298.162	807.7	2617	807.7	2618
6.18	298.184	809.8	2688	809.9	2689
9.12	298.187	811.9	2753	811.9	2755
12.26	298.217	814.0	2828	814.1	2832
15.30	298.199	816.1	2901	816.1	2904
18.34	298.202	818.1	2975	818.1	2978
21.38	298.199	820.0	3050	820.1	3053
24.42	298.197	821.9	3116	822.0	3119
27.66	298.248	823.9	3186	824.0	3191
		$T_{nom} = 3$	23.15 K		
0.10	323.223	786.2	1394	786.3	1397
3.14	323.123	788.9	1434	788.9	1433
6.18	323.168	791.4	1474	791.4	1475
9.22	323.205	793.8	1511	793.8	1514
12.26	323.181	796.2	1553	796.2	1555
15.30	323.150	798.5	1593	798.5	1593
18.34	323.165	800.7	1635	800.8	1636
21.38	323.165	803.0	1679	803.0	1680
24.42	323.159	805.1	1719	805.1	1719
28.27	323.132	807.8	1770	807.8	1769

Table VII. Viscosity of 1-Butanol as a Function of Pressure

measurements to 2%, the aforementioned deviation could be attributed to a typographical error. Isdale et al. [10] measured the viscosity of methanol employing a calibrated falling-body viscometer, with a quoted uncertainty of $\pm 2\%$. This set of measurements at atmospheric pressure agrees with the present measurements to 0.9%, which is well within the mutual uncertainty

Table VIII. Coefficients in Eq. (1)

Alcohol	<i>A</i> (μPa⋅s)	<i>В</i> (К)	σ (%)
Methanol	8.203 ± 0.032	1251.4 ± 1.2	±0.03
Ethanol	3.517 ± 0.040	1708.1 ± 3.5	<u>+</u> 0.09
1-Propanol	1.394 ± 0.006	2160.3 ± 1.3	±0.04
1-Butanol	1.080 ± 0.005	2315.2 ± 1.3	± 0.05

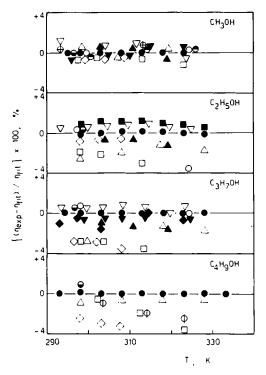


Fig. 1. Percentage deviations of the atmospheric-pressure viscosity measurements, from Eq. (1). (\bullet) Present measurements; (\bigcirc) Ref. 9; (\bullet) Ref. 10; (Φ) Ref. 11; (\bullet) Ref. 12; (\triangle) Ref. 13; (\blacktriangle) Ref. 14; (\bullet) Ref. 15; (\blacksquare) Ref. 16; (\square) Ref. 17; (\diamond) Ref. 18; (\triangledown) Ref. 19; (\triangledown) Ref. 20; (∇) Ref. 21; (Φ) Ref. 22.

of the instruments. Isakova and Oshueva [11] measured the viscosity of methanol under pressure, employing a calibrated capillary viscometer with a quoted uncertainty of ± 1 %, while Papaioannou [12] employed a calibrated falling-body viscometer for high-pressure measurements in all four alcohols, with a quoted uncertainty of 0.7%. At atmospheric pressure, both these sets of measurements agree with the present work within the mutual uncertainty of the instruments. The other investigators presented in Fig. 1 have performed measurements only at atmospheric pressure employing Ubbelohde, Cannon-Fenske, or Ostwald viscometers. In such cases the absolute value of the viscosity is directly related to the accuracy of the calibration of the instrument. It is a well-established practice to use water as the calibrant liquid and, furthermore, to quote the calibration conditions and values. Since some investigators do not adhere to this practice, discrepancies are to be expected. For the atmospheric-pressure measurements of the viscosity of the alcohols, an Ubbelohde type of viscometer was used by Rauf et al. [13] (no calibrant liquid quoted), Crabtree and O'Brien [14] and Paez and Contreras [15] (both calibrated with water), and Phillips and Murphy [16] (calibrated with diethyl ether). Although they all quote uncertainties of about $\pm 0.2\%$, their values deviate from the present measurements up to -3, -1.6, -1.7, and +1.2%, respectively. A Cannon-Fenske viscometer was employed by Garcia et al. [17] (calibrated with water) and Aminabhavi et al. [18] (no calibrant liquid quoted), both with a +0.2% quoted uncertainty. These sets of measurements show deviations from the present set of up to -4 and -3.3% respectively. The measurements of Mikhail and Kimer [19, 20] and Kikuchi and Oikawa [21], performed in calibrated Ostwald viscometers, show deviations from the present set of up to 1.5%. Finally, the measurements of Dakshinamurty et al. [22], also performed in a watercalibrated Ostwald viscometer with a quoted reproducibility of +1%. show deviations from the present set up to 2.5%. It is of interest to note that although most of the investigators mentioned have performed the measurements in the last decade, the discrepancies between the data sets, in some cases, far exceed the quoted uncertainties.

The high-pressure viscosity measurements of the four alcohols have been correlated with pressure along each isotherm, for the purpose of interpolation only, by a Tait-like equation as

$$\ln\left[\frac{\eta}{\eta_0}\right] = E \ln\left[\frac{D+P}{D+P_0}\right]$$
(2)

Alcohol	Т (К)	η ₀ (μPa·s)	E (-)	D (MPa)	σ (%)
Methanol	298.15	545.86	0.441	79.5	+ 0.03
	323.15	394.21	0.680	118.0	± 0.07
Ethanol	298.15	1080.80	0.309	40.0	±0.16
	323.15	694.12	0.556	69.5	<u>+</u> 0.05
1-Propanol	298.15	1954.45	1.256	151.8	±0.03
	323.15	1114.28	1.006	116.2	± 0.02
I-Butanol	298.15	2547.48	1.026	111.5	± 0.09
	323.15	1396.96	1.576	173.2	± 0.11

Table IX. Coefficients in Eq. (2)

where η_0 represent the experimental viscosity at the atmospheric pressure P_0 (0.101 MPa), and P the pressure (in MPa). The values of the constants for each isotherm for all alcohols are shown in Table IX. In the same table, the standard deviation of each fit is shown. It can be seen that the maximum standard deviation is $\pm 0.16\%$.

In Figs. 2 and 3 the deviations of the present high-pressure measurements of the viscosity of the four alcohols at 298.15 and 323.15 K from those correlated by Eq. (2) are presented. The maximum deviation of all present measurements is 0.25%. In the same figures four other sets of high-pressure measurements are also included. With the exception of the measurements of methanol at 298.15 K, all other measurements of Tanaka et al. [9] agree with the present values within the mutual uncertainty of the instruments (see also discussion for the atmospheric-pressure measurements). Isdale et al. [10] and Isakova and Oshueva [11] per-

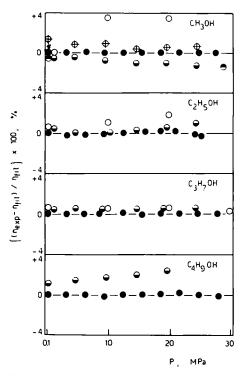


Fig. 2. Percentage deviations of the high-pressure viscosity measurements at 298.15 K, from Eq. (2). (\bullet) Present measurements; (\bigcirc) Ref. 9; (\bigcirc) Ref. 10; (\diamondsuit) Ref. 11; (\bigcirc) Ref. 12.

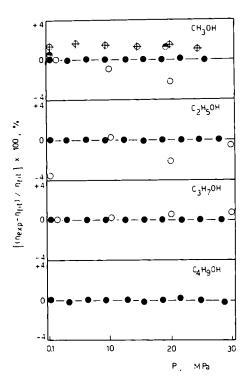


Fig. 3. Percentage deviations of the high-pressure viscosity measurements at 323.15 K, from Eq. (2).
(●) Present measurements; (○) Ref 9; (●) Ref. 10;
(♦) Ref. 11.

formed high-pressure measurements only on methanol. Their values agree with the present set of values within the mutual uncertainty of the instruments. Finally, Papaioannou [12] performed measurements in all four alcohols at 298.15 K. Except in the case of 1-butanol, where higher deviations of up to 2.8% are noticed, all other measurements agree with the present values within the mutual uncertainty of the instruments.

4. CONCLUSIONS

New measurements of the viscosity of methanol, ethanol, 1-propanol, and 1-butanol have been presented. The measurements were performed in a recently modified vibrating-wire instrument; at atmospheric pressure they cover a temperature range of 290–340 K, while at 298.15 and 323.15 K they extend up to 30 MPa. The overall uncertainty in the reported data is estimated to be better than $\pm 0.5\%$, an estimate confirmed by the measurement of the viscosity of water.

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