The Viscosity of Toluene in the Temperature Range from 210 to 370 K at Pressures up to 30 MPa

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The paper presents new measurements of the viscosity of toluene over a temperature range from 210 to 370 K, from the saturation line up to pressures of 30 MPa. The measurements were performed with a vibrating-wire viscometer. The uncertainty of the measurements, confirmed above room temperature with the measurement of the viscosity of water, is estimated to be ±0.5%.

KEY WORDS: toluene; vibrating-wire technique; viscosity.

1. INTRODUCTION

This paper presents new measurements for the viscosity of toluene under pressure. The measurements cover the temperature range 210 to 370 K, for pressures up to 30 MPa. The measurements along the saturation line have already been reported [1].

Toluene has long been considered as a primary viscosity standard, especially where conditions of application or the temperature range required make the employment of water impractical. In the case of the thermal conductivity of toluene, a standard reference equation along the saturation line that covers the temperature range 190 to 550 K has recently been proposed [2] by the Subcommittee of Transport Properties of the International Union of Pure and Applied Chemistry. The development, however, of a standard reference equation for the viscosity of toluene has been hindered by a distinct lack of measurements below room temperature. Indeed, only one investigator [3] has reported measurements below room temperature along the saturation line.

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To our knowledge, there are no other high-pressure measurements of the viscosity of toluene below room temperature. Hence, the present measurements, that attempt to fill this gap, can help in the development of a standard reference equation for the viscosity of toluene under pressure.

2. EXPERIMENTAL

2.1. Viscometer

A description of the vibrating-wire viscometer employed for these high-pressure measurements, has already been presented elsewhere [1, 4, 5] and is only briefly described here. The vibrating wire employed is made from tungsten with a nominal diameter of 100 μm. It is suspended from a 316 stainless-steel chuck, supported in the upper plate of the pressure vessel. At its lower end, the wire, also placed in a similar chuck, carries a two-weight assembly that ensures its constant tensioning [4] during measurements. Two permanent samarium–cobalt magnets placed around the wire provide the required magnetic field. The magnets are plated with an impervious gold layer to guard against chemical attack and are linked by a magnetic stainless-steel yoke to achieve as high a magnetic field as possible. As the viscometer was also designed for water and polar fluids, exceptional care was taken to diminish possible electrolytic effects arising from the presence of dissimilar metals. Hence, with the exception of the wire, the inner weight, the magnets, and their yoke, all the other parts of the viscometer, the leads, and the pressure vessel are made of stainless steel, while all connections are spot-welded.

2.2. Assembly

The viscometer is placed in the pressure vessel, which is made of stainless steel for a maximum working pressure of 100 MPa. Electrical contacts out of the pressure vessel are accomplished by employing a chromel–alumel stainless steel-shielded thermocouple wire. Sealing the pressure vessel for the temperature range 210 to 370 K and up to 30 MPa was not that easy. After many attempts, we employed successfully stainless-steel springs coated with graphite–carbon-filled PTFE o-rings made by Bal Seal Engineering Europe BV.

The pressure vessel is placed in a 20-liter thermostatic bath made especially for this temperature range. Above room temperature, ethylene glycol is employed in the bath, while at lower temperatures propanol is used. The temperature of the bath is controlled by circulating a second heat-transfer

fluid, whose temperature is controlled by a Julabo F81-MV external circulator. This arrangement ensures that the temperature in the bath is very stable and the temperature gradients are kept at a tolerable level. Above room temperature ethylene glycol was also used as the heat-transfer liquid, while at lower temperatures ethanol was employed. The temperature of the liquid is recorded by three platinum resistance thermometers embedded along the pressure-vessel wall. The thermometers are calibrated over the whole temperature range of 200 to 370 K vs a Class 1 NPL-certified, Tinsley platinum resistance thermometer, to an uncertainty of better than ±20 mK. All temperatures refer to ITS-90.

The pressure vessel is filled with toluene under vacuum. Vacuum is achieved with an E2M1.5 Edwards rotary vacuum pump. Following prolonged vacuum, toluene is pressurized by a A0-612 Stanstead "mini-air" hydraulic pump. Finally, the pressure of the toluene inside the pressure vessel is measured by a Druck PTX520 pressure transmitter, with an uncertainty of 0.1 MPa.

3. WORKING EQUATIONS

According to the ideal model of the technique [4], a thin vertical wire, constrained not to move at its two ends, is placed in the liquid. If an oscillation is initiated by the displacement of the wire from its equilibrium position, then, following a short-lived initial transient, the motion conforms to a damped, simple harmonic motion,

$$y = y_0 e^{(i - \Delta)\omega t} \tag{1}$$

with an angular frequency ω and a logarithmic decrement Δ. It has been shown [4] that in certain well-specified circumstances, the working equation for the evaluation of the viscosity, η, from the above experimentally obtained quantities takes the form

$$\Delta = \frac{(\rho/\rho_w) k' + 2\Delta_0}{2[1 + (\rho/\rho_w) k]} \tag{2}$$

where Δ_0 is the logarithmic decrement in vacuum, ρ is the liquid density, and ρ_w is the density of the wire material. The quantities k and k' are given by

$$k = -1 + 2 \operatorname{Im}(A) \tag{3}$$

$$k' = 2 \operatorname{Re}(A) + 2\Delta \operatorname{Im}(A) \tag{4}$$

where

$$A = (i - \Delta) \left\{ 1 + \frac{2K_1(s)}{sK_0(s)} \right\} \tag{5}$$

and

$$s = [(i - \Delta)\,\Omega]^{1/2} \tag{6}$$

$$\Omega = \rho\omega R^2/\eta \tag{7}$$

In these equations, R is the radius of the vibrating wire and K_0 and K_1 are modified Bessel functions of the zero and first order, respectively.

The viscosity can be obtained as a function of the density, employing the above set of equations, from the measurements of the frequency of oscillation in the liquid and the decrement in the liquid and in vacuum. However, this implies that both the radius R and the density ρ_w of the wire can be measured with sufficient accuracy. Since with present technology this cannot be accomplished, their values were refined by employing the measurement of the viscosity of water in the fashion already described elsewhere [5]. Hence, taking all parameters into account, the uncertainty of the measurements is estimated to be $\pm 0.5\%$, and their reproducibility and precision $\pm 0.1\%$.

4. DENSITY EQUATION

A very important factor for the correct interpretation of the measurements is the density equation employed [1], since the value of the viscosity is very sensitive to the actual density and particularly at low temperatures. Most investigators employ an equation of state published in 1989 by Goodwin [6]. This equation, however, was found to show large deviations below room temperature, from the measurements of Muringer et al. [7] done in 1985 (but not included in the correlation) and the more recent ones performed by Magee and Bruno [8] in 1996. Specifically, at a temperature of 180 K, the value produced by Goodwin's equation of state differs by 1.6% from the above measurements. This is probably attributed to the fact that Goodwin reports only one data point at 178 K, while the next one is at 293 K.

Hence, Goodwin's equation of state was not employed and the recent measurements of Magee and Bruno [8], which agreed very well with the measurements of Muringer et al. [7], were correlated with the following Tait-type equation:

$$\frac{\rho - \rho_0}{\rho} = C \log\left(\frac{B + P}{B + 0.1}\right) \tag{8}$$

Table I. Coefficients b_k, c_k, d_k, and h_k

k	b_k (MPa)	c_k	d_k (kg·m^{-3})	h_k
0	422.7205	34.054	1166.816	8.657415
1	− 882.595	−219.46	−749.510	0.373310
2	481.901	556.183	467.299	0.013137
3	0	−653.601	−360.279	0.282222
4	0	292.762	0	0.055111

In this equation, ρ is the calculated density, the coefficient $C = 0.216$ was proposed by Dymond et al. [9], and the density at 0.1 MPa, ρ_o, and the coefficient B are

$$\rho_o = \sum_{k=0}^{3} d_k T_r^k \tag{9}$$

$$B = \sum_{k=0}^{2} b_k T_r^k \tag{10}$$

where $T_r = T/T^c$, the critical temperature $T^c = 591.75$ K, and the constants d_k and b_k are reported in Table I. The above equation is valid for temperatures from 180 to 400 K and pressures up to 35 MPa and fits the experimental values with a maximum deviation of less than ±0.09%.

5. MEASUREMENTS

The toluene employed was supplied by BDH (ARISTAR grade), 99.9% pure. The largest impurities included were water (200 ppm), benzene (200 ppm), and sulfur compounds (30 ppm). Remaining impurities were below 1 ppm. To avoid ice formation [1], toluene was dried over molecular sieves. The toluene was introduced in the vessel under vacuum.

5.1. Measurements at Atmospheric Pressure

The measurements of the viscosity of toluene at atmospheric pressure are given in Table II. These measurements were fitted to the following equation:

$$\ln \left(\frac{\eta}{\eta(293.15 \text{ K})} \right) = \sum_{k=0}^{4} c_k T_r^k \tag{11}$$

Table II. Measurements of the Viscosity of
Toluene at Atmospheric Pressure

T (K)	ρ (kg·m^{-3})	η (μPa·s)
363.088	799.6	291.6
353.096	809.4	317.6
342.527	819.7	349.1
332.613	829.2	382.4
322.789	838.5	421.9
312.935	847.9	466.9
303.765	856.5	517.1
293.330	866.2	585.8
283.572	875.3	662.6
273.280	884.9	765.0
262.952	894.4	896.7
252.856	903.8	1067
243.049	912.8	1290
233.299	921.9	1593
223.644	930.8	2030
213.722	940.1	2720

where the viscosity at 293.15 K is found to be 586.9 μPa·s. The coefficients c_k are given in Table I. The maximum deviation of the experimental viscosity values from the above fit is 0.4%. These measurements have been presented and discussed elsewhere [1].

5.2. Measurements at Higher Pressure

The measurements of toluene at higher pressures are shown in Table III. For interpolation purposes these were fitted to the following equation:

$$\eta(\rho_r, T_r) = h_0 \exp\left(\frac{h_1}{T_r} + \frac{h_2}{T_r^4}\right) \frac{\rho_r}{1 - \rho_r(h_3 + h_4 T_r^2)} \qquad (12)$$

In the above equation $\rho_r = \rho/\rho^c$, the critical density $\rho^c = 290.2$ kg·m^{-3}, and values of the coefficients h_k are shown in Table I. In Fig. 1, the deviations of the present measurements from the values correlated by the above equation are shown. It can be seen that the maximum deviation is 0.5%.

In Fig. 2 deviations of the high-pressure viscosity measurements of other investigators from the values calculated from Eq. (12) are shown. It should be noted that no investigator has reported values under pressure

Table III. Measurements of the Viscosity of Toluene
as a Function of Pressure

T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
219.362	0.101	934.8	2302
219.324	1.35	935.5	2331
219.286	3.43	936.7	2376
219.217	5.35	937.8	2423
217.726	6.63	939.9	2577
217.751	9.14	941.1	2608
217.720	11.43	942.3	2669
217.713	13.43	943.3	2720
217.600	15.04	944.2	2774
233.931	0.101	921.3	1572
233.931	2.23	922.5	1603
233.893	4.22	923.7	1636
233.924	6.32	924.8	1662
233.946	8.74	926.2	1696
233.965	10.77	927.3	1725
233.975	12.48	928.2	1747
234.000	14.58	929.3	1778
234.019	15.99	930.0	1803
253.528	0.101	903.1	1050
253.537	2.25	904.5	1070
253.550	4.28	905.7	1086
253.515	6.21	907.0	1102
253.521	8.18	908.2	1122
253.518	9.88	909.2	1137
253.521	12.08	910.5	1159
253.521	14.24	911.8	1179
253.508	16.24	913.0	1198
253.505	18.00	914.0	1213
253.528	19.43	914.8	1228
273.289	0.101	884.8	763.3
273.289	2.08	886.2	775.2
273.164	4.15	887.8	786.8
273.158	6.09	889.1	799.0
273.161	8.25	890.5	811.8
273.161	10.24	891.9	824.7
273.158	12.31	893.2	838.7
273.151	14.16	894.4	851.9
273.145	16.20	895.7	865.9
273.164	18.39	897.1	880.6
293.210	0.101	866.3	584.2
293.207	2.13	867.9	592.5
293.181	4.20	869.5	603.5
293.129	6.18	871.1	613.0
293.142	8.15	872.5	622.5

Table III. *(Continued)*

| T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
293.161	10.16	874.0	631.2
293.158	12.17	875.4	640.8
293.158	14.18	876.8	649.1
293.148	16.14	878.2	660.2
293.142	18.14	879.6	669.1
293.142	20.16	881.0	679.1
293.155	22.30	882.4	691.3
313.276	0.101	847.5	464.6
313.279	2.22	849.4	471.8
313.263	4.20	851.1	480.2
313.162	6.43	853.0	488.6
313.146	8.14	854.5	494.3
313.149	10.19	856.1	502.6
313.149	12.13	857.7	509.9
313.149	14.18	859.3	517.2
313.146	16.16	860.8	525.3
313.143	18.12	862.3	533.0
313.143	20.12	863.8	541.1
313.146	22.16	865.3	549.6
313.146	24.01	866.7	556.4
313.146	25.53	867.8	562.4
333.090	0.101	828.7	380.3
333.090	2.09	830.7	385.9
333.093	4.22	832.7	393.1
333.057	6.36	834.8	399.8
333.044	8.17	836.4	405.3
333.067	10.15	838.2	411.3
333.070	12.16	840.0	418.0
333.064	14.10	841.7	424.5
333.054	16.15	843.4	430.8
333.047	18.13	845.1	437.5
333.054	20.11	846.8	444.0
333.064	22.17	848.4	450.7
353.481	0.101	809.0	316.7
353.494	2.15	811.3	322.0
353.517	4.16	813.5	327.3
353.517	6.17	815.6	332.7
353.520	8.17	817.7	338.7
353.520	10.10	819.6	343.5
353.520	12.14	821.7	349.5
353.507	14.13	823.6	354.8
353.507	16.10	825.5	360.8
353.510	18.16	827.4	366.5
353.507	20.07	829.2	371.9
353.501	22.15	831.1	377.9
353.520	23.91	832.6	382.6
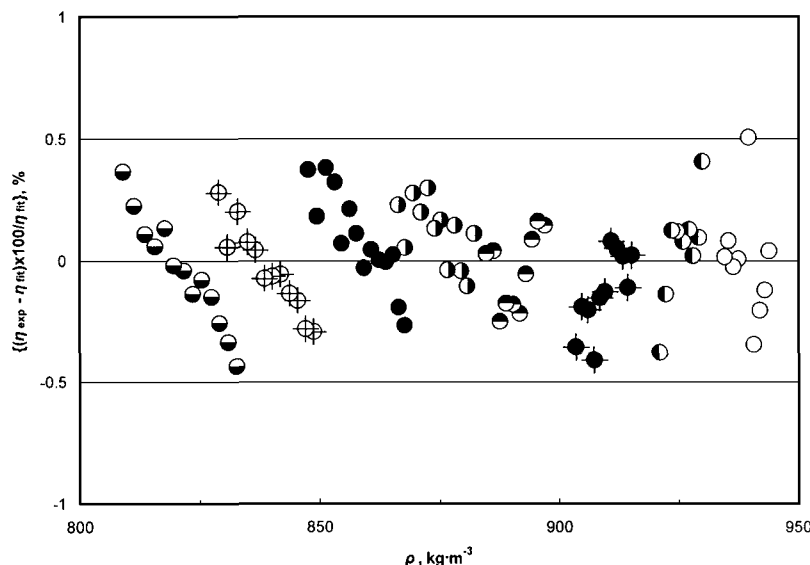
Fig. 1. Deviations of the present viscosity measurements from those calculated from Eq. (12): (O) 218 K; (◑) 233 K; (◈) 253 K; (◔) 273 K; (◖) 293 K; (●) 313 K; (⊕) 333 K; (◗) 353 K.

below room temperature. It should also be mentioned that only Krall et al. [10] employed water as the calibration fluid. These measurements, performed in an oscillating-disk viscometer with an uncertainty of $\pm 0.5\%$, are in excellent agreement with the present results.

Oliveira [11] employed a very similar vibrating-wire instrument for the measurement of the viscosity of toluene, calibrated with a series of hydrocarbons with an uncertainty of $\pm 0.5\%$. Except for the one point at the highest temperature, the agreement between the two sets is within the mutual uncertainties of the two instruments.

The measurements of Vieira dos Santos and Nieto de Castro [12] were performed in a quartz-crystal viscometer calibrated with toluene at 1 atm. The uncertainty of these measurements is $\pm 0.5\%$. Their agreement with the present values is excellent.

The measurements of Dymond et al. [13], performed in a falling-body viscometer calibrated with a series of hydrocarbons and an uncertainty of $\pm 3\%$, agree very well with the present values. Also, there is very good agreement with the older values reported by Dymond et al. [14]. A falling-body viscometer, calibrated with toluene at 1 atm, was also employed by Harris et al. [15]. These values, with an uncertainty of $\pm 2\%$, agree very well with the present results.
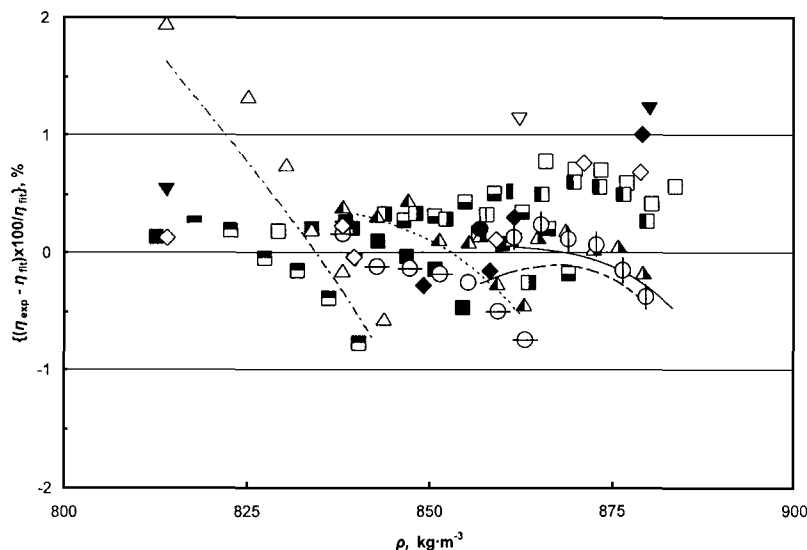
Fig. 2. Deviations of other viscosity measurements from those calculated from Eq. (12). Krall et al. [10]. (□) 298 K; (▣) 303 K; (▤) 313 K; (▨) 323 K; (■) 333 K; (▥) 350 K. Oliveira [11]: (▲) 303 K; (▲) 323 K; (△) 348 K. Vieira dos Santos and Nieto de Castro [12]: (◇). Dymond et al. [13]: (▽). Dymond et al. [14]: (▼). Harris et al. [15]: (◆). Kashiwagi and Makita [16]: (——) 298 K; (— —) 303 K; (---) 323 K; (— ·) 348 K. Assael et al. [17]: (Φ) 303 K; (⊖) 323 K.

In Fig. 2 the older measurements, performed by Kashiwagi and Makita [16] in a torsional vibrating-crystal viscometer with an uncertainty of ±2%, are also shown. These measurements are in good agreement with the present results.

Finaly, in Fig. 2 our older measurements are included. The instrument employed at that time was a vibrating-wire viscometer, but it was calibrated with toluene at 1 atm. These older measurements, performed with an uncertainty of ±0.5%, are in very good agreement with the present results.

6. CONCLUSIONS

The present viscosity measurements cover a temperature range from 210 to 370 K and from atmospheric pressure to 30 MPa. The uncertainty of these measurements is ±0.5%. Above room temperature, these measurements are in excellent agreement with all other measurements in these temperature and pressure ranges. Below room temperature, no comparison could be made, as no other measurements under pressure have been reported.

Hence, these measurements can form the basis of a new IUPAC recommendation for the viscosity of toluene.

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