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The Viscosity of Toluene in the Temperature Range 210 to 370 K[1]

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The paper reports new measurements of the viscosity of toluene along the saturation line over a temperature range of 210 to 370 K. The measurements were performed in a vibrating-wire viscometer, properly adjusted for these low-temperature measurements. 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: measurements; toluene; vibrating-wire technique; viscosity.

1. INTRODUCTION

Toluene has long been considered as a primary viscosity standard, especially where conditions of application or the temperature range required make the use of water impractical. Indeed, in the case of the thermal conductivity of toluene a standard equation that covers the temperature range 190 to 550 K has recently been proposed [1] by the Subcommittee of Transport Properties of the International Union of Pure and Applied Chemistry. Nevertheless, the development of a standard equation for the viscosity of toluene along the saturation line has been hindered by a distinct lack of measurements below room temperature. Indeed below 288 K, to our knowledge, only one investigator [2] has reported measurements that extend down to 218 K. Therefore, the present measurements that extend from 370 K down to 210 K attempt to fill this gap and help in the

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development of a wide range standard reference equation for the viscosity of toluene.

2. THE VISCOMETER

The vibrating-wire viscometer employed for the present measurements has been described in detail elsewhere [3, 4] and thus will only briefly be presented here. It consists of a 100-μm-diameter straight tungsten wire suspended from the top plate of a pressure vessel and carrying tensioning weights on its lower end. Except for the wire itself and the inner weight [3, 4], which are made out of tungsten, all other components and electrical leads are made out of stainless steel, spot-welded together where necessary. This arrangement was found to be necessary to eliminate electrolytic effects [4] in the specific case of polar liquids, due to the dissimilar metals. The wire is set into transverse vibration electromagnetically, and the subsequent motion of the wire within the liquid is observed by electromagnetic induction. The magnetic field is provided by two samarium–cobalt magnets plated with an impervious gold layer to guard against chemical attack and linked by a yoke made of magnetic stainless steel. The decay of the transverse vibrations, which conform to a damped sinusoidal oscillation, is related to the viscosity and the density of the liquid by the working equation

$$\Delta = \frac{(\rho/\rho_{\mathrm{w}})\,k' + 2\Delta_o}{2[1 + (\rho/\rho_{\mathrm{w}})\,k]} \tag{1}$$

Where Δ represents the logarithmic decrement of the oscillation in the liquid, Δ_o the logarithmic decrement *in vacuo*, ρ the fluid density, and ρ_{w} the density of the wire material. In addition, k and k' are quantities that depend [3] upon the viscosity of the fluid through the equations

$$k = -1 + 2\,\mathrm{Im}(A) \tag{2}$$

$$k' = 2\,\mathrm{Re}(A) + 2\Delta\,\mathrm{Im}(A) \tag{3}$$

where

$$A = (i - \Delta)\left\{1 + \frac{2K_1(s)}{sK_0(s)}\right\} \tag{4}$$

and

$$s = [(i - \Delta)\Omega]^{1/2} \tag{5}$$

$$\Omega = \rho\omega R^2/\eta \tag{6}$$

Here, R is the radius of the vibrating wire and ω the frequency of the oscillation. K_0 and K_1 are modified Bessel functions [4].

Equations (1)–(6) form a consistent set of equations from which the viscosity η can be obtained as a function of the density from measurements of the frequency of oscillation in the liquid and the decrement in the liquid and *in vacuo*, provided the radius of the wire and its density are known. Since, however, these two last quantities cannot be measured directly with sufficient accuracy, they can be determined by the use of liquids of known viscosity as described elsewhere [4]. The modifications described earlier allow the use of water as a calibrant. Hence, water, whose viscosity is very accurately known, was used for the calibration of the viscometer. Taking all parameters into account, the uncertainty of the instrument is thus estimated to be ±0.5% , while the precision and the reproducibility of the measurements are about ±0.1% . The use of water in the instrument served also as a check that no electrolytic effects are present [4].

The viscometer, suspended from the cap of the pressure vessel—since the whole arrangement is constructed for pressure measurements also—is placed in the pressure vessel and the pressure vessel in the bath. A Julabo F81-MV external circulator controls the temperature of the heat transfer fluid, which in turn circulates inside the tubes that control the temperature in the bath. This arrangement ensures that the bath temperature is very stable and that temperature gradients are kept to a tolerable level. The temperature of the liquid in the pressure vessel is monitored by three platinum-resistance thermometers embedded along the pressure vessel wall. These were calibrated over the complete experimental range (200 to 370 K) versus a Class 1 NPTL-certified, Tinsley platinum resistance thermometer to within an uncertainty of better than ± 10 mK. The calibration, and consequently all temperatures, were adjusted to ITS 90. Above 290 K ethylene glycol was employed as both the heat transfer liquid and the bath liquid, while below this temperature ethanol was used as the heat transfer liquid and propanol as the bath liquid.

3. MEASUREMENTS

The toluene was supplied by BDH (ARISTAR grade), 99.9% pure. Major impurities were water (200 ppm), benzene (200 ppm), and sulfur compounds (30 ppm). Other impurities were below 1 ppm. Among these impurities, the 200 ppm of water presents the main problem if measurements below 273 K are to be conducted, since ice particles may be formed on the wire surface. In the vibrating-wire technique this effect is very easily detected as it results in a very large superficial increase of viscosity. After analysis of the problem, removal of water by distillation over an anhydrous agent was ruled out, as the close boiling points of the chemicals results in a simultaneous loss of purity. Hence, drying over molecular sieves was preferred. After long exposure to 3A-Type Merck molecular sieves, the water content was found by Karl-Fischer analysis to decrease to less than 100 ppm. This dilution resulted in no effect of the ice particles on the viscosity measurements. The toluene was introduced into the vessel under vacuum.

Another factor that was crucial to the correct interpretation of the measurements involved the density values employed. Initially the Goodwin [5] equation of state was employed, since most investigators use it. However, comparison of the liquid density at 180 K calculated by the Goodwin equation with the measurements of Muringer et al. [6] showed a 1.6% difference. Careful investigation of the values Goodwin employed shows that in the case of the liquid density, only one data point at 178 K was used, while the next data point was at 293 K. Furthermore, the very recent measurements of Magee and Bruno [7] that extended from 180 to 400 K agreed with the values of Muringer et al. Hence, we believe that the Goodwin equation of state should not be employed below 273 K.

Since Magee and Bruno [7] did not give equations for the liquid density, their measurements were fitted over the range 180–400 K and up to 35 MPa to the following Tait-type equation with a maximum uncertainty of less than ±0.09%:

$$\frac{\rho-\rho_o}{\rho}=C\log_{10}\left(\frac{B+P}{B+0.1}\right) \tag{7}$$

where ρ_o is the density at 0.1 MPa and the constant C is equal to 0.216 as proposed by Dymond et al. [8], and

$$\rho_o=\sum_{k=0}^{3} d_k(T/T^c)^k \tag{8}$$

$$B=\sum_{k=0}^{2} b_k(T/T^c)^k \tag{9}$$

where T is the absolute temperature (K), P is the pressure (MPa), and the critical temperature T^{c} is 591.75 K. The constants d_k and b_k are given in Table I.

Table II gives the viscosity measurements of toluene. For comparison purposes the measurements were fitted to an equation of the form

$$\ln\left(\frac{\eta}{n(293.15\ \mathrm{K})}\right)=\sum_{k=0}^{4} c_k(T/T^c)^k \tag{10}$$

Table I. Coefficients b_k, c_k, and d_k

k	b_k (MPa)	c_k	d_k (kg · m^{-3})
0	422.7205	34.054	1166.816
1	−822.595	−219.46	−749.510
2	481.901	556.183	467.299
3	0	−653.601	−360.279
4	0	292.762	0

where the viscosity at 293.15 K is found to be equal to 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%.

The uncertainty of the measurements, as already discussed, is estimated to be ±0.5%. In the very low temperature region, however, this value might be slightly higher due to the strong temperature influence of the viscosity.

In comparing the present measurements with those of other investigators, we will restrict ourselves to investigators who carried out measurements at atmospheric pressure during the past 20 years. Furthermore, in our analysis we shall not include measurements performed in instruments calibrated with atmospheric pressure values of the viscosity of toluene for obvious reasons (this includes our earlier measurements).

Table II. Viscosity Measurements 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

Table III. Toluene Viscosity Measurements of Other Investigators at Atmospheric Pressure

Year	First author	Ref.	T range (K)	Method[a]	Number of points	Calibration fluid employed
1992	Krall	9	298–350	OD	6	Water
1987	Gonçalves	10	298–348	CF	6	Water
1995	Dymond	11	299, 323	FB	2	*n*-Octane, isooctane, *n*-hexadecane, oil Shell Vitrea No. 21
1992	Oliveira	14	303, 323, 348	VW	3	Toluene, *n*-hexane, *n*-heptane, *n*-octane, *n*-decane
1991	Dymond	12	298, 323, 348, 373	FB	4	*n*-Octane, isooctane, *n*-hexadecane, oil Shell Vitrea No. 21
1991	Kaiser	2	218–378	CF	18	Standard oils
1985	Dymond	13	288–393	CF	7	Benzene, toluene
1984	Bauer	15	293, 298	CF	2	Standard oils

[a] OD, Oscillating disk; CF, capillary flow; FB, falling body; VW, vibrating wire.

To our knowledge, only two investigators have employed water for calibration of their instruments. Although sometimes water is more difficult to employ, the accuracy with which its viscosity value is known makes these instruments of greater importance when measurements for standard values are concerned. Table III reports these two investigations. Krall et al. [9] employed an oscillating-disk viscometer with an uncertainty of ±0.5%. These measurements are in excellent agreement with the earlier measurements of Gonçalves et al. [10] performed in a capillary-flow viscometer with a ±0.3% uncertainty. All these measurements are in excellent agreement with the present values as can be seen in Fig. 1.

The remaining investigators employed a variety of fluids for calibration of their instruments as shown in Table III. Dymond et al. reported measurements of toluene both with a falling-body viscometer [11, 12], with an uncertainty of ±2%, and a capillary-flow viscometer [13], with an uncertainty ±0.5%. All measurements are in excellent agreement with the present ones.

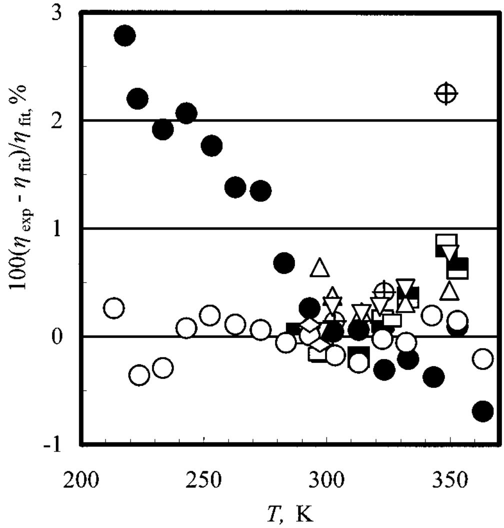

Fig. 1. Deviations of the viscosity at atmospheric pressure from the values calculated by Eq. (10). (○) Present work; (□) Dymond et al. (1995) [11]; (⬓) Dymond et al. (1991) [12]; (⬒) Dymond and Roberston (1985) [13]; (△) Krall et al. (1992) [9]; (▽) Gonçalves et al. (1987) [10]; (●) Kaiser et al. (1991) [2]; (◇) Bauer and Meerlander (1985) [15]; (⊕) Oliveira (1991) [14].

Oliveira [14] employed a novel vibrating-wire viscometer carefully calibrated with a large selection of liquids, mostly alkanes, with an uncertainty of better than ±0.5%. This set of measurements is in agreement with the present ones, except at 348 K, where a higher value than for all other investigators is noted.

As already mentioned, the only other set of measurements that extends from 378 K down to 218 K is that of Kaiser et al. [2] performed in a capillary-flow viscometer with an uncertainty of about ±1%, which increases to ±1.4% at the lowest temperature. In this region their values are higher than the present results by up to 2.5%, which is just about the mutual uncertainty of the two instruments at low temperatures. The distinct difference in slope is, however, noted.

Bauer and Meerlender [15] employed a capillary-flow viscometer, calibrated with standard oils, with an uncertainty of ±0.2%. These values are also in excellent agreement with the present results.

4. CONCLUSIONS

New measurements of the viscosity of toluene along the saturation line over a temperature range from 210 to 370 K are presented. These measurements were performed in a vibrating-wire viscometer calibrated with water, with an uncertainty of ±0.5%. The measurements are in good agreement with most measurements in this temperature range and thus form the basis of a new IUPAC recommendation for the viscosity of toluene at atmospheric pressure from 210 to 370 K.

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