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Reference Correlation for the Viscosity of Liquid Toluene from 213 to 373 K at Pressures to 250 MPa

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A correlation in terms of temperature and molar volume is recommended for the viscosity of liquid toluene as a reference for high-pressure viscosity measurements. The temperature range covered is from 213 to 373 K, and the pressure range from atmospheric up to 250 MPa. The standard deviation of the proposed correlation is 1.36%, and, within a 95% confidence limit, the error is 2.7%. It is estimated that for densities up to 920 $\mathrm{kg \cdot m^{-3}}$ the uncertainty of the viscosity values generated by this correlation is about $\pm 2\%$.

KEY WORDS: density; pressure; reference; toluene; viscosity.

1. INTRODUCTION

Although high-pressure viscometry has many applications, until now only water, based on recommendations by the International Association for the Properties of Water and Steam, has been established as a viscosity reference fluid [1]. The use of water in viscometry is, however, hindered by the facts that it is a polar liquid and, hence, unsuitable in certain viscometers and, furthermore, that its application (at atmospheric pressure) is restricted to temperatures above 273.15 K.

Hence, over the last two decades the Subcommittee of Transport Properties of Commission I.2 of the International Union of Pure and Applied Chemistry has undertaken the responsibility of examining other

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liquids for use as viscosity reference fluids. Thus, in addition to the recommended values for the viscosity of water [1, 2], values for the viscosity of *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane, and *n*-tetradecane [3] at various temperatures and at atmospheric pressure were also recommended.

Toluene was the first reference liquid to be proposed (after water), as it is widely used as a basic compound for chemical synthesis and as an organic solvent. Furthermore, its unusually wide temperature range in the liquid phase (178 to 384 K) makes it an ideal reference liquid for viscosity calibration purposes and apparatus validation. Standard reference data on the thermal conductivity of liquid toluene have already been established [4].

The formulation of the viscosity of toluene over a wide range of temperatures and pressures, proposed in this paper, was undertaken under the auspices of the Subcommittee of Transport Properties of the International Union of Pure and Applied Chemistry.

2. DENSITY

Since the proposed viscosity correlation is a function of temperature and density, a density formulation covering the whole temperature and pressure range was necessary.

The sources [5–8], temperature ranges, and nominal uncertainties of the sets of toluene density data at 0.1 MPa that were used in the present work are shown in Table I. The resulting correlation of the density at 0.1 MPa, $\rho_0(T)$ $(\mathrm{kg \cdot m^{-3}})$, as a function of the absolute temperature, T (K), is

$$\rho_0(T) = 1188.631 - 1.49777T + 0.002158T^2 - 2.69 \times 10^{-6}T^3 \tag{1}$$

with a standard deviation of $\pm 0.03\%$. The deviations of these data from the values calculated by Eq. (1) are shown in Fig. 1. The maximum deviation is 0.06%, while the average deviation of all data is 0.03%.

In Table I, the sources [5–10], temperature and pressure ranges, and nominal uncertainties of the sets of high-pressure density data of toluene used in the present work are also shown. The data cover the temperature range from 198 to 380 K and the pressure range from 0.1 to 280 MPa. The smoothed density data published by Kashiwagi et al. [5] at the highest pressures (>200 MPa) have not been retained in the fitting, as most of them exhibit significant systematic deviations from the fitting equations.

Table I. Measurements of the Density of Liquid Toluene

Year	First author	Ref. No.	Temperature range (K)	Maximum pressure (MPa)	Number of data	Uncertainty (%)[a]
			At 0.1 MPa			
1982	Kashiwagi	[5]	273–373	0.1	6[b]	0.1
1985	Muringer	[6]	198–320	0.1	4	0.2
1988	Dymond	[7]	298–373	0.1	6	0.1
2000	Avelino	[8]	222–348	0.1	7	0.06(0.1)
			At high pressure			
1969	Mopsik	[9]	223–298	203	42	Not known
1982	Kashiwagi	[5]	273–373	240	76[b]	0.1
1985	Muringer	[6]	198–320	264	133	0.2
1988	Dymond	[7]	298–373	279	48	0.1
1996	Magee	[10]	198–380	34	214	0.05
2000	Avelino	[8]	222–348	80	83	0.06(0.1)

[a] Below 273.15 K, the uncertainty is shown parentheses.
[b] Smoothed data.

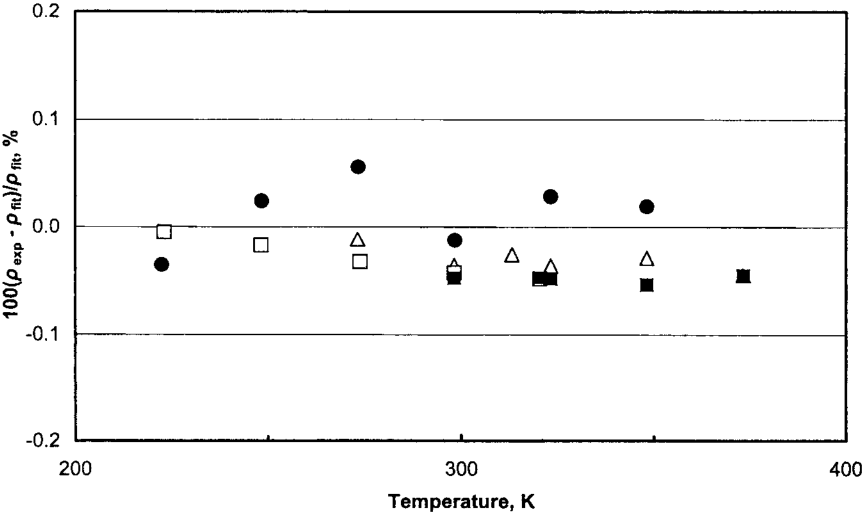

Fig. 1. Percentage deviations of the density measurements at atmospheric pressure as a function of the temperature from the values calculated with Eq. (1). (△) Kashiwagi et al. [5]; (□) Muringer et al. [6]; (■) Dymond et al. [7]; (●) Avelino et al. [8].

The Tait-type equation employed for the data correlation is

$$\frac{\rho - \rho_0}{\rho} = 0.216 \log\left[\frac{B+P}{B+0.1}\right] \tag{2}$$

where ρ is the density ($\mathrm{kg \cdot m^{-3}}$) at temperature T (K) and pressure P (MPa), while parameter B (MPa) is obtained from

$$B = -4.100 + 82.54043\Theta + 198.1896\Theta^2 - 6.61293\Theta^3 + 307.6237\Theta^4 \tag{3}$$

where

$$\Theta = 1 - (T/T_c) \tag{4}$$

and $T_c = 591.8$ K denotes the critical temperature of toluene. The deviations of the density measurements from this correlation are shown in Fig. 2. These equations were found to reproduce the aforementioned data with a standard deviation of ±0.05% over the whole range of conditions.

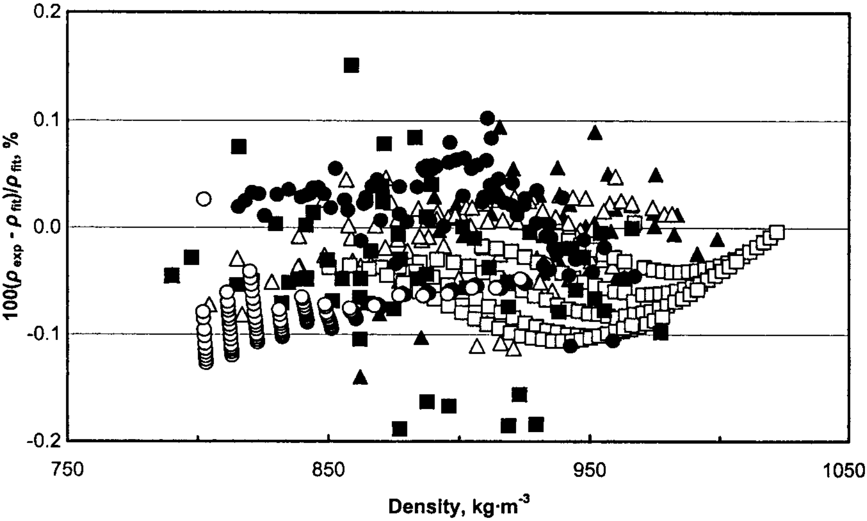

Fig. 2. Percentage deviations of the density measurements at higher pressures as a function of the density from the values calculated with Eqs. (1)–(4). (▲) Mopsik [9]; (△) Kashiwagi et al. [5]; (□) Muringer et al. [6]; (■) Dymond et al. [7]; (○) Magee and Bruno [10]; (●) Avelino et al. [8].

3. VISCOSITY

3.1. Measurements

The data sets considered in the present formulation are listed in Table II. Seventeen sets of measurements performed during the last two decades were included [8, 11–26]. All measurements were separated into two groups according to whether the quoted uncertainty is more or less than 1.5%. This separation was chosen only so as to facilitate the comparison of the measurements.

The purity of each sample employed, the temperature range of the data set, the maximum pressure and method used, the number of points in the set, and the uncertainty in the viscosity measurements are also presented in Table II. The maximum pressure of each data set was determined essentially by the pressure range of the available density data, as shown in Table I. Where high pressures or low temperatures are involved, the uncertainty is increased, and this higher uncertainty is indicated in parentheses. In the same table, the fluids employed for the calibration of each viscometer are shown. It should be pointed out that instruments calibrated with water are expected to produce more accurate measurements. A point that should be made is that only the data of Krall et al. [16] below 380 K were included, this being the limit of the density equations employed here. The maximum pressure considered was 250 MPa, this being the limit of the density equations employed here. For all these viscosity measurements the density was recalculated as described above. No correction to ITS 90 was considered necessary, as the four sets of measurements performed before 1990 employ a very limited temperature range in which the correction is negligible.

We note, finally, that the lowest temperature considered was 213 K, the highest temperature was 373 K, and the highest pressure was 250 MPa.

3.2. Correlation

Since the temperature and pressure ranges were quite wide, resulting in a range for the viscosity of toluene of 234 to 5569 $\mu\mathrm{Pa}\cdot\mathrm{s}$, a correlation in temperature and pressure would not seem plausible. Hence, it was preferred to express the viscosity as a function of the temperature and density. It was decided to employ the hard-sphere scheme developed successfully by Dymond and Assael for the correlation of the *n*-alkanes [27] and the aromatic hydrocarbons [28]. However, as the correlation had to focus on toluene and be as accurate as possible, it was preferred to optimize the form of the equation employed rather than use the generalized form developed by Dymond and Assael [27] for the dimensionless viscosity η^*.

Table II. Measurements of the Viscosity of Liquid Toluene

Year	First author	Ref. No.	Min. purity (%)	Method^a	Calibration fluid(s) employed	Temperature range (K)^b	Max. pressure (MPa)^b	Number of data	Uncertainty (%)^c	Correlation (%)	
										Average	Maximum
1984	Bauer	[11]	99.5	CF	Standard oils	293, 298	0.1	2	0.2	0.4	0.5
1985	Dymond	[12]	99.95	CF	Benzene, toluene	288–373	0.1	6	0.5	1.4	4.4
1987	Gonçalves	[13]	99.9+	CF	Water	298–348	0.1	6	0.3	0.4	1.1
1991	Assael	[14]	99.5	VW	Toluene	303, 323	70	30	0.5	0.3	0.6
1991	Kaiser	[15]	99^{d,e}	CF	Standard oils	218–373	0.1	17	1(1.5)	0.8	2.1
1992	Krall	[16]	99.9	OD	Water	298–373	30	42	0.5	0.3	0.9
1992	Oliveira	[17]	99.95	VW	Toluene, alkanes	303–348	250	46	0.5	1.2	8.6
1997	Vieira dos Santos	[18]	99.9^{d,e}	QC	Toluene	298–373	200	31	0.5	1.3	4.5
1998	Dymond	[19]	99.9^d	CF	Water	260–320	0.1	10	0.5(2)	0.5	2.0
1999	Assael	[20]	99.9^d	VW	Water	218–353	25	90	0.5(1)	0.7	1.5
1982	Kashiwagi	[21]	>99	QC	Hydrocarbons	298–348	110	Equation	2	0.5	2.2
1991	Dymond	[22]	99.9	FB	Alkanes, standard oils	298–373	200	28	2(5)	2.5	7.8
1995	Dymond	[23]	99.9	FB	Alkanes, standard oils	299, 323	200	16	3(5)	0.9	2.8
1997	Harris	[24]	99.8^f	FB	Toluene	298, 323	250	14	2	0.8	2.8
2000	Avelino	[8]	99.8^d	VW	Toluene	248–348	65	82	1.5(2.5)	1.1	2.9
2000	Harris	[25]	99.8^f	FB	Toluene	255–323	250	163	2	1.0	3.5
2000	Caetano	[26]	99.8^d	VW	Toluene	213–298	20	56	1.5	0.6	2.1

[a] CF, capillary flow; VW, vibrating wire; OD, oscillating disk; QC, oscillating quartz crystal; FB, falling body.

[b] Ranges restricted to $\leqslant 250$ MPa and $\leqslant 373$ K.

[c] At the lowest temperatures or highest pressures the uncertainty is shown in parentheses.

[d] Treated with molecular sieves to remove water content.

[e] Further distilled under vacuum.

[f] Dried over Na wire.

Hence, after a thorough optimization, based on all the aforementioned investigators, of all parameters involved, the viscosity, η (Pa · s), written as a function of the dimensionless viscosity η^*, the molar volume V ($\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$), the molar mass M ($=0.09214\ \mathrm{kg} \cdot \mathrm{mol}^{-1}$), and the gas constant R, as

$$\eta = \eta^* \{6.035 \times 10^8 V^{2/3} (MRT)^{-0.5}\}^{-1} \tag{5}$$

can be obtained from the dimensionless viscosity η^*,

$$\frac{1}{\eta^*} = 0.524367 - 1.34765 V_\mathrm{r} + 1.081113 V_\mathrm{r}^2 - 0.25609 V_\mathrm{r}^3 \tag{6}$$

In the above equation the reduced volume $V_\mathrm{r} = V/V_0$, where the characteristic molar volume V_0 ($\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$) is given by

$$V_0 \times 10^6 = 129.770 - 0.2793623T + 6.7699 \times 10^{-4} T^2 - 6.36347 \times 10^{-7} T^3 \tag{7}$$

Equations (5)–(7) form a consistent scheme by which the viscosity can be calculated as a function of the temperature and the density.

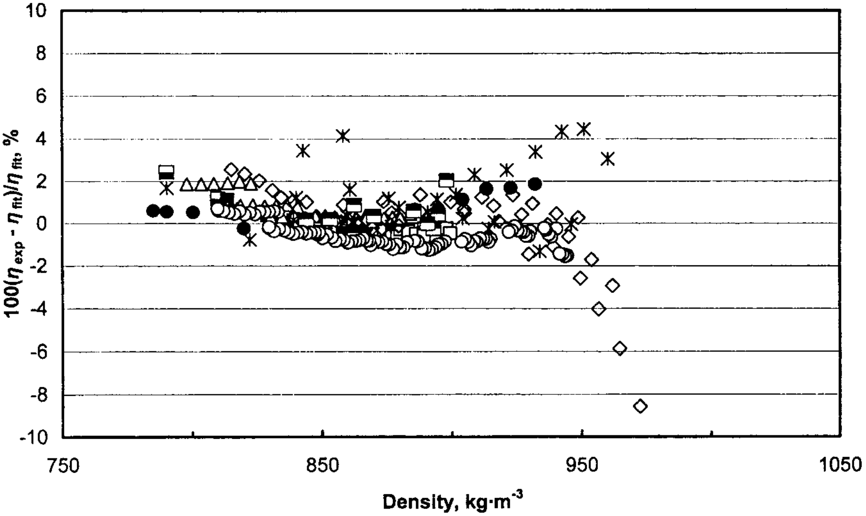

Fig. 3. Percentage deviations of the viscosity of data sets (quoted uncertainty, <1.5%) from the values calculated with the proposed formulation, Eqs. (5)–(7). (◆) Bauer and Meerlender [11]; (⬓) Dymond and Robertson [12]; (■) Gonçalves et al. [13]; (□) Assael et al. [14]; (●) Kaiser et al. [15]; (△) Krall et al. [16]; (◇) Oliveira and Wakeham [17]; (∗) Vieira dos Santos and Nieto de Castro [18]; (⬒) Dymond and Simoiu [19]; (○) Assael et al. [20].

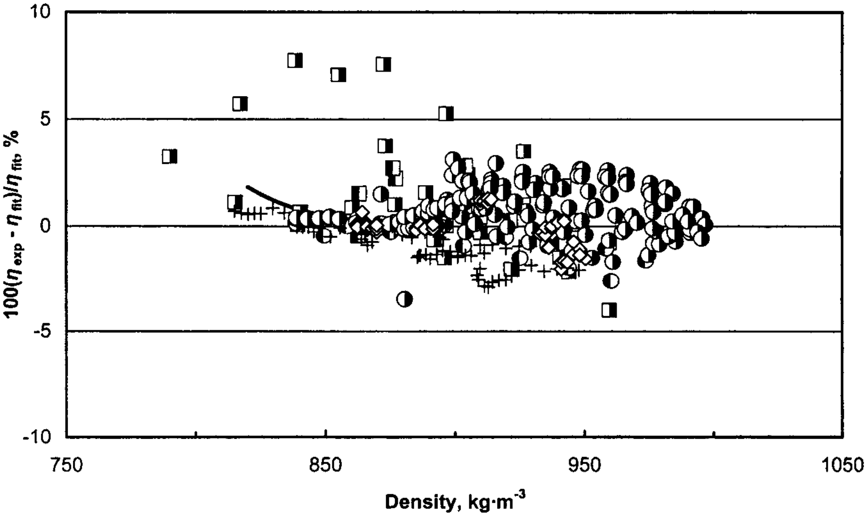

Fig. 4. Percentage deviations of the viscosity of data (quoted uncertainty, >1.5%) from the values calculated with the proposed formulation, Eqs. (5)–(7). (▬) Kashiwagi and Makita [21]; (◨) Dymond et al. [22]; (◧) Dymond et al. [23]; (◐) Harris et al. [24]; (+) Avelino et al. [8]; (◑) Harris [25]; (◇) Caetano et al. [26].

The deviations of all the measurements from the proposed correlation are shown in Figs. 3 and 4, separated according to the experimental level of uncertainty quoted, as noted earlier, and listed in Table II. In the same table, the average and maximum deviations of each data set from the present correlation are shown as percentages.

Considering measurements with a quoted uncertainty of less than 1.5%, we note, in Table II and Fig. 3, that only a relatively small number of points (one datum of Dymond et al. [12], seven data of Oliveira et al. [17], and eight data of Santos et al. [18]) deviate by more than 2%, which is more or less within the mutual quoted uncertainties of the investigators. The deviations noted are at the extreme conditions, i.e., at the highest pressures, highest temperatures, or lowest temperatures.

The same comment can be made in the case of investigators with quoted uncertainties of more than 1.5%, as shown in Table II and Fig. 4. Larger deviations are observed in areas where pressures are higher than 200 MPa. It should also, however, be pointed out that these deviations might be attributed in part to the failure of the model itself to describe the viscosity over such a wide range of conditions.

The standard deviation of the proposed correlation is 1.36%, and, within a 95% confidence limit, the error is 2.7%. Based upon this

Table III. Recommended Values for the Viscosity of Liquid Toluene

	223.15 K		248.15 K		273.15 K		298.15 K		323.15 K		348.15 K		373.15 K	
P (MPa)	ρ $(\mathrm{kg \cdot m^{-3}})$	η $(\mu\mathrm{Pa \cdot s})$	ρ $(\mathrm{kg \cdot m^{-3}})$	η $(\mu\mathrm{Pa \cdot s})$	ρ $(\mathrm{kg \cdot m^{-3}})$	η $(\mu\mathrm{Pa \cdot s})$	ρ $(\mathrm{kg \cdot m^{-3}})$	η $(\mu\mathrm{Pa \cdot s})$	ρ $(\mathrm{kg \cdot m^{-3}})$	η $(\mu\mathrm{Pa \cdot s})$	ρ $(\mathrm{kg \cdot m^{-3}})$	η $(\mu\mathrm{Pa \cdot s})$	ρ $(\mathrm{kg \cdot m^{-3}})$	η $(\mu\mathrm{Pa \cdot s})$
0.1	931.9	2072	908.7	1170	885.6	771	862.5	555	839.0	421	815.0	330	790.2	265
10	936.9	2274	914.4	1270	892.1	833	869.9	599	847.6	455	825.0	359	801.9	289
20	941.7	2496	919.8	1377	898.3	899	876.9	646	855.6	491	834.2	388	812.4	313
30	946.4	2739	925.0	1490	904.1	968	883.5	693	863.0	527	842.5	417	821.9	338
40	950.8	3003	929.9	1611	909.6	1039	889.7	743	869.9	565	850.2	447	830.5	362
50			934.7	1739	914.9	1114	895.5	794	876.4	603	857.4	477	838.5	387
60			939.2	1876	919.9	1193	901.1	847	882.5	642	864.1	508	845.9	412
70			943.6	2022	924.7	1276	906.3	902	888.3	683	870.5	539	852.8	437
80			947.8	2178	929.3	1362	911.4	959	893.8	724	876.5	571		
90			951.9	2344	933.7	1453	916.2	1018	899.0	767	882.1	604		
100			955.8	2522	938.0	1549	920.8	1080	904.0	811	887.5	638		
120			963.3	2917	946.1	1756	929.5	1211	913.4	904	897.6	708		
140			970.3	3371	953.7	1986	937.7	1354	922.1	1003	906.9	782		
160			977.0	3897	960.8	2242	945.3	1508	930.2	1109	915.5	860		
180			983.3	4508	967.5	2527	952.4	1677	937.8	1222	923.6	942		
200			989.3	5221	973.9	2847	959.2	1861	945.0	1344	931.2	1030		
220					980.0	3206	965.6	2063	951.8	1476	938.3	1123		
240					985.8	3610	971.8	2284	958.2	1617	945.1	1223		

uncertainty and the preceding discussion, it is estimated that for densities up to 920 $\mathrm{kg \cdot m^{-3}}$ the uncertainty of the viscosity values generated by this correlation is about ±2%; above that density, the uncertainty deteriorates to about ±4% reflecting the discrepancies of some of the data in that region.

In Table III, recommended values for the viscosity of toluene are given for pressures up to 240 MPa.

4. CONCLUSIONS

A correlation in terms of temperature and molar volume is recommended for the viscosity of liquid toluene as a reference for high-pressure viscosity measurements. The temperature range covered is from 213 to 373 K, and the pressure range from atmospheric up to 250 MPa. The standard deviation of the proposed correlation is 1.36%, and, within a 95% confidence limit, the error is 2.7%. It is estimated that for densities up to 920 $\mathrm{kg \cdot m^{-3}}$ the uncertainty of the viscosity values generated by this correlation is about ±2%.

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