Measurements of the Viscosity of Liquid Toluene in the Temperature Range $218-378 K^1$

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New relative measurements of the viscosity of liquid toluene are reported for the temperature range 218 to 378 K. They supplement the existing data, which have been obtained mostly above 273.15 K. The relative accuracy of the results is estimated between -1 and 1.38% at 218 K, narrowing to one of -0.74 and 1.12% at 378 K. The experimental data have been correlated well within these estimates by an empirical temperature function. A comparison with previous experimental and compiled or evaluated data includes references since 1894 and is the most comprehensive survey so far. The agreement with the present data is generally very good. There is a need for further measurements with instruments other than capillary viscometers and in the low-temperature range from the triple point (178.15 K) to 273.15 K.

KEY WORDS: capillary viscometer; viscosity; toluene.

1. INTRODUCTION

Toluene is widely used as a basic compound for chemical syntheses and as an organic solvent. Because of its lower carcinogeneous potential it is seen as a replacement for benzene. Beyond these implications, scientific interest in toluene arises because of its unusually wide liquid temperature range, which makes it a suitable reference fluid for calibration purposes and apparatus validation. Standard reference data of the thermal conductivity of liquid toluene have already been established [1]. The members of the

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Subcommittee on Transport Properties of the International Union for Pure and Applied Chemistry (IUPAC) have started a program to provide data for the formulation of a standard reference of the viscosity of liquid toluene. The present work is a contribution to this effort.

2. EXPERIMENTAL

2.1. Sample Preparation

A toluene sample *pro analysi* from J. T. Baker Chemicals with a stated purity of greater than 99% was used for the measurements. The sample was kept under phosphorous pentoxide or silica gel to remove water and to avoid further water absorption from the ambient air. The formation of ice crystals below 273.15 K during first viscosity measurements with the original sample indicated water as a major impurity.

The toluene was distilled under vacuum before all subsequent viscosity determinations and its purity checked by refractive index measurements. The distillation was performed from product fractions of 100% in volume to 25% in steps of 5%. Samples of the products were taken with sterile syringes and immediately measured in an Abbé refractometer at (293.15 ± 0.2) K. The temperature fluctuation of ± 0.2 K causes an uncertainty in the refractive index of ± 0.0001 . This can be tolerated since the fourth decimal of the measured refractive index has to be interpolated with the refractometer that was used. The value of the refractive index was obtained for each sample as an average of two independent measurements. The results are sown in Fig. 1. The refractive index decreased from



Fig. 1. Dependence of the refractive index of the toluene samples on the distillation product fraction at 293.15 K.

 $n_{\rm D}^{20} = 1.4972$ toward the reference value $n_{\rm D}^{20} = 1.4961$ [2, 3] with decreasing product fractions. For fractions smaller than 50%, a change of the sample value $n_{\rm D}^{20} = 1.4967$ could not be observed anymore within the resolution of the refractometer. The total absolute accuracy of the refractive index measurement is estimated to be within ± 0.00061 , corresponding to $\pm 0.4\%$ relative to the reference value. Although this value was not reached completely, the distillation increased the purity of the toluene significantly. There were no other purification methods available to the authors.

2.2. Equipment Modifications

The viscosity was measured with Ubbelohde glass capillary viscometers and peripheral equipment as described earlier [4]. Before the toluene campaign, all capillaries were recalibrated in this apparatus with standard oils from Physikalisch-Technische Bundesanstalt (PTB, Braunschweig, Germany). It turned out that the calibration constants K [see Eq. (2) below] as stated by the manufacturer were incorrect between 2.4 and -0.5% in the extremes. The accuracy of the recalibration is estimated to be better than $\pm 0.28\%$. Capillary types 0 and 0a were used for the toluene measurements.

Due to the usually high humidity at Siegen, the viscometer was modified further to avoid intrusion of water into the instrument, particularly at temperatures below 273.15 K. The control unit (AVS 300) and the capillary in the measuring stand were connected to a vessel. This system was filled with dry nitrogen so that the sample was separated from the atmosphere during the measurements.

The thermostat was additionally insulated so that the temperature was constant to ± 0.02 K in the middle of the capillary. A calibrated platinum resistance thermometer was used to determine the temperature at the capillary with an accuracy of ± 0.2 K below 273.15 K and ± 0.1 K above.

2.3. Accuracy Considerations

The working equation of Ubbelohde capillary viscometers reads [4]

$$v = \frac{\pi R^4 g h}{8 l V} \tau - \frac{m V}{8 \pi l \tau} \tag{1}$$

with v the kinematic viscosity, R the radius of the capillary, (gh) the driving hydrostatic pressure difference, l the length of the capillary, m the Hagenbach-Couette correction factor, and V the liquid volume which

passes the capillary during the measured efflux time τ . Usually the simplified equation

$$v = K(\tau - \vartheta) \tag{2}$$

is employed, with the calibration constant K of a capillary and ϑ a tabulated correction time.

The accuracy of the viscosity measurements is estimated by analyzing the sensitivity of Eq. (1) to different experimental errors. The maximum relative error of the viscosity is obtained by

$$\left(\frac{\Delta v}{v}\right) = \pm \frac{1}{v} \sum_{i=1}^{5} |\Delta v_i|$$
(3)

with the individual contributions

$$|\Delta v_i| = \left| \left(\frac{\partial v}{\partial y_i} \right)_{y_j \neq i} \right| \Delta y_i \tag{4}$$

The calculation included the following quantities y_i and their estimated variations Δy_i :

| $\Delta m = 0.1;$ |
|--|
| $\Delta \tau = 0.01 \text{ s};$ |
| $\Delta \phi = 2^{\circ};$ |
| |
| |
| $(T-T_{\text{calib}});$ |
| $\Delta T = 0.2 \text{ K} (T < 273.15 \text{ K}),$ |
| $\Delta T = 0.1 \text{ K} (T > 273.15 \text{ K}).$ |
| |

The last contribution has to be calculated individually for each liquid that is measured from the temperature dependence of its viscosity. This requires a correlation of the experimental results, which can be established only after the measurements. Yet the accuracy of the temperature determination is a predominant contribution to the total experimental accuracy as is illustrated in Fig. 2. The correlation presented in Section 3 was used to calculate that contribution. It decreases from $\pm 0.56\%$ at 218.11 K to $\pm 0.068\%$ at 378.18 K.

Two other effects on the calibration constant K have to be considered, which arise from differences between the properties of the standard oils and those of the actually measured liquid. An additional bouyancy effect occurs if the density of the measured liquid differs significantly from the density of the standard oil. Similarly, differences in the surface tension may result in



Fig. 2. Individual contributions to the estimated experimental accuracy of the toluene viscosity measurements.

changes of K. To account for these influences the calibration constant K_{calib} as determined in the measurements with standard oils is corrected by two terms,

$$K = K_{\text{calib}} \left[1 - \left(\frac{\rho_{\text{air}}}{\rho} - \frac{\rho_{\text{air}}}{\rho_0} \right) \right] \left[1 - \kappa \left(\frac{\sigma_0}{\rho_0} - \frac{\sigma}{\rho} \right) \right]$$
(5)

yielding the actual calibration constant K for the liquid measurements [5]. The bracket terms include the density of air ρ_{air} , the density and surface tension of the standard oil, ρ_0 and σ_0 , and those of measured liquids, ρ and σ . The correction factor κ has to be determined from experiments as explained below.

The buoyancy correction can be calculated. With the densities of the standard oils 5A and 1B as stated by PTB and the density of toluene [5], this effect amounts to changes in the calibration constants of 0.007% for capillary type 0a and of 0.01% for capillary type 0 at 293.15 K. Compared to the other uncertainties of the measurements, these corrections are negligibly small in the case of toluene.

The influence of surface tension differences is largely, but not completely, compensated by the trumpet shape of the measuring bulb and the suspending level of Ubbelohde viscometers. In principle, the residual influence of the surface tension could be calculated if the geometrical factors of a particular viscometer would be known. Since these data are difficult to obtain, the second correction term is introduced in Eq. (5) and the factor κ determined by measurements of two liquids which have differing ratios σ/ρ but the same viscosity. Thus after inserting Eq. (5), Eq. (2) can be equated for the two liquids and κ is obtained from the measured efflux times. According to DIN 51 562 part 3, the following combination was chosen:

- (i) anhydrous acetone pro analysi at T = 297.78 K, and
- (ii) trichloroethylene pro analysi at T = 293.15 K.

At these temperatures those liquids have a viscosity of $0.3850 \text{ mm}^2 \cdot \text{s}^{-1}$ but σ/ρ ratios of 29 and 19.5 cm³ · s⁻², respectively. Using capillary 0, efflux times were measured four times for each liquid at the above temperatures ± 0.01 K. The resulting values of the correction factor ranged between -0.00075 and $-0.00115 \text{ s}^2 \cdot \text{cm}^{-3}$, with an average of $\kappa = -0.00092$ $s^2 \cdot cm^{-3}$. The negative sign indicates a surface tension effect opposite to gravity as it is found for most Ubbelohde viscometers. Applying the average κ value to toluene, which has a σ/ρ ratio of 32.9 cm³ s⁻² at 293.15 K, results in a correction of the calibration constant of that capillary of $K/K_{calib} = 1.0038$ equivalent to a unilateral increase of the viscosity of 0.38%. This value was taken as an estimate for the influence of surface tension effects on all the measurements which were performed. It differs for each capillary and changes due to the temperature dependence of the density and surface tension. According to Bauer and Meerlender [5] surface tension effects amount usually to uncertainties of 0.1 to 0.3% in the viscosity. The present value can therefore be regarded as a conservative estimate.

The individual contributions to the relative accuracy of the present measurements are summarized in Fig. 2. The transitions in $\Delta \varphi$, Δm , and $\Delta \tau$ from capillary 0a to capillary 0 at 273.15 K are marked by broken lines, as is the change in the accuracy of the temperature determination ΔT . The smallest contribution arises from the uncertainty of the timing $\Delta \tau$. Efflux times ranged between 505 and 171 s in capillary 0a and between 738 and 278 s in capillary 0. The contribution ΔK is the estimated accuracy of the viscometer recalibration as stated in Section 2.2. An estimate of the total experimental accuracy is obtained by summing up these individual contributions with positive and negative signs. The contribution due to surface tension effects $\Delta(\sigma/\rho)$ is counted only in positive direction. These accuracy margins are included in Figs. 4 to 8. At the low-temperature end the range is from -1 to 1.38%, and at the high-temperature end, from -0.74 to 1.12%. The best accuracy prevails at the calibration temperature 293.15 K, where it is limited by -0.58 and 0.96%, respectively.

3. EXPERIMENTAL RESULTS AND CORRELATION

The viscosity measurements were performed at ambient pressure and at temperatures from 218 to 378 K in steps of 5 and 10 K. A total of 18 data points is quoted in Table I. Each table entry is based on four independent measurements. At 273.15 K the viscosity was measured with both capillaries. The method of Schwen and Puhl [6] was employed to correlate the data with an appropriate temperature function. It is common experience that the simple Andrade or Arrhenius equation is not suitable for an accurate representation of liquid viscosities over an extended temperature range. Therefore, a total of 26 empirical expressions was tested to find the best correlation of the data. The best fit was obtained wih the four-parameter equation

$$\frac{v}{v_0} = e^{\left[b_1 + b_2(T/1000) + b_3(1000/T) + b_4(1000/T)^2\right]}$$
(6)

where v is the kinematic viscosity and T the temperature in Kelvin. The

| 1 | 105010 |
|----------|---|
| Т (К) | $(10^{-6} \text{ m}^2 \cdot \text{s}^{-1})$ |
| 218.11 | 2.61203 |
| 223.09 | 2.26951 |
| 233.19 | 1.77103 |
| 243.20 | 1.43687 |
| 253.19 | 1.19292 |
| 263.17 | 1.01198 |
| 273.11 | 0.87772 |
| 283.13 | 0.76673 |
| 293.13 | 0.67943 |
| 303.12 | 0.60905 |
| 313.10 | 0.55143 |
| 323.19 | 0.49989 |
| 333.16 | 0.45834 |
| 343.19 | 0.42117 |
| 353.16 | 0.39203 |
| 363.13 | 0.36284 |
| 373.19 | 0.33690 |
| 378.18 | 0.32516 |
| | |

 Table I.
 Experimental Results for the Kinematic Viscosity of Toluene as a Function of Temperature at Atmospheric Pressure

reduction constant v_0 accounts for the units of the kinematic viscosity and may be set to $10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$. With the parameter values

$$b_1 = 2.710\ 058$$

 $b_2 = -6.146\ 481\ \mathrm{K}^{-1}$
 $b_3 = -1.220\ 728\ \mathrm{K}$
 $b_4 = 0.246\ 5344\ \mathrm{K}^2$

the tabulated data are reproduced with an average deviation of -0.0086%and an associated standard deviation of $\pm 0.27\%$. The extreme deviations are 0.52% and -0.49%. Thus, the correlation represents the data well within their estimated accuracy. Other equations with five and six adjustable parameters did not yield a better fit. The tabulated experimental data and the correlation are shown in Fig. 3 on an absolute scale. Figure 4 displays the percentage deviations between all measurements, the tabulated data, and the correlation, Eq. (6). The extreme deviations occur at either end of the temperature range, which indicates that the correlation does not follow the upward curvature at low temperatures or the downward curvature toward the normal boiling point at 383.764 K. The scatter of the data at each temperature, i.e., the precision of the measurements, is found to be well within $\pm 0.2\%$. Thanks to the recalibration, the four measurements with either capillary at 273.15 K agree very well. Systematic trends which might be typical for each capillary cannot be identified.



Fig. 3. Experimental data and correlation of the viscosity of toluene.



Fig. 4. Percentage deviations between all measurements, the tabulated data, and the correlation, Eq. (6). Here and in the following figures the nozzle-shaped lines represent the estimated accuracy margins of the present measurements.

4. COMPARISON WITH LITERATURE DATA

A total of 40 previous publications on the viscosity of liquid toluene was found suitable for comparisons after a comprehensive literature search: 32 papers present original experimental data, and 8 references are compilations or evaluations of data. Only six papers report experimental data below 273.15 K. Most of the measurements were performed between room temperature and 373.15 K. Capillary viscometers were used with six exceptions. The data of Bridgman [7] were obtained with a falling-body instrument, those of Medani and Hasan [8] with a rolling-ball instrument, while Kashiwagi and Makita [9] used a torsionally vibrating quartz viscometer for relative measurements. Preliminary absolute measurements were reported from the same type of instrument by Vieira dos Santos and Nieto de Castro [10]. Kyropoulos [11] reported one data point which was obtained in a Couette viscometer and the data of Linke [12] were measured in a Höppler viscometer.

All data were compared with the correlation, Eq. (6), as reported over the temperature range of the present measurements. Adjustments for different temperature scales were not made. Dynamic viscosities from previous publications were converted to kinematic viscosities using density data of the respective publication where provided. Otherwise the equation

| f Toluene ^a |
|------------------------|
| 5 |
| Viscosity |
| the |
| of |
| Comparison |
| Table II. |

| | ļ | | | | 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 | | | |
|---------------------|--------------------|----------|------------|------------|---|---------------------|-------------------|-------|
| Author(s) | Year (Ref. No.) | T (K) | p (MPa) | Method | $\Delta_{\rm av} \pm {\rm s}$ (%) | Δ_{\max} (%) | A_{\min} (%) | Data |
| | | | Experime | ental data | | | | |
| Thorpe, Rodger | 1894(19) | 273-342 | 0.1 | CP | 0.67 + 1.87 | 4.6 | -0.61 | × |
| Heydweiller | 1896 (30) | 293373 | 0.1 | CP | 0.77 + 0.97 | 1.81 | -0.12 | о (г. |
| Linebarger | 1896 (40) | 298.15 | 0.1 | CP | -2.36 ± 0.26 | -2.18 | -2.54 | . 6 |
| Kendall, Monroe | 1917 (41) | 298.15 | 0.1 | CP | -0.14 ± 0.08 | -0.081 | -0.19 | 1 (1 |
| Miller | 1924 (42) | 282, 293 | 0.1 | CP | -1.73 ± 0.81 | -1.15 | -2.30 | 5 |
| Lewis | 1925 (43) | 298.15 | 0.1 | CP | -0.16 | | | ı — |
| Bridgman | 1926 (7) | 303, 348 | 0.1 | FB | -0.4 ± 1.03 | 0.33 | - 1.13 | 5 |
| Timmermans, Martin | 1926 (32) | 288-333 | 0.1 | CP | 0.52 ± 1.25 | 1.85 | -0.64 | m ا |
| Puschin, Pinter | 1929 (44) | 303.15 | 0.1 | CP | - 16.0 | | | , |
| Kyropoulos | 1932 (11) | 307 | 0.1 | 00 | 0.89 | | | |
| Linke | 1941 (12) | 286-323 | 0.1 | QН | 5.82 ± 0.74 | 6.7 | 4.9 | 5 |
| Geist, Cannon | 1946 (20) | 273-313 | 0.1 | CP | -0.053 ± 0.4 | 0.36 | 0.44 | ŝ |
| Lima | 1952 (31) | 298–308 | 0.1 | CP | -0.26 ± 1.01 | 0.71 | -1.30 | e |
| Mamedov, Panchenkov | 1955 (18) | 253-353 | 0.1 | CP | -1.02 ± 2.7 | 0.86 | -7.9 | - 11 |
| Hammond, | | | | | 1 | | | 4 |
| Howard, McAllister | 1958 (21) | 293-353 | 0.1 | C | 0.25 ± 0.30 | 0.72 | -0.06 | 7 |
| Barlow, Lamb, | | | | | ł | | | |
| Matheson | 1966 (23) | 223-303 | 0.1 | СР | 0.92 ± 1.77 | 3.48 | -0.57 | 4 |
| Neduzhii, Khmara | 1968 (16) | 220-360 | Sat. liq. | CP | -3.52+4.97 | 0.20 | -17.7 | 15 |
| Akhundov, | | | ſ | | I | | | |
| Ismail-zade, Tairov | 1970 (24) | 297–373 | 0.1 | CP | 1.39 ± 0.98 | 2.56 | 0.25 | 4 |
| Karbanov, Geller | 1975 (22) | 223-363 | 0.1 | Cb | 0.68 ± 0.90 | 2.03 | -0.62 | 12 |
| Medani, Hasan | 1977 (8) | 353-373 | Sat. liq. | RB | 1.17 ± 0.52 | 1.77 | 0.83 | £ |
| Rabe | 1981 (17) | 220-300 | 0.1 | CP | 1.69 + 2.18 | 6.53 | -2.38 | 14 |
| Teja, Rice | 1981 (27) | 298-323 | 0.1 | CP | 0.28 ± 0.64 | 0.90 | -0.37 | 5 |
| Kashiwagi, Makita | 1982 (9) | 298–348 | 0.1 | TVC | 0.64 ± 0.99 | 2.05 | -0.17 | 4 |

| 1984 (29) | 298-333 | 0.1 | Ċ | 1.21 ± 1.40 | 5.29 | 07.0- | n |
|-----------------|---|---|---|--|---|---|--|
| 1984 (5) | 293, 298 | 0.1 | Cb | -0.19 ± 0.03 | -0.16 | -0.22 | m |
| 1985 (25) | 288-373 | Sat. liq. | C | 0.39 ± 0.73 | 1.44 | -0.44 | 9 |
| | | | | | | | |
| 1986 (15) | 288-308 | 0.1 | СР | -13.9 ± 0.79 | -13.4 | | en. |
| | | | | | | | |
| 1986 (14) | 258-378 | 0.1 | Cb | -12.2 ± 3.29 | -6.95 | -16.5 | 25 |
| 1987 (26) | 298–358 | 0.1 | CP | 0.045 ± 0.46 | 0.71 | -0.54 | 8 |
| | | | | | | | |
| 1987 (28) | 297–332 | 0.1 | CP | 0.50 ± 0.28 | 0.98 | 0.22 | 9 |
| | | | | | | | |
| 1987 (10) | 298.15 | 0.1 | TVC | 5.05 ± 1.28 | 5.96 | 4.15 | 7 |
| 1988 (6) | 273-373 | 0.1 | CP | 1.24 ± 0.86 | 2.15 | -0.30 | 21 |
| 1989 | 218-378 | 0.1 | CP | -0.0086 ± 0.27 | 0.52 | -0.49 | 18 |
| | | Correlations/ | compilations | | | | |
| 1975 (38) | 273-373 | Sat. liq. | | 0.19 ± 0.63 | 1.40 | -0.66 | 10 |
| 1977 (37) | 233-373 | 0.1 | | 0.55 ± 0.78 | 1.77 | -0.43 | 8 |
| 1977 (33) | 218-378 | Sat. liq. | | -1.49 ± 1.53 | 0.65 | -4.64 | 33 |
| 1979 (35) | 295-380 | 0.1 | | 1.33 ± 0.87 | 2.42 | 0.22 | 10 |
| 1986 (39) | 248378 | 0.1 | | -0.48 ± 0.36 | 0.05 | -1.43 | 27 |
| 1987 (34) | 233-378 | Sat. liq. | | -1.29 ± 1.28 | 0.56 | -2.88 | 30 |
| | | | | | | | |
| 1988 (36) | 220-370 | 0.1, | | 0.41 ± 1.09 | 2.43 | -1.20 | 16 |
| | | sat. liq. | | | | | |
| | | | | | | | |
| 1989 (3) | 273–313 | 0.1 | | 0.40 ± 0.58 | 1.08 | -0.15 | Ś |
| onological orde | r. The tempera | tture range in c | olumn "T (K | ()" refers to the range of | of the compari | son and does | not show |
| | 1984 (2) 1984 (5) 1985 (25) 1986 (15) 1986 (14) 1987 (26) 1987 (28) 1988 (6) 1988 (6) 1977 (33) 1977 (33) 1977 (33) 1977 (33) 1977 (33) 1977 (33) 1977 (33) 1978 (6) 1988 (6) 1988 (39) 1988 (39) 1988 (36) 1988 (36) 19 | 1984 (29) 298-333 1984 (5) 293, 298 1985 (25) 288-373 1986 (15) 288-378 1986 (15) 288-378 1987 (26) 298-358 1987 (26) 298-358 1987 (26) 298-358 1987 (26) 298-358 1987 (28) 297-332 1987 (10) 298.15 1988 (6) 273-373 1989 218-378 1975 (38) 273-373 1975 (38) 273-373 1977 (37) 233-373 1977 (37) 233-373 1977 (37) 233-373 1977 (37) 233-373 1978 (39) 248-378 1977 (37) 233-373 1978 (36) 248-378 1979 (35) 295-380 1988 (36) 248-378 1988 (36) 233-373 1988 (36) 233-373 1988 (36) 233-373 1988 (36) 218-378 1988 (36) 218-378 1989 (3) 273-313 | 1984 (29) 298-333 0.1 1984 (5) 293, 298 0.1 1985 (25) 288-373 Sat. liq. 1986 (15) 288-308 0.1 1986 (15) 288-308 0.1 1986 (15) 288-378 0.1 1987 (26) 298-358 0.1 1987 (26) 298-358 0.1 1987 (28) 297-332 0.1 1987 (28) 297-332 0.1 1987 (10) 298.15 0.1 1987 (10) 298.15 0.1 1988 (6) 273-373 0.1 1988 (6) 273-373 0.1 1975 (38) 273-373 0.1 1975 (38) 273-373 0.1 1977 (37) 233-373 0.1 1977 (37) 233-373 0.1 1977 (37) 233-373 0.1 1977 (37) 233-373 0.1 1977 (35) 295-380 0.1 1977 (37) 233-378 0.1 1977 (35) 295-380 0.1 1977 (35) 298-378 <td>1984 (29)298-333 298-3730.1CP1984 (5)293, 2980.1CP1985 (25)288-373Sat. liq.CP1986 (15)288-3780.1CP1986 (14)258-3780.1CP1987 (26)298-3580.1CP1987 (26)298-3580.1CP1987 (28)297-3320.1CP1987 (28)297-3320.1CP1987 (10)298.150.1CP1987 (10)298.150.1CP1987 (10)298.150.1CP1987 (10)298.150.1CP1988 (6)273-3730.1CP1978 (6)273-3730.1CP1988 (6)273-3730.1CP1978 (33)273-373Sat. liq.1977 (33)218-378Sat. liq.1977 (33)218-378Sat. liq.1977 (33)218-378Sat. liq.1977 (33)218-378Sat. liq.1977 (34)233-373Sat. liq.1978 (36)220-3700.11988 (36)220-3700.11989 (3)273-3130.11989 (3)273-3130.11989 (3)273-3130.11989 (3)273-3130.11989 (3)273-3130.11989 (3)273-3130.11989 (3)273-3130.11989 (3)273-3130.11989 (3)273-3130.1</td> <td>1984 (29) 298-333 0.1 CP 1.21 ± 1.40 1984 (5) 293,298 0.1 CP -0.19 ± 0.03 1985 (15) 288-373 Sat. liq. 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the entire range of the respective literature data set. $\Delta_{av} \pm s$ is the percentage average and its standard deviation compared with the correlation, Eq. (6). A_{max} and A_{min} are the extreme deviations of this comparison. CO, Couette viscometer; CP, capillary viscometer; FB, falling-body viscometer; HÖ, Höppler viscometer; RB, rolling-ball viscometer; TVC, torsionally vibrating crystal viscometer.

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of state and the saturated liquid density correlation of Goodwin [13] were used. A summary of all comparisons is compiled in Table II. Data sets with three or more points are also included in the deviation plots, Figs. 5 to 8.

Data sets which deviate considerably from the present correlation are included in Fig. 5. The data of Linke [12] are on the average too high by 6%. Systematic discrepancies from -8 to -16% are found in the results of Trumpakaj and Lewandowska [14]. These authors noted already themselves "some oddity" in their measurements around room temperature. Since the results are reported as a correlating equation, it cannot be decided whether the measurements are in error or the discrepancies are due to misprinted parameter values of the correlating equation. A systematic offset of -15% is found for the data of Ritzoulis et al. [15] as well. A maximum deviation of -18% occurs for the saturated liquid data of Neduzhii and Khmara [16] at 218 K. It reduces systematically with higher temperatures and comes close to the lower accuracy margin of the present work above 273.15 K. Nevertheless, these results are systematically too low and not confirmed by other saturated liquid studies. The measurements of Rabe [17] have been carried out down to 193 K and over an extended pressure range. Those values which fall in the present temperature range exhibit considerable scatter and are mostly too high with an extreme deviation of 6.5% at 223.5 K. The best agreement is found in Fig. 5 for the measurements of Mamedov and Panchenkov [18]. Excluding two points below 273.15 K, the deviations range within the estimated accuracy band of the present work.



Fig. 5. Percentage deviations between literature data and the correlation, Eq. (6).



Fig. 6. Percentage deviations between literature data and the correlation, Eq. (6).

It is remarkable that the first data, obtained nearly a century ago by Thorpe and Rodger [19], are in far better agreement than some of the more recent results. Figure 6 illustrates that most of the deviations fall within the estimated accuracy band of this work, with an extreme value of only -0.7% at 273.15 K. The measurements at 343.15 and at 380.25 K



Fig. 7. Percentage deviations between literature data above 283.15 K and the correlation, Eq. (6).



Fig. 8. Percentage deviations between recommended values from data evaluations and the correlation, Eq. (6).

appear to be outliers. Two data points of Geist and Cannon [20] almost coincide with the respective points of Thorpe and Rodger [19]. A similar deviation pattern is found for the data of Hammond et al. [21], which join well to the former but with mostly positive deviations. The trend which may be inferred from these two data sets continues with two data points of Medani and Hasan [8] but the deviation of their value at 373.15 K exceeds the upper accuracy margin of the present work. Systematically increasing deviations with increasing temperature are also observed in the data of Karbanov and Geller [22] from 263.15 K up and in the values of Schwen and Puhl [6] which have been calculated from their correlation. The shift, compared to the results of Thorpe and Rodger [19] and Hammond et al. [21], is about 1%. The data of Karbanov and Geller [22] exceed the estimated accuracy margins of this work only above 313.15 K. Below 273.15 K these are the only experimental data which agree favorably with the present measurements. The data of Barlow et al. [23] which extend into the supercooled liquid region could be compared only at four temperatures. The deviations of three points fall within the estimated accuracy band of this work but there is a systematic trend, diagonally increasing from -0.6% at 303.15 K to 3.5% at 223.15 K, which resembles partly the deviations of the data of Rabe [17] in Fig. 5. Further lowtemperature measurements are necessary to resolve these differences. An atypical trend of deviations is found for the data of Akhundov et al. [24], which appear somewhat too high.

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The remaining literature data above 283.15 K are compared in Fig. 7. Among these investigations, only the measurements of Dymond and Robertson [25] cover this temperature range entirely. They agree with the present results within the estimated accuracy margins except at 373.15 K, where the deviation amounts to 1.4%. The data of Dymond and Robertson [25] exhibit a trend at higher temperatures which was found similarly in the saturated liquid data of Medani and Hasan [8] in Fig. 6. The measurements of Byers and Williams [26] have been carried out in equipment of the same manufacturer as was used in this investigation. The results agree mutually very well within the estimated experimental accuracy. Although the average deviation is only 0.045%, the deviations rise systematically with temperature but are shifted by -0.7% compared to those of Dymond and Robertson [25]. Nevertheless, this series supports the present results best overall. Very good agreement is found, besides, with the data of Teja and Rice [27] and Gonçalves et al. [28]. Three data points of Kashiwagi and Makita [9] deviate also within the accuracy margins, with an apparent outlier at 348.15 K. Two values of Singh and Sinha [29] at 303.15 and 313.15 K deviate up to 3.3% and seem to be outliers, too. One of the three data points which Heydweiller obtained in 1896 [30] deviates by 1.81% at 373.15 K. The value of Lima [31] at 308.15 K is clearly too low, while the measurement of Timmermans and Martin [32] at 333.15 K is too high.

It is noted that the viscosity values calculated from Eq. (6) at 293.15 and 298.15 K agree with the very carefully determined data of Bauer and Meerlender [5] within or just above the accuracy wich is quoted by these authors (0.18%).

Finally, comparisons are provided with data from eight previous compilations or evaluations. For engineering applications such sources are usually accessed first since it is too time consuming to screen original experimental data. Figure 8 illustrates the reliability which may be expected. A strikingly singular trend of deviations is observed for the correlation which was presented by Yaws [33] in terms of the kinematic viscosity. The handbook of Reid et al. [34] recommends this correlation but in terms of the dynamic viscosity. This may be the reason of the slight differences which occur. Overall, these calculated viscosities are too small, particularly below 243.15 and above 303.15 K, and not confirmed by any measurements which were taken into account in this work. The values recommended by Stephan and Lucas [35] (10 points) were generated from the data of Akhundov et al. [24] (4 points) and exhibit consequently the same deviation trend as seen in Fig. 6. They are too high below 323.15 K. Liley et al. [36] used also the data of Akhundov et al. [24] and supplemented them with unspecified information from 296 K down to the triple point. The result of

this synthesis appears to be inconsistent because the deviations from the correlation of the present measurements are negative up to 273.15 K but then reach a maximum of 2.4% at 300 K which is due to the data of Akhundov et al. [24]. The saturated liquid values of Liley et al. [36] are identical to those which are quoted for the 0.1-MPa isobar from 300 K to the normal boiling point.

The other compiled data agree with the present correlation mostly within the estimated accuracy margins. The data of Geller [37], Vargaftik [38], Stephan and Lucas [35], and of Liley et al. [36] join mutually very closely above 333.15 K and show increasing deviations with temperature up to 2.2% at 378.15 K. The best overall agreement is found for the data of the TRC Thermodynamic Tables [39]. They differ considerably from the other compilations above 333.15 K.

Results of comparisons with the remaining experimental data from Refs. 7, 10, and 40–44 are presented in Table II only. The four values of Linebarger [40] and Miller [42] are too low, while the preliminary values by Vieira dos Santos and Nieto de Castro [10] are on the average 5% too high. Otherwise, the deviations are within the estimated accuracy of the present measurements.

5. CONCLUSIONS

The new measurements of the viscosity of liquid toluene which are presented in this work are among the few investigations which cover an extended temperature range and bridge to temperatures below 273.15 K. The preceding comparisons show that the available data are scarce and contradictory in that region. Further measurements appear necessary to resolve the discrepancies. They should be conducted down to the triple-point temperature at 178.15 K.

In general, the measurements agree very well with literature data. One may attribute this in part to the relatively wide accuracy margins which were estimated for the present results. However, the accuracies of other experiments are stated globally and are not reported in such details as here.

Toward the normal boiling point, there is a trend of some literature data to higher viscosities than obtained in this work. Such a difference should not exist because the saturated liquid boundary and the atmospheric pressure isobar meet at that temperature (383.764 K). Presumably, these differences are caused by sample impurities. The sample purity was found in this work to have a significant effect on the viscosity of toluene.

This work is a contribution toward a future standard reference formulation of the viscosity of liquid toluene and presents the most comprehensive data survey so far. The available data provide a considerably accurate knowledge of this property, more accurate than for many other liquids. However, the entire temperature range of liquid toluene has yet to be explored. Further measurements are necessary to complete the data base for a standard reference formulation. Preferably, they should be carried out with instruments other than capillary viscometers since these have been used often to measure toluene. Particularly desirable are studies with the oscillating-body instrument at the University of Trondheim [45] and with the torsionally vibrating crystal viscometers at the National Institute of Standards and Technology in Boulder, which can cover the entire temperature range [46, 47].

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