Viscosity of Toluene and Benzene Under High Pressure[1]

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The viscosity of toluene and benzene was measured at the temperatures of 298.15, 323.15, 348.15, and 373.15 K (ITS-90) from atmospheric pressure up to 200 MPa, by a torsionally vibrating quartz-crystal viscometer, with an estimated accuracy of 0.5%. The experimental data for each temperature were fitted with a Tait-like equation, by a non linear iterative program based on the Marquardt Levenberg method. A comparison between present data and available data from other authors, whenever possible, was made in terms of the dispersion of each data set with respect to the Tait-like equation.

KEY WORDS: benzene; high pressure; quartz-crystal viscometer; toluene; viscosity.

1. INTRODUCTION

This paper presents new data for the viscosity of toluene and benzene at temperatures from 298.15 to 373.15 K (ITS-90) and pressures up to 200 MPa. This set of measurements was made to overlap with existing data on toluene and benzene to check the operating conditions of the viscometer and to try to establish its accuracy [1, 2]. The current interest in toluene as a possible reference substance for viscosity measurements, as discussed in the current projects of the IUPAC Subcommittee on Transport Properties of Fluids, was also an important factor on the selection of this fluid for the first measurements of this new instrument.

2. METHOD

The torsionally vibrating quartz-crystal viscometer, introduced in 1947 by Mason [3], is especially suitable for high-pressure measurements because of its simplicity, small size, absence of macroscopically moving parts, no use of pressure differences, and reduced number of required electrical connections. It consists of a quartz cylinder, 0.05 m high and 0.005 m in diameter, with four very thin ($\approx 3 \times 10^{-7}$ m) gold electrodes deposited on the lateral surface. A sinusoidal wave applied to the electrodes produces a torsional vibration of the same frequency as the excitation wave, damped by the fluid around the crystal. The amount of damping is measured by the change in the electrical impedance of the crystal and reflects the product *viscosity · density* of the surrounding fluid. The torsional wave is heavily damped, and completely extinguished a few micrometers away from the crystal's surface, so that a thin layer of fluid around the transducer, about 0.004 m thick, is sufficient to allow the measurement of the fluid viscosity.

The working equation,

$$\eta = \frac{\pi f}{\rho} \left[\frac{M}{S} \left(\frac{\Delta f}{f} - \frac{\Delta f_0}{f_0} \right) \right]^2 \tag{1}$$

was established semiempirically by Welber and Quimby [4] and relates the resonance frequency, f, and bandwidth, Δf, of the resonance curve of the crystal when vibrating in the fluid to the same values when in vacuum, f_0 and Δf_0, and the quartz-crystal mass, M, and total surface area, S, to the fluid density, ρ, and viscosity, η. Experimental determinations consist of measuring the transducer electrical impedance as a function of excitation frequency, for a frequency range of about 1 kHz around the fundamental torsional vibration frequency. The electrical properties used are conductance and capacitance and curves like the ones presented in Fig. 1 have been obtained for any fluid.

The (M/S) term was calculated for each temperature and pressure from measurements of the quartz crystal dimensions at 293.15 K, published values for quartz and gold densities at 293.15 K and 298.15 K, and the best available estimates for quartz and gold linear and volumetric temperature and pressure coefficients. The dependence of the quartz electrical properties on temperature and pressure was estimated but not taken in account due to their small influence on the measured properties. The strong anisotropy of quartz [5] had to be considered because of the wide temperature range
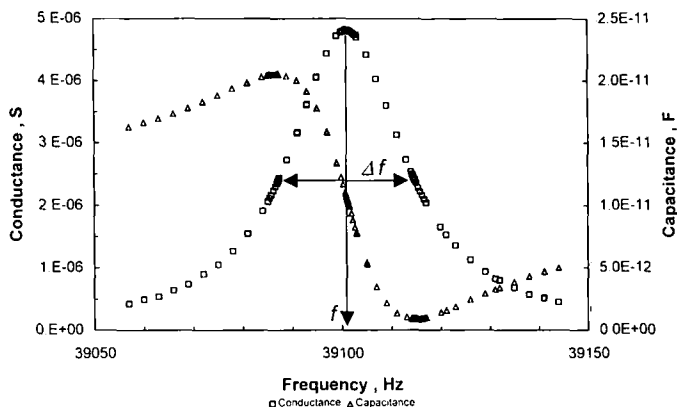
Fig. 1. Resonance curve for the torsional vibrating quartz-crystal in toluene (298.15 K, P_{atm}).

covered in this work: at the highest temperatures and/or pressures, the transducer cross section is significantly different from the circle verified at 298.15 K.

The residual damping of the transducer, $\Delta f_0/f_0$, was not determined by vacuum measurements as used with other instruments of the same kind, because several determinations made it clear that in vacuum we cannot measure the quartz crystal temperature, and the applied power (to promote the torsional oscillations) has no way of being dissipated to the surroundings so as to maintain the reference temperature for the determination. So we used a fluid around the crystal to establish the thermal equilibrium with the cell and the thermostatic bath. As a consequence, we used the fluid viscosity, measured with another viscometer, to calculate the residual damping of the transducer. The fluid could be a gas but a liquid provides better thermal equilibrium, so toluene was used at atmospheric pressure, for each of the experimental temperatures. An average of the best available data for the viscosity of toluene with an estimated uncertainty better than 0.5% was used [1]. As the damping factor does not contribute to Eq. (1) by more than 6%, this procedure contributes to the uncertainty in the viscosity determination less than 0.03%. No contribution from pressure to this term was considered [1]. This kind of problem in establishing the residual damping of an oscillator is common, has been reported by van der Gulik [6] and Assael et al. [7] regarding vibrating-wire viscometers and Diller [8] and Kashiwagi et al. [9] in relation to torsionally vibrating quartz-crystal viscometers.

The resonance frequency and bandwidth, f and Δf, were obtained by fitting the experimental conductance of the quartz crystal as a function of frequency to a Lorentzian distribution function, as shown in Eq. (2).

$$G(f_i) = \frac{A_1}{\pi} \frac{(\Delta f/2)}{[(f_i - f)^2 + (\Delta f/2)^2]} \tag{2}$$

where $G(f_i)$ is the electrical conductance at frequency f_i, and A_1 is just a normalization factor whose physical meaning is not relevant to the fit.

The density of toluene and benzene as a function of pressure was obtained from Kashiwagi et al. [10, 11], whose correlations were considered suitable for the pressure range covered by this work. Kashiwagi et al. [10] presents a Tait equation which allows the calculation of toluene density for any temperature (IPTS-68) between 298.15 and 373.15 K for pressures up to 200 MPa. However, Kashiwagi et al. [11] present polynomial correlations of density as a function of pressure only for the temperatures they authors used. To obtain benzene density for the temperatures and pressures in this work, a Tait equation, identical in form to the one used for toluene, for temperatures as defined by IPTS-68, was established based on a large amount of data generated from the correlations in Kashiwagi et al. [11]. Densities for toluene and benzene were calculated from the experimental temperatures in this work (ITS-90), converted to their IPTS-68 equivalent values by the equations provided by Goldberg and Weir [12].

3. EXPERIMENTAL PROCEDURE

Toluene and benzene, both p.a. from Merck, were purified as previously described [1, 13], and their purity checked by GC and GC-MS; the results are presented in Table I. The high-pressure viscosimetric cell uses a metallic bellow to isolate the fluid in test from the hydraulic oil used in the pressure line and is described in Ref. 14.

Table I. Purity of Toluene and Benzene

Fluid	Purity (%)	Estimated water content (ppm)
Benzene	>99.99	<0.10
Toluene	>99.99	<0.10

The experimental apparatus, with the exception of the hydraulic pump operation, is completely automated, all measuring instruments connected to a computer through an IEEE-488 interface. A specially built multiplexer and temperature-control system allow the use of just one digital multimeter to measure temperature, pressure, and resistance standards every few seconds, so as to maintain the ultimate stability require by this instrument because of the sensitivity of quartz to temperature and pressure effects. One viscosity measurement takes about 2–3 min to allow for very stable operation of the quartz crystal, although it could be made in a period as short as 30 s. A general description of the viscosity apparatus prior to automation was published previously [13]; a scheme of the present one is presented in Fig. 2.

All measurements were made with calibrated sensors and instruments, in terms of ITS-90 and Ω-90, and care has been taken to maintain the highest possible accuracy at all stages. Temperature measurements were made on the outside of the high-pressure vessel, using 2 PRT, under conditions such that preliminary tests proved that no temperature difference existed between the inside and the outside of the vessel. The temperature was measured with a resolution of 0.1 mK and an accuracy of 10 mK. The pressure was measured inside the high-pressure vessel with a Manganin resistance gauge, on the outside of the viscosimetric cell, under similar provisions, with a resolution of 0.04 MPa and an accuracy of 0.4 MPa.

The experimental data for the different temperatures as a function of pressure are presented in Tables II and III, while Figs. 3 and 4 show the plots of viscosity as a function of pressure.
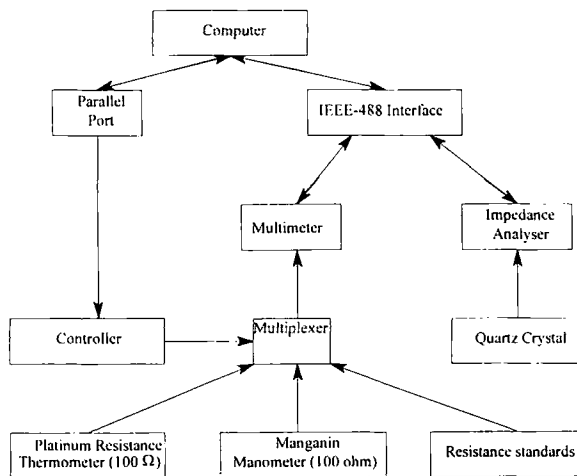

Fig. 2. Data acquisition system.

Table II. Viscosity of Toluene

Pressure (MPa)	Viscosity × density (kg · m^{-1} · s^{-1})	Density (kg · m^{-3})	Viscosity (Pa · s)	Number of data points
		$T = 298.15$ K		
0.1	0.4786	862.50	0.0005549	10
23.9	0.5888	879.84	0.000669	4
47.7	0.7073	894.57	0.000791	6
74.7	0.8637	909.14	0.000950	3
100.7	1.0250	921.53	0.001112	11
126.4	1.2104	932.33	0.001298	3
152.3	1.4232	942.68	0.001510	4
176.0	1.6315	951.24	0.001715	5
203.0	1.8704	960.33	0.001948	6
		$T = 323.15$ K		
0.1	0.3536	838.90	0.0004215	4
25.3	0.4399	859.78	0.000512	6
50.5	0.5297	876.95	0.000604	5
76.8	0.6362	892.33	0.000713	4
100.2	0.7364	904.37	0.000814	3
126.7	0.8591	916.55	0.000937	5
152.0	0.9846	927.12	0.001062	5
177.2	1.1270	936.78	0.001203	3
203.0	1.2890	945.92	0.001363	4
		$T = 348.15$ K		
0.1	0.2709	814.78	0.0003325	6
27.0	0.3470	840.19	0.000413	7
54.7	0.4300	860.84	0.000499	4
78.5	0.5019	875.78	0.000573	4
106.0	0.5899	890.75	0.000662	5
128.3	0.6743	901.63	0.000748	6
156.6	0.7715	914.00	0.000844	7
180.4	0.8700	923.53	0.000942	4
207.2	0.9789	933.44	0.001049	5
		$T = 348.15$ K		
0.1	0.2126	790.13	0.0002691	7
30.4	0.2765	822.50	0.000336	3
55.7	0.3497	843.09	0.000415	5
78.0	0.4093	858.29	0.000477	4

Table III. Viscosity of Benzene

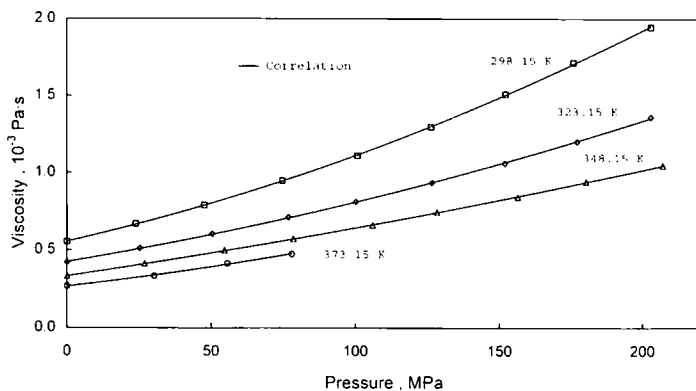| Pressure (MPa)	Viscosity × density (kg·m^{-1}·s^{-1})	Density (kg·m^{-3})	Viscosity (Pa·s)	Number of data points
		$T = 298.15$ K		
0.1	0.5302	873.66	0.000607	52
15.5	0.6032	885.73	0.000681	3
25.3	0.6661	892.68	0.000746	3
32.5	0.7044	897.51	0.000785	4
41.5	0.7569	903.27	0.000838	5
50.9	0.8222	908.94	0.000905	3
61.7	0.9007	915.10	0.000984	4
71.7	0.9849	920.50	0.001070	2
75.9	1.0174	922.69	0.001103	2
76.6	1.0218	923.01	0.001107	4
77.7	1.0321	923.57	0.001117	6
		$T = 323.15$ K		
0.1	0.3748	846.73	0.000443	11
24.6	0.4718	868.36	0.000543	6
50.9	0.5887	887.21	0.000664	4
51.2	0.5898	887.41	0.000665	4
77.2	0.7155	903.12	0.000792	4
101.6	0.8426	916.04	0.000920	5
127.3	0.9959	928.17	0.001073	5
151.0	1.1502	938.36	0.001226	4
168.9	1.2915	945.46	0.001366	4
		$T = 348.15$ K		
0.10	0.2616	819.42	0.000319	4
25.9	0.3406	846.00	0.000403	3
27.1	0.3484	847.12	0.000416	3
51.2	0.4352	866.47	0.000502	4
77.2	0.5244	883.88	0.000593	4
104.4	0.6301	899.50	0.000701	4
127.4	0.7264	911.17	0.000797	5
152.1	0.8399	922.50	0.000911	1
152.3	0.8421	922.57	0.000913	4
177.6	0.9651	933.14	0.001034	2

Fig. 3. Experimental data points and fitted equation for toluene isotherms.

4. CORRELATION

The curves in Figs. 3 and 4 represent values calculated from a fit to Eq. (3),

$$\ln\left(\frac{\eta}{\eta_0}\right) = E \ln\left(\frac{D+P}{D+P_0}\right) \tag{3}$$

where η_0 is the viscosity of the liquid at pressure $P_0 = 0.1$ MPa. The values of the parameters η_0, E, and D for toluene and benzene are presented in Tables IV and V.
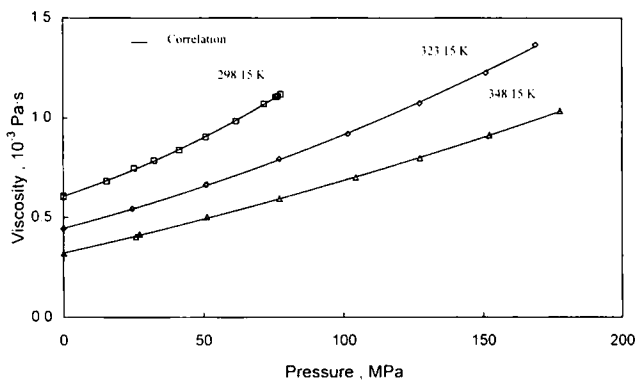

Fig. 4. Experimental data points and fitted equation for benzene
isotherms.

Table IV. Parameters of Eq. (3) for Toluene

Temperature (ITS-90) (K)	η_0 (μPa·s)	E	D (MPa)	Number of data points
298.15	553.5	2.6 ± 0.3	326.146 ± 0.002	52
323.15	422.1	2.0 ± 0.4	259.074 ± 0.002	39
348.15	337.5	1.4 ± 0.5	168.598 ± 0.003	49
373.15	270.0	4.5 ± 0.08	569.693 ± 0.0006	16

Measurements of viscosity have been performed at 298.15, 323.15, 348.15, and 373.15 K (ITS-90) and pressures up to 200 MPa. The experimental data for the viscosity obtained for each of the fluids were fitted to a Tait-like equation, Eq. (3), in terms of pressure. The maximum deviation of the experimental viscosity data from Eq. (3) does not exceed 1%. The highest viscosities measured for each of the fluids were those corresponding to the highest pressures: 1.95 mPa·s for toluene at 203 MPa and 298.15 K and 1.37 mPa·s for benzene at 170 MPa and 323.15 K.

A Tait-like equation for the viscosity is rather inadequate for large ranges of pressure because of the exponential dependence of viscosity on pressure, and does not have any physical meaning as it does for the density dependence on pressure, where it originated. However, we have not found another correlating equation as simple to use that could provide to same degree of fit to the experimental data. Work is in progress to establish a fit of the viscosity as a function of temperature and pressure, of a different kind, yet simple enough to be easily calculated.

Table V. Parameters of Eq. (3) for Benzene

Temperature (ITS-90) (K)	η_0 (μPa·s)	E	D (MPa)	Number of data points
298.15	602.2	8.69 ± 0.04	1052.5658 ± 0.0003	88
323.15	442.7	2.2 ± 0.3	253.622 ± 0.002	46
348.15	319.2	1.5 ± 0.5	147.812 ± 0.004	34

5. DISCUSSION

Comparisons with other authors were made in terms of deviations to our fitting Eq. (3) for each temperature of each fluid and are grouped for toluene in Fig. 5 and for benzene in Fig. 6. Although no experimental data points were measured at pressures over 203 MPa, the comparison was extended to around 300 MPa to see if Eq. (3) could prove to have any predictive value outside of its definition range. Figures 5 and 6 prove that this is not the case: Eq. (3) should be used just for interpolation inside its definition range.

Other data have been obtained with different kinds of viscometers such as oscillating disk [15], falling body [16–19], vibrating wire [20, 21] and also by other torsionally vibrating quartz-crystal viscometers [9, 22].

A discussion of the comparisons between the present data and those from different authors for toluene has been presented elsewhere [13] and we refer the reader to it. Essentially that discussion and Fig. 5 show a good agreement within the mutual uncertainty between the present data and data obtained by other authors, especially with vibrating-wire or oscillating-disk viscometers.

For benzene, data have been obtained by Collings and McLaughlin [22] at 303, 313, and 323 K and pressures up to 175 MPa, by Isdale and Spence [18] at temperatures between 298 and 373 K and pressures up to 110 MPa, by Parkhurst and Jonas [19] between 303 and 433 K and pressures up to 400 MPa, and by Kashiwagi and Makita [9] from 298.15
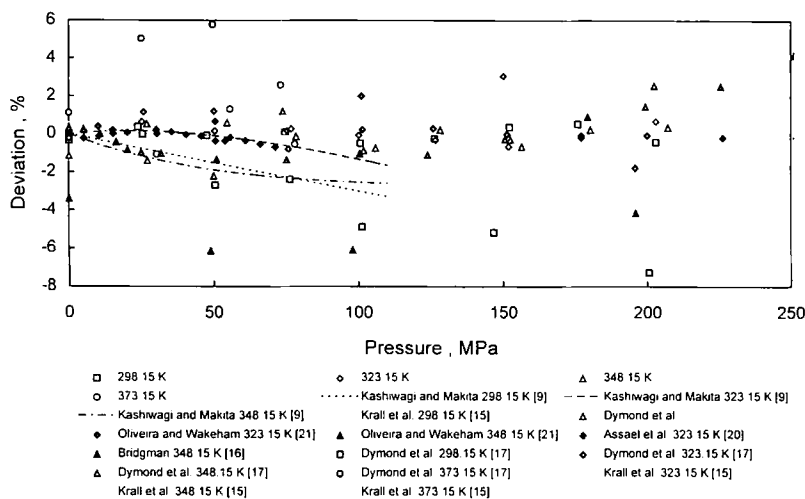

Fig. 5. Deviations of existing viscosity data for toluene from the fit with parameters in Table IV.
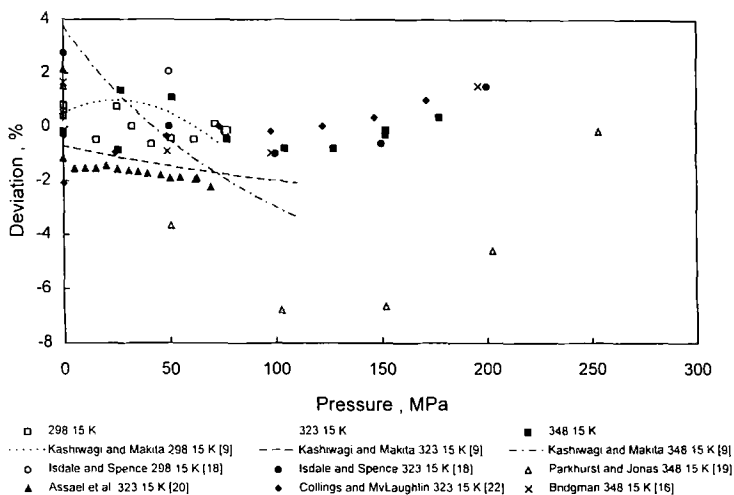
Fig. 6.   Deviations of existing viscosity data for benzene from the fit with
parameters in Table V.

to 348.15 K and pressures up to 110 MPa. Comparisons are shown in
Fig. 6. At 298.15 K the data of Kashiwagi and Makita [9] and of Isdale
and Spence [18] agree with the present data within their mutual uncer-
tainty. These authors have used commercial benzene without further
purification. For 323.15 K there is also agreement within their mutual
uncertainty with the data of Refs. 9 and 22, although these last authors
show a divergence increasing with pressure. The data of Assael et al. [20]
show a systematic deviation between −1.5 and −2.2%, with a trend
similar to the data of Kashiwagi and Makita [9]. These authors have also
used commercial benzene without further purification, while Collings and
McLaughlin [22] did purify benzene.

At 348.15 K the values of Isdale and Spence [18] and Bridgman [16]
agree with the present data, an agreement also found with the data of
Kashiwagi and Makita [9] for pressures up to 75 MPa. However, the
pressure coefficient of viscosity is very different from what other authors
and this work show. The values of Parkhurst and Jonas [19] deviate
significantly (up to −7%) from the present results.

6. CONCLUSIONS

The comparison of the data obtained with a torsionally vibrating
quartz-crystal viscometer for benzene in this work with the data obtained

by other laboratories using the same or another type of viscometer, covering viscosities between $320\,\mu\text{Pa}\cdot\text{s}$ and $1.4\,\text{mPa}\cdot\text{s}$, supports the proposed accuracy of 0.5% and confirms the conclusions obtained previously for toluene [13].

New data for the viscosity of toluene and benzene at 298.15, 323.15, 348.15, and 373.15 K (ITS-90) at pressures up to 200 MPa obtained with a torsionally quartz-crystal viscometer have been presented. The accuracy of the data is estimated to be 0.5%.

Without further refinement of the method's theory, it is not expected to obtain further improvements in the quality of the measurements obtained with the torsionally vibrating quartz-crystal viscometer. We hope in the future to contribute to the solution of this problem.

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