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High-Temperature, High-Pressure Viscosities and Densities of Toluene

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Virginia Commonwealth University.

by

Aaron James Rowane Masters of Science Virginia Commonwealth University

Director: Dr. Bernard F. Gupton and Dr. Mark A. M^cHugh Department of Chemical and Life Science Engineering Virginia Commonwealth University Richmond, Virginia May, 2016

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Abstract

High-Temperature, High-Pressure Viscosities and Densities of Toluene

By Aaron James Rowane, M.S.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Virginia Commonwealth University

Virginia Commonwealth University, 2016.

Major Director: Dr. Bernard F. Gupton, and Dr. Mark A. M^cHugh Department of Chemical and Life Science Engineering

High-temperature, high-pressure (HTHP) conditions are exemplified in ultra-deep petroleum reservoirs and can be exhibited within diesel engines. Accurate pure component hydrocarbon data is essential in understanding the overall behavior of petroleum and diesel fuel at these conditions. The present study focuses on the HTHP properties of toluene since this hydrocarbon is frequently used to increase the octane rating of gasoline and toluene occurs naturally in crude oil. In this thesis experimental densities and viscosity are presented to 535 K and 300 MPa extending the database of toluene viscosity data to higher temperature than previous studies. The data is correlated to a Tait-like equation and a Padè approximate in conjunction with a single mapping of the isotherms. Free-volume theory and a superposition of the viscosity in relation to the Leonnard-Jones repulsive force are both used to model the toluene viscosity data. It was found that the data are in good agreement with the available literature data.

Chapter 1 Introduction

The high-temperature, high-pressure (HTHP) conditions exhibited within automobile and diesel engines^{1, 2} and found in ultra-deep petroleum reservoirs ³ place a premium on accurately modeling hydrocarbon fluid properties, such as density and viscosity at extreme conditions. The present study focuses on the HTHP properties of toluene since this hydrocarbon is frequently used to increase the octane rating of gasoline 4 and toluene occurs naturally in crude oil 5 . Toluene is also a prime candidate for viscometer calibration since it remains a liquid from 178 to 384 K at atmospheric pressure ⁶. Avgeri and coworkers present a very detailed review and analysis of toluene viscosity data where they note the dearth of available toluene viscosity data at pressures greater than ~50 MPa at temperatures greater than ~ 373 K 7 . The experimental challenges for measuring high-temperature, high-pressure viscosity are evident given the variety of different viscometric techniques reported in the literature, such as the falling body viscometer ⁸⁻¹², vibrating wire viscometer ¹³⁻²¹, quartz-crystal viscometer ^{22, 23}, and the rolling ball viscometer ^{24, 25}. Harris reports toluene viscosity data with a very low uncertainty of $\pm 1\%$ using a falling-body viscometer operated from 255 to 323 K and pressures to 400 MPa⁹. Dymond et al. also push the limits of the falling-body viscometer technique by measuring toluene viscosity data to 373 K and 519 MPa ¹⁰. In a different approach, Oliveira and Wakeham employ a more involved technique, a vibratingwire viscometer, to measure the viscosity of five different liquid hydrocarbons, including toluene, to 348 K and 252 MPa¹⁷. Toluene and benzene viscosities are reported by Vieira dos Santos and Nieto de Castro, who use a vibrating quartz-crystal viscometer to maximum conditions of 348 K and 207 MPa²³. Wilbur and Jonas, utilize a rolling ball viscometer to measure the viscosity of toluene- d_8 , a deuterated isotope of toluene, to a maximum temperature and pressure of 473 K and 350 MPa respectively ²⁵.

As mentioned, the experimental challenges for measuring high-temperature, high-pressure viscosity are evident given the variety of different viscometric techniques reported in the literature, such as the falling body viscometer ⁸⁻¹², vibrating wire viscometer ¹³⁻²¹, quartz-crystal viscometer ^{22, 23}, and the rolling ball viscometer ^{24, 25}. Assael *et al.*²⁶ presents and Kashiwagi and Makita²² describe the operation and construction of the vibrating wire viscometer and crystal-quartz viscometer respectively. Both the vibrating wire and quartz-crystal viscometers require electronics to be housed within the pressure vessel of the system that experiences approximately the same temperature as the sample volume. It has been well established that the reliability of electronics diminishes at high temperature conditions. The falling body and rolling ball viscometers mentioned before are less reliant on electronics for viscosity measurement however, the previously employed systems do not include a window for sample observation and do not have the capability of simultaneous density measurement. The window not only provides the ability to observe sample solidification, but also allows for the observation to ensure that the ball within our system is rolling, not sliding.

In this thesis, toluene viscosity data are measured using a windowed, variable-volume, rolling ball viscometer/densimeter (RBVD) at temperatures from 295 to 535 K and pressure to ~300 MPa. The RBVD allows for simultaneous measurements of density and viscosity. It is important to recognize that this apparatus is manufactured from Inconel 718, which is a high strength, corrosion-resistant, and non-magnetic nickel chromium steel. Inconel 718 is used in the aerospace and petrochemical industry for high temperature applications²⁷ because of its ability to maintain high a tensile strength at high temperatures. Special Metals Corporation reports that

Inconel 718 maintains a tensile strength of 156,000 psi (1,075 MPa) for temperatures to 600°F $(315^{\circ}C)^{28}$. Inconel 718, an austenitic steel, has a permeability of 1.001, which means this metal does not respond to electromagnetic fields and it is feasible, therefore, to use an external magnet to drive a stir bar located in the RBVD. A select amount of experimental toluene density data is measured to demonstrate the accuracy of this apparatus. The toluene viscosity data presented in this thesis demonstrate the ability of the RBVD to obtain reliable data and the toluene viscosity database is extended with original data at temperatures from 373 to 535 K and pressures to 300 MPa. The viscosity data are correlated with two different methods to facilitate the reliable interpolation of data within the ranges of temperatures and pressures investigated in this study and for ease of comparison of toluene viscosity data from the literature. One method is a Tait-like equation that has been used by several other research groups to represent viscosity as function of temperature and pressure ^{19, 22, 23}. In a recent study, Caudwell et al. ²⁹ propose a methodology for calculating the Tait parameters that is applied in the present study. The second method used in this study is the correlation proposed by Harris⁹, who implements a Padé approximation paired with a mapping function, capable of collapsing multiple isotherms onto a single reference isotherm. In addition to these two correlation methods, the Free Volume Theory (FVT) is used to model the experimental viscosity data measured in this study. Here the densities required for FVT calculations are obtained either from experimental data or from predictions using the Perturbed-Chain Statistical Association Fluid Theory (PC-SAFT) equation of state (EoS) ³⁰ that allows for viscosity predictions from a minimum amount of viscosity data.

Chapter 2 Experimental Apparatus and Methods

In this chapter the features of the RBVD are described and the calibration method is demonstrated. In the first section basic specifications are presented for octane and decane that are used as calibration fluids for density and viscosity, respectively. Section 2.2 describes the features and components of the RBVD. Section 2.3 and 2.4 describe the internal volume and viscosity calibrations, respectively.

2.1. Materials

Octane (anhydrous, purity \geq 99 wt. %, CAS: 111-65-9, lot SHBF6351V), and decane (anhydrous, purity \geq 99 wt. %, CAS: 124-18-5, lot SHBG2472V) are obtained from Sigma-Aldrich Corporation and used without further purification.

2.2 Rolling–Ball Viscometer/Densimeter

Figure 1 shows a schematic diagram of the RBVD used in this study. Many of the equipment details of the RBVD are similar to the rolling–ball viscometer used in our previous studies, which are described in detail elsewhere.^{3, 31} Those key similarities and differences are briefly described here. The RBVD body, constructed from Inconel 718, has an inside diameter (ID) of 1.5875 cm and a maximum working volume of approximately 50 cm³ (3D Design and Manufacturing LLC). The ball used here has an outside diameter of 1.5796 cm (Industrial Tectonics Inc.), which is 99.5% of the internal diameter of the RBVD. The ball is also made of

Inconel 718 to minimize the effects of temperature on the clearance between the ball and ID of the viscometer. A borescope is positioned against the window at the front end of the viscometer to confirm that a single fluid phase exits and to verify that the ball continuously rolls without sliding during a measurement. The rolling speed of the ball is determined using a fiber optic, light detection technique³² (sensor: Model R55FVWQ; cables: Model IF23SM900, Banner Engineering Corp.) interfaced to small sapphire windows secured in ports³³ located radially on the viscometer. The sensor is monitored with a computer using a data acquisition program that records the ball roll time $(\pm 0.001 \text{ s})$ between two sets of opposing ports. A pressure transducer (0 to 414 MPa, Model 245-BZS, Viatran Corp., accurate to within \pm 0.41 MPa) measures the system pressure. The internal viscometer temperature is measured at two axial locations with type-K thermocouples (Omega Corp.) calibrated against an immersion thermometer (Fisher Scientific Inc., precision and accuracy to within \pm 0.1 K, recalibrated using methods traceable to NIST standards). For temperatures below 400 K, each location is maintained constant to within \pm 0.1 K and the temperature difference between each location is within ± 0.2 K. At temperatures from 400 to 535 K, each location is maintained constant to within ± 0.3 K and the temperature difference between each location is within ± 0.4 K.



Figure 1. Schematic diagram of the rolling–ball viscometer/densimeter used in this study. T1 and T2 are thermocouples.

2.3 Internal Volume Calibration

The internal cell volume of the RBVD is measured with a linear, variable, differential transformer (LVDT, Schaevitz Corporation, Model 2000 HR) attached to the end of the RBVD apparatus.^{34, 35} The LVDT core moves through the sensor region of the LVDT while the opposite end is connected to the inner surface of a metal bellows (1.72 cm OD, BellowsTech, LLC). Water is pressurized using a high-pressure generator (HIP Inc., Model 37-5.75-60) and is delivered to or removed from the internal volume of the bellows that expands/contracts to increase/decrease system pressure. The cell volume is calibrated using highly accurate n-octane density data reported by Caudwell, *et al.*²⁹ to 473 K and 200 MPa and by NIST³⁶ at temperatures greater than 473 K and

pressures less than 100 MPa. Figure 2 exhibits a plot of the internal cell volume vs. the transducer reading. The calibration is done at 347, 452, and 535 K and 67 pressures from 14 to 195 MPa, which allows for the full linear extension of the bellows. The expanded uncertainty in the reported densities, $U_c(\rho)$, is 0.7% of the value of the density, at a confidence level of 95% with a coverage factor, k = 2.



Figure 2. Relationship between the internal cell volume, V and the transducer reading. Calibration is done with octane at 347, 452, and 535 K and 67 pressures from 14 to 195 MPa.

2.4 Viscosity Calibration

The working equation for determining the calibration constant, K, of a rolling-ball viscometer is

$$K = \frac{\eta}{t \cdot \left(\rho_b - \rho_{fl}\right) \sin \theta} \tag{1}$$

where *K* has units of (cm²•s⁻²), η is viscosity (mPa•s), *t* is the time for the ball to roll between the ports (s), while ρ_b and ρ_{fl} are ball density and fluid density (g•cm⁻³), respectively, and θ is angle of inclination. The viscometer is calibrated over the entire temperature and pressure ranges of interest to account for the influence of high temperature and pressure on the ball diameter and viscometer ID. As described in our earlier work,^{3, 31} the viscometer is calibrated with n-decane viscosity data obtained from NIST,³⁶ which implements a viscosity correlation proposed by Huber, Laesecke, and Xiang.³⁷ Figure 3 exhibits a plot of the calibration constant, K, vs. Pressure, *p* including the linear relationship between the two quantities. The standard uncertainties are u(t) = 0.001 s and $u(\theta) = 0.02^{\circ}$. The expanded uncertainty, $U_c(\eta)$, in the reported viscosities is calculated by applying the law of error propagation to Equation 1 and is equal to 2.0% at a confidence level of 95% with a coverage factor, k = 2.



Figure 3. Viscosity calibration with decane. The relationship between the calibration constant, *K* and pressure, *p* at O - 373.1 K, \Box - 422.7 K, \diamond - 470.5 K, and \triangle - 522.7 K. The data here is for WP, Ball rolling from window to piston, and PW, the ball rolling from piston to window.

Hubbard and Brown³⁸ derived relationships for the Reynolds number, Re, and the resistance factor, f, represented in equations 2 and 3 respectively.

$$\operatorname{Re} = \frac{vd^2}{(D+d)} \frac{\rho_{fl}}{\eta} \tag{2}$$

$$f = \frac{5\pi}{42} g \frac{(D+d)^2}{v^2 d} \frac{\left(\rho_b - \rho_f\right)}{\rho_f} \sin\theta$$
(3)

where D (cm) is the internal diameter of the view cell, d (cm) is the diameter of the ball, v (cm/s) is the velocity of the ball, and g (cm·s⁻²) is the gravitational acceleration. Table 1 lists calibration constants, Re, and f at each temperature and pressure used with decane to calibrate the RBVD. The Reynolds number ranges from 0.5 to ~100 and it increases with increasing temperature. Conversely, the resistance factor ranges from 22,000 to 231,200, and decreases with an increase in temperature. Figure 4 shows a log-log plot of f vs. Re for the calibration data. The data exhibit a linear relationship which establishes laminar flow throughout the calibration process.

<i>p</i> /MPa	$K \cdot 10^4 / \text{cm}^2 \cdot \text{s}^{-2}$	Re	f [.] 10 ⁻⁵	γ·10 ⁻⁴ / s ⁻¹	<i>p</i> /MPa	$K \cdot 10^4$ /cm ² ·s ⁻²	Re	f [.] 10 ⁻⁵	γ·10 ⁻⁴ / s ⁻¹
	<i>T</i> /K =	319.9				<i>T</i> /K =	422.7		
25.9	4.42	5.82	3.00	0.55	20.0	4.08	38.6	0.54	1.37
26.2	4.44	5.94	3.12	0.53	20.0	4.09	37.3	0.52	1.42
26.5	4.97	6.19	4.84	0.42	20.0	4.22	37.2	0.68	1.19
26.5	5.01	5.78	4.78	0.42	20.0	4.36	37.4	0.62	1.27
67.4	5.37	3.28	6.91	0.35	34.9	4.66	28.6	0.92	1.01
67.6	5.46	3.43	6.80	0.35	34.9	4.69	29.0	0.88	1.05
67.8	5.88	3.38	9.32	0.30	35.0	4.71	30.6	0.87	1.06
67.9	5.82	3.42	9.43	0.30	35.0	5.15	28.7	1.09	0.94
103.8	6.30	2.18	11.98	0.26	69.8	5.58	19.1	1.34	0.84
104.1	7.36	2.13	22.64	0.19	69.9	5.58	18.2	1.42	0.79
104.2	4.29	2.21	3.31	0.51	69.9	6.12	19.2	1.64	0.73
104.2	4.27	2.21	3.31	0.51	70.0	6.60	19.8	1.93	0.67
138.5	4.76	1.47	5.26	0.41	70.1	6.55	19.9	1.93	0.67
138.6	4.82	1.50	5.05	0.42	70.1	6.94	18.1	2.08	0.63
138.9	5.22	1.42	7.40	0.34	103.9	4.01	14.6	0.55	1.36
139.2	5.23	1.50	7.23	0.35	103.9	4.04	13.7	0.54	1.37
169.1	5.62	1.05	10.29	0.28	138.2	4.20	11.0	0.67	1.21
169.5	5.61	1.09	9.99	0.29	138.2	4.20	10.3	0.68	1.19

Table 1. Calibration constant, *K*, Reynolds number, *Re*, and Resistance Factor, *f*, for the decane viscosity data used to calibrate the RBVD.

<i>p</i> /MPa	$K \cdot 10^4 / \text{cm}^2 \cdot \text{s}^{-2}$	Re	f·10 ⁻⁵	γ·10 ⁻⁴ / s ⁻¹	<i>p</i> /MPa	$K \cdot 10^4 / \text{cm}^2 \cdot \text{s}^{-2}$	Re	f·10 ⁻⁵	γ·10 ⁻⁴ / s ⁻¹
238.8	6.06	0.51	12.89	0.25	138.3	4.62	10.3	0.98	0.96
240.7	7.02	0.49	23.12	0.19	138.4	4.64	10.4	0.92	1.02
	<i>T</i> /K =	340.7			173.5	4.63	8.2	0.98	0.96
50.4	4.77	6.72	2.49	0.60	173.5	5.09	8.0	1.18	0.88
50.4	4.76	6.78	2.54	0.59	208.0	5.50	6.5	1.45	0.79
50.5	5.00	6.47	3.08	0.53	208.0	5.54	6.4	1.44	0.79
50.6	5.46	6.93	4.16	0.45	208.1	5.99	6.4	1.72	0.71
69.6	5.43	5.33	4.07	0.46	208.2	6.48	6.5	1.98	0.66
69.6	5.42	5.19	4.21	0.44	227.7	6.46	5.7	2.00	0.66
102.6	5.89	3.60	5.32	0.40	227.9	6.77	5.7	2.14	0.63
102.7	6.37	3.64	6.81	0.35		T/K =	470.5		
102.9	6.35	3.72	6.84	0.35	22.2	4.15	62.1	0.31	1.85
103.3	6.73	3.61	9.43	0.29	22.2	4.22	63.3	0.31	1.87
103.4	6.77	3.62	9.12	0.29	23.2	4.36	63.5	0.37	1.69
103.5	4.59	3.54	2.77	0.56	23.3	4.94	62.6	0.47	1.47
138.5	4.63	2.62	2.64	0.58	35.5	5.41	51.6	0.58	1.30
138.6	4.85	2.51	3.27	0.52	35.6	5.38	51.8	0.58	1.31
172.1	5.28	1.89	4.40	0.44	69.2	5.43	35.8	0.59	1.29
172.3	5.30	1.71	4.30	0.45	69.4	5.84	34.2	0.72	1.15
172.5	5.24	1.89	4.31	0.45	104.1	6.24	26.0	0.88	1.01
172.7	5.69	1.82	5.77	0.38	104.2	6.90	26.3	0.95	0.96

204.1 6.14 1.37 7.35 0.34 104.2 6.92 25.9 0.97 0.97 204.7 6.16 1.33 7.81 0.32 104.3 7.18 23.9 1.05 0.92 205.0 6.55 1.31 9.60 0.29 104.3 4.04 24.8 0.33 1.32 205.4 6.53 1.30 9.20 0.30 104.3 4.16 24.8 0.32 1.42 $T/K =$ 373.1 139.3 4.34 19.5 0.37 1.62	,
204.76.161.337.810.32104.37.1823.91.050.9205.06.551.319.600.29104.34.0424.80.331.3205.46.531.309.200.30104.34.1624.80.321.3 $T/K =$ 373.1139.34.3419.50.371.6	0.94
205.0 6.55 1.31 9.60 0.29 104.3 4.04 24.8 0.33 1.32 205.4 6.53 1.30 9.20 0.30 104.3 4.16 24.8 0.32 1.32 $T/K =$ 373.1 139.3 4.34 19.5 0.37 1.62	0.90
205.4 6.53 1.30 9.20 0.30 104.3 4.16 24.8 0.32 1.30 $T/K =$ 373.1 139.3 4.34 19.5 0.37 1.60	1.82
T/K = 373.1 139.3 4.34 19.5 0.37 1.0	1.85
	1.69
20.7 4.27 18.89 1.02 0.97 139.5 4.80 18.8 0.50 1.4	1.41
20.7 4.30 19.52 0.98 1.00 173.1 5.28 15.0 0.65 1.	1.19
20.7 4.40 18.91 1.23 0.88 173.4 5.30 15.0 0.63 1.2	1.24
20.7 4.84 19.25 1.69 0.75 207.1 5.30 12.5 0.63 1.2	1.24
20.7 4.86 19.11 1.70 0.74 207.3 5.78 12.3 0.76 1.	1.11
35.1 5.14 15.20 2.39 0.61 207.3 6.23 12.3 0.88 1.0	1.01
35.1 5.31 15.39 2.22 0.64 207.4 6.73 12.3 0.99 0.9	0.95
69.1 5.30 9.82 2.26 0.63 227.9 6.72 10.9 0.99 0.93	0.95
69.1 5.79 10.06 2.80 0.56 228.1 7.03 11.0 1.06 0.9	0.91
69.1 5.70 9.97 2.93 0.55 $T/K = 522.7$	
69.1 6.18 9.78 3.55 0.49 23.2 3.85 97.1 0.22 2.3	2.31
104.0 6.07 6.82 3.65 0.49 23.2 4.18 98.4 0.25 2.0	2.08
104.0 6.68 6.70 4.30 0.45 35.1 4.59 81.9 0.33 1.7	1.79
104.1 6.73 6.82 4.28 0.44 35.1 5.30 79.0 0.39 1.4	1.58
104.1 6.70 6.97 4.27 0.45 69.8 5.43 53.8 0.37 1.0	1.62
104.1 4.19 6.85 1.04 0.97 69.8 5.40 53.6 0.38 1.0	1.60

<i>p</i> /MPa	$K \cdot 10^4 / \text{cm}^2 \cdot \text{s}^{-2}$	Re	f·10 ⁻⁵	γ·10 ⁻⁴ / s ⁻¹	<i>p</i> /MPa	$K \cdot 10^4 / \text{cm}^2 \cdot \text{s}^{-2}$	Re	f·10 ⁻⁵	γ·10 ⁻⁴ / s ⁻¹
104.1	4.20	6.84	1.02	0.99	103.4	5.90	39.4	0.44	1.48
138.8	4.18	5.08	1.03	0.98	103.4	6.21	39.7	0.51	1.37
138.8	4.37	4.95	1.22	0.89	103.5	6.75	39.4	0.58	1.26
138.8	4.75	4.98	1.76	0.73	103.6	6.87	40.6	0.56	1.29
138.8	4.77	4.92	1.76	0.73	103.6	7.25	39.4	0.61	1.19
138.9	5.19	4.97	2.32	0.63	103.7	7.12	40.0	0.62	1.20
172.9	5.19	3.75	2.32	0.63	138.3	3.99	31.8	0.21	2.34
172.9	5.22	3.73	2.30	0.63	138.3	4.22	30.7	0.24	2.15
172.9	5.64	3.71	2.94	0.55	172.8	4.79	25.8	0.32	1.79
207.6	5.66	2.88	2.92	0.55	172.8	5.25	25.0	0.40	1.57
207.6	5.65	2.85	2.93	0.55	207.2	5.27	21.0	0.40	1.58
207.6	6.07	2.86	3.63	0.49	207.2	5.28	20.6	0.40	1.57
207.6	6.56	2.84	4.42	0.44	207.3	5.76	20.6	0.46	1.43
207.6	6.59	2.79	4.47	0.43	207.3	6.27	21.5	0.52	1.33
					227.5	6.76	18.6	0.59	1.24
					227.6	6.78	18.7	0.59	1.24
					227.6	7.10	18.7	0.62	1.20
					227.6	7.09	18.7	0.62	1.20



Figure 4. Relationship between the resistance factor, *f* and the Reynolds number, Re. O - 319.9 K, \Box - 340.7 K, \triangle - 373.1 K, \diamondsuit - 422.7, ∇ - 470.5 K, and \triangle - 522.7 K.

Šesták and Ambros³⁹ derived the following expression for the average shear rate of the rolling ball viscometer,

$$\overline{\dot{\gamma}} = 2.4v \frac{D}{\left(D-d\right)^2} \tag{4}$$

where the variables are previously defined in equations 2 and 3. In order to obtain useful information the shear rate must be varied at a fixed temperature and pressure. This can be done most easily by varying the angle of inclination however, this method is indirect and not as easily controlled as in other rheometers. The range of the shear rate provides insight on the internal consistency between the calibration and data acquisition. The range of shear rates for the calibration in this study was 1891 - 23360 s⁻¹.

Chapter 3 Toluene Study

The following chapter describes a study using toluene to demonstrate the validity of the RBVD and to present original toluene viscosity data at temperatures greater than 373K and pressures to 300 MPa. The first section presents basic information pertaining to toluene. Section 3.2 presents toluene density data measured in this study and provides a comparison to literature data. Section 3.3 presents the experimental toluene viscosity data obtained in this study with subsequent sections on correlational work and Free Volume Theory.

3.1 Materials

Toluene (CHROMASOLV Plus grade, purity \geq 99.9 wt.%, CAS: 108-88-3, lot SHBC8894V) is obtained from Sigma-Aldrich Corporation and used as received.

3.2 Toluene density

Table 2 lists density data for toluene obtained in this study at 347, 452, and 535 K. Although the density data are listed in an increasing order of pressure, the experimental density data are obtained in a non-monotonic manner to minimize any potential experimental artifacts. Figure 5 shows a deviation plot for these data relative to NIST data.³⁶ The accuracy of the density data is characterized by absolute average deviation (AAD) defined in Equation 5,

.

$$AAD / \% = 100 \cdot \frac{1}{N} \sum_{i=1}^{N} \left| \frac{x_{i,\exp} - x_{i,cal}}{x_{i,\exp}} \right|$$
(5)

where *N* is the number of data points, $x_{i,exp}$ represents an experimental data point, and $x_{i,cal}$ represents a calculated or literature data point. The *AAD* thus obtained is within ± 0.25% signifying good agreement with toluene density data reported by NIST. Figure 5 shows the density data are distributed uniformly about zero deviation, and all of the data are well within the experimental uncertainty of ± 0.7%.

<i>p/</i> MPa	$\rho/\mathrm{kg}\mathrm{\cdot m}^{-3}$	<i>p</i> /MPa	$\rho/\text{kg} \cdot \text{m}^{-3}$	p/MPa	$\rho/\mathrm{kg}\mathrm{\cdot m}^{-3}$	p/MPa	$\rho/\text{kg} \cdot \text{m}^{-3}$
	T/K =	347.4			T/K =	534.9	
8.6	820.0	138.8	907.3	37.4	697.2	124.0	794.7
8.7	820.1	138.9	907.3	37.4	696.5	124.1	793.8
34.7	844.5	158.7	916.5	51.6	721.5	168.8	818.8
34.8	844.5	158.8	916.5	51.8	720.7	168.9	818.8
80.8	876.5	180.2	925.6	68.3	743.2	169.1	820.6
81.0	876.5	180.3	925.6	68.3	742.4	209.2	843.1
104.9	890.3	180.3	925.6	88.5	764.8	209.4	844.9
105.0	890.3	180.4	925.6	88.5	764.8	234.4	859.2
138.6	907.3	202.1	934.3	88.6	764.0	254.3	865.3
138.6	907.3	202.3	934.3	88.6	764.0	254.6	867.2
	T/K =	451.9		104.3	778.9	276.3	877.0
18.0	737.1	114.9	833.5	104.4	778.1	277.5	878.3
42.0	771.0	131.7	840.7				

Table 2. Toluene density, ρ , obtained in this study at temperatures of 347.4, 451.9, and 534.9 K.

p/MPa	$ ho/kg \cdot m^{-3}$	<i>p/</i> MPa	$ ho/kg \cdot m^{-3}$	p/MPa	$ ho/kg \cdot m^{-3}$	<i>p</i> /MPa	$\rho/\mathrm{kg}\cdot\mathrm{m}^{-3}$
42.2	771.2	131.9	840.0				
69.3	798.4	172.6	864.0				
69.3	798.6	172.7	863.4				
84.1	811.0	213.8	884.2				
84.2	811.3	214.0	883.6				
98.0	821.6	235.6	895.7				
98.1	821.6	255.9	905.1				
98.1	821.8	256.2	904.4				
111.2	826.2	276.2	911.8				
111.4	825.6	276.8	912.7				
114.8	833.2	276.8	912.0				



Figure 5. Deviation plot of experimental toluene density (ρ_{exp}) obtained in this study to that obtained from NIST³⁶ (ρ_{NIST}). \triangle - 347 K, \bigcirc - 452 K, and \square - 535 K. Note that at virtually every pressure multiple data points superpose.

3.3 Toluene viscosity

Table 3 lists the toluene viscosity data obtained in this study from 296 to 535 K and pressures to nearly 300 MPa, and the associated Reynolds numbers, resistance factors, and shear rates for each measurment . For convenience, the fluid density needed for calculating the viscosity using Equation 1 is obtained from NIST. Figure 6 shows experimental toluene viscosity as a function of pressure at eight different temperatures. The data for a given isotherm are fit to a quadratic function in pressure and that function is used subsequently when comparisons to literature data are made to minimize the experimental fluctuations in the data. The fit of the curves are characterized using Equations 5 to 7, which represent the *AAD*, the maximum deviation (D_{max}), and the *bias*, respectively. Table 4 lists the *AAD*, the standard deviation of the absolute deviations (*SD*), D_{max} , and *bias* for each smoothing curve. Note that the *AAD* for each curve is well within the experimental uncertainty of 2.0% of the data and the *SD* is less then 1.2% for data at each isotherm. The *bias* values shown in Table 4 establish that the deviations are evenly distributed about zero.

p/MPa	η/mPa∙s	Re	f·10 ⁻⁵	$\gamma \cdot 10^{-4} \ /s^{-1}$	<i>p</i> /MPa	η/mPa⋅s	Re	f ⁻¹⁰⁻⁵	γ ·10 ⁻⁴ /s ⁻¹
	T/K=	295.9				T/K=	421.5		
14.7	0.626	11.4	1.80	0.63	9.6	0.221	83.6	0.25	1.87
14.7	0.616	12.4	1.65	0.67	9.7	0.219	86.2	0.24	1.91
36.1	0.734	9.3	2.06	0.59	21.1	0.243	72.4	0.28	1.75
36.2	0.721	9.5	2.01	0.59	21.2	0.240	73.6	0.27	1.76
55.3	0.845	7.7	2.34	0.55	35.4	0.266	63.6	0.30	1.65
55.3	0.839	7.2	2.51	0.51	35.4	0.263	65.8	0.29	1.69
75.8	0.953	6.4	2.65	0.51	48.8	0.296	54.4	0.34	1.55
75.9	0.971	6.1	2.77	0.50	48.9	0.291	57.2	0.32	1.60
90.9	1.043	5.7	2.83	0.50	69.8	0.337	48.1	0.36	1.52
110.9	1.193	4.7	3.30	0.46	69.8	0.334	47.1	0.37	1.48
110.9	1.216	4.3	3.58	0.43	86.5	0.368	41.8	0.39	1.42
111.5	1.214	4.4	3.51	0.44	86.5	0.368	41.2	0.40	1.40
111.6	1.191	4.6	3.33	0.45	104.7	0.400	38.9	0.40	1.41
131.0	1.351	3.8	3.87	0.42	104.7	0.407	37.0	0.42	1.37
131.0	1.404	3.5	4.16	0.41	120.2	0.435	34.9	0.43	1.36
152.9	1.521	3.1	4.50	0.38	120.2	0.428	35.7	0.42	1.37
153.0	1.542	3.1	4.44	0.39	131.4	0.452	33.9	0.43	1.37

Table 3. Toluene viscosity data obtained in this study at 295.9, 323.5, 347.4, 392.5, 421.5, 451.9, 500.3, and 534.9 K.

T/K= 323.5 131.4 0.452 32.3 0.45 21.0 0.488 18.5 1.09 0.81 138.0 0.475 30.8 0.47	1.30 1.30 1.31 1.25
21.0 0.488 18.5 1.09 0.81 138.0 0.475 30.8 0.47	1.30 1.31 1.25
	1.31 1.25
21.0 0.478 20.6 0.97 0.89 138.0 0.466 31.8 0.45	1.25
30.9 0.552 15.6 1.25 0.77 158.6 0.501 28.4 0.48	
30.9 0.522 18.0 1.08 0.84 158.6 0.509 27.9 0.49	1.25
55.7 0.623 13.7 1.31 0.75 173.5 0.546 24.9 0.53	1.18
55.7 0.625 14.0 1.29 0.76 175.4 0.535 26.0 0.51	1.21
55.7 0.637 12.9 1.39 0.72 186.2 0.566 23.9 0.54	1.17
55.8 0.648 12.3 1.46 0.70 186.3 0.563 24.3 0.53	1.18
76.3 0.722 9.9 1.70 0.62 194.0 0.585 24.1 0.52	1.22
76.4 0.732 9.9 1.71 0.62 194.1 0.576 24.4 0.52	1.21
108.8 0.872 7.8 1.97 0.58 213.6 0.627 20.9 0.58	1.12
108.9 0.873 7.6 2.02 0.56 213.6 0.621 21.1 0.58	1.12
131.3 0.951 7.6 1.91 0.61 235.0 0.672 19.7 0.59	1.12
131.4 0.973 7.3 2.00 0.59 235.1 0.672 19.5 0.59	1.11
147.1 1.054 6.5 2.16 0.57 255.0 0.723 17.5 0.64	1.06
147.2 1.034 6.5 2.15 0.56 255.4 0.714 18.0 0.62	1.08
151.8 1.087 5.5 2.52 0.50 270.9 0.754 16.4 0.66	1.03
151.9 1.070 5.9 2.34 0.53 271.2 0.757 16.2 0.67	1.02
151.9 1.101 4.9 2.82 0.45 292.6 0.802 15.7 0.66	1.04
152.0 1.052 5.5 2.50 0.48 294.5 0.811 15.4 0.68	1.03

p/MPa	η/mPa∙s	Re	f [.] 10 ⁻⁵	γ ·10 ⁻⁴ /s ⁻¹	<i>p</i> /MPa	η/mPa∙s	Re	f·10 ⁻⁵	γ ·10 ⁻⁴ /s ⁻¹
180.2	1.222	5.1	2.54	0.51		T/K=	451.8		
180.2	1.239	5.1	2.54	0.52	18.0	0.206	95.5	0.21	2.05
200.4	1.357	4.5	2.75	0.50	18.1	0.201	100.0	0.20	2.09
200.4	1.354	4.4	2.81	0.49	42.0	0.246	76.9	0.24	1.88
217.2	1.459	4.1	2.93	0.49	42.2	0.246	75.2	0.25	1.85
217.4	1.484	3.7	3.21	0.45	42.2	0.255	70.0	0.27	1.78
220.4	1.548	3.5	3.38	0.44	69.3	0.287	61.2	0.28	1.69
220.6	1.483	3.8	3.13	0.46	69.3	0.298	57.2	0.30	1.64
	T/K=	347.4	`		84.1	0.311	53.5	0.31	1.58
8.6	0.353	36.3	0.58	1.19	84.2	0.314	53.8	0.31	1.60
8.7	0.347	34.3	0.61	1.11	98.0	0.332	51.9	0.31	1.61
34.7	0.431	27.0	0.71	1.06	98.1	0.333	52.3	0.30	1.63
34.8	0.424	26.8	0.72	1.03	98.1	0.329	50.2	0.32	1.54
80.8	0.592	15.9	1.05	0.82	111.2	0.357	46.5	0.33	1.53
81.0	0.584	15.9	1.05	0.81	111.4	0.355	48.9	0.31	1.60
104.9	0.659	14.2	1.10	0.80	114.8	0.363	45.2	0.34	1.51
105.0	0.670	13.8	1.13	0.80	114.9	0.367	43.7	0.35	1.48
138.6	0.786	11.0	1.31	0.73	131.7	0.394	42.1	0.35	1.51
138.6	0.798	10.4	1.37	0.71	131.8	0.395	41.2	0.35	1.48
138.8	0.805	10.3	1.38	0.70	131.9	0.402	41.0	0.36	1.50
138.9	0.792	11.0	1.30	0.74	172.6	0.461	33.1	0.40	1.35

p/MPa	η/mPa∙s	Re	f ⁻ 10 ⁻⁵	γ ·10 ⁻⁴ /s ⁻¹	p/MPa	η/mPa∙s	Re	f·10 ⁻⁵	γ·10 ⁻⁴ /s ⁻¹
158.7	0.862	10.0	1.37	0.72	172.7	0.461	34.6	0.38	1.42
158.8	0.876	9.1	1.49	0.67	213.8	0.531	28.5	0.42	1.32
180.2	0.967	8.2	1.59	0.66	214.0	0.542	28.1	0.43	1.33
180.3	0.971	8.1	1.61	0.65	235.6	0.589	24.7	0.47	1.25
180.3	0.944	8.8	1.48	0.69	255.9	0.606	24.0	0.46	1.24
180.4	0.947	8.8	1.48	0.69	256.2	0.610	23.4	0.48	1.22
202.1	1.056	7.6	1.64	0.66	276.2	0.647	22.0	0.49	1.21
202.3	1.047	7.6	1.62	0.66	276.8	0.643	22.8	0.47	1.24
	T/K=	392.5			276.8	0.643	22.8	0.47	1.24
16.2	0.268	58.5	0.35	1.52		T/K=	500.3		
16.2	0.269	61.2	0.33	1.60	22.8	0.182	119.8	0.17	2.39
34.4	0.308	47.8	0.40	1.39	22.9	0.182	120.9	0.17	2.40
34.4	0.319	44.9	0.43	1.36	55.4	0.225	91.6	0.20	2.10
34.4	0.311	49.1	0.39	1.45	55.5	0.224	97.5	0.18	2.23
34.5	0.305	50.6	0.38	1.47	83.0	0.260	76.6	0.22	1.96
47.5	0.336	45.0	0.41	1.41	83.1	0.258	81.1	0.20	2.06
47.6	0.330	43.9	0.42	1.35	103.5	0.286	67.2	0.23	1.85
63.6	0.378	36.1	0.49	1.26	103.6	0.284	71.6	0.22	1.96
63.7	0.379	35.9	0.49	1.25	127.9	0.320	60.0	0.25	1.81
77.2	0.407	33.6	0.50	1.24	128.0	0.316	63.4	0.23	1.89
77.3	0.408	33.7	0.50	1.25	166.1	0.369	49.6	0.27	1.68

p/MPa	η/mPa∙s	Re	f [.] 10 ⁻⁵	γ ·10 ⁻⁴ /s ⁻¹	p/MPa	η/mPa∙s	Re	f·10 ⁻⁵	γ·10 ⁻⁴ /s ⁻¹
89.2	0.437	29.9	0.55	1.17	166.3	0.362	54.3	0.25	1.80
89.3	0.436	28.7	0.57	1.13	186.0	0.390	47.0	0.27	1.66
111.5	0.491	25.8	0.60	1.12	186.2	0.386	50.9	0.25	1.78
111.6	0.495	26.5	0.58	1.16	212.4	0.426	40.9	0.30	1.55
131.8	0.540	22.6	0.64	1.07	212.6	0.424	45.8	0.27	1.73
131.9	0.537	21.7	0.67	1.02	232.9	0.450	41.0	0.28	1.63
152.4	0.598	19.5	0.71	1.01	233.0	0.445	42.2	0.28	1.65
152.4	0.599	19.4	0.71	1.01	235.7	0.455	38.1	0.30	1.53
172.7	0.652	17.5	0.75	0.98	235.9	0.448	43.0	0.27	1.70
192.7	0.701	15.7	0.81	0.93	255.0	0.481	37.9	0.29	1.59
192.8	0.697	15.9	0.80	0.94	255.3	0.477	38.6	0.29	1.61
192.8	0.704	15.8	0.80	0.95	276.3	0.513	34.3	0.31	1.52
214.3	0.754	14.7	0.82	0.93	276.9	0.506	35.6	0.30	1.56
214.5	0.752	14.7	0.83	0.93		T/K=	534.9		
235.9	0.813	13.1	0.88	0.89	37.4	0.182	125.3	0.15	2.51
236.1	0.818	13.2	0.87	0.90	37.4	0.182	125.5	0.15	2.51
255.6	0.869	11.9	0.94	0.85	51.6	0.199	111.7	0.16	2.37
255.9	0.879	12.2	0.91	0.89	51.8	0.201	114.0	0.16	2.44
275.9	0.928	11.2	0.96	0.85	68.3	0.218	99.4	0.17	2.24
276.5	0.933	11.1	0.97	0.85	68.3	0.218	101.4	0.17	2.28
					88.5	0.242	86.3	0.19	2.10

<i>p</i> /MPa	η/mPa∙s	Re	f ⁻¹⁰⁻⁵	$\gamma \cdot 10^{-4} \ /s^{-1}$	p/MPa	η/mPa∙s	Re	f [.] 10 ⁻⁵	γ ·10 ⁻⁴ /s ⁻¹
					88.5	0.240	88.5	0.18	2.13
					88.6	0.241	92.1	0.18	2.23
					88.6	0.241	91.6	0.18	2.22
					104.3	0.259	81.1	0.19	2.07
					104.4	0.259	86.6	0.18	2.21
					124.0	0.281	73.7	0.20	2.00
					124.1	0.278	79.4	0.19	2.14
					168.8	0.330	61.0	0.22	1.88
					168.9	0.329	64.0	0.21	1.97
					169.1	0.330	64.5	0.21	1.98
					209.2	0.371	55.1	0.22	1.86
					209.4	0.375	54.5	0.22	1.86
					234.4	0.400	51.0	0.23	1.83
					254.3	0.422	47.7	0.23	1.79
					254.6	0.426	48.1	0.23	1.82
					276.3	0.445	45.4	0.24	1.77
					277.5	0.443	44.1	0.24	1.72



Figure 6. Effect of pressure and temperature on the viscosity of toluene, η_{exp} , obtained in this study. O - 295.9 K, \Box - 323.4 K, \triangle - 347.3 K, \diamondsuit - 392.5 K, \bigtriangledown - 421.5 K, + - 452.1 K, \varDelta - 500.2, and × - 534.9 K. The lines are drawn to guide the eye.

$$D_{\max} / \% = 100 \bullet Max \left(\left| \frac{x_{i, \exp} - x_{i, cal}}{x_{i, \exp}} \right| \right)$$
(6)

$$bias / \% = 100 \bullet \frac{1}{N} \sum_{i=1}^{N} \left(\frac{x_{i, \exp} - x_{i, cal}}{x_{i, \exp}} \right)$$
(7)
<i>T</i> /K	AAD/%	SD/%	D _{max} /%	bias/%
295.9	1.0	0.7	3.3	0.0
323.5	1.6	1.2	4.6	0.0
347.4	0.9	0.5	1.7	0.1
392.5	0.7	0.7	3.2	0.0
421.5	0.7	0.6	1.8	-0.1
451.8	1.0	1.0	4.1	0.1
500.3	0.6	0.5	1.4	-0.1
534.9	0.4	0.3	1.3	0.3

Table 4. Average absolute deviation (*AAD*), standard deviation (*SD*), maximum deviation (D_{max}), and *bias* for each smoothed curve fit to experimental viscosity isotherms.

Figure 7 shows the relationship between f and Re for all of the toluene data obtained in this study and listed in Table 3. The relationship for each isotherm can be seen to be linear confirming that there is laminar flow. The shear rates are listed in Table 3 and with the exception of 6 data points shear rates are within the range used for the calibration of the RBVD. The outlying six data points are at the highest temperatures and lower pressures where the resistance factor is much lower.



Figure 7. Relationship between the resistance factor (*f*) and Reynolds number (Re) for the toluene viscosity data obtained in this study. O - 295.9 K, □ - 323.4 K, △ - 347.3 K, ◇ - 392.5 K, ▽ - 421.5 K, + - 452.1 K, ⊿ - 500.2, and × - 534.9 K.

3.3.1 Tait Equation

Viscosity data are correlated with Equation 8 using a method similar to that reported by Caudwell et al. ²⁹ Equation 8 is a Tait-like expression with three parameters, *D*, *E*, and η_0 , which is a reference viscosity at $p_0 = 0.1$ MPa ^{19, 22, 23}. Initially, Equation 8 is fit to each set of isothermal data by minimizing the *AAD* between calculated and smoothed experimental viscosities. Table 5 shows that η_0 , *D*, and *E* decrease with increasing temperature. The *AAD* and *SD* values are all less than 0.3% showing that this Tait expression provides an excellent representation of the high-pressure toluene viscosities measured at each temperature.

$$\eta = \eta_0(T) \left(\frac{p+E}{p_0+E}\right)^D \tag{8}$$

295.9 8 - 172 0.554 2.897 360.5 0	.05 0.17
323.4 21 - 221 0.432 2.559 352.4 0	.06 0.03
347.3 9 - 202 0.324 1.458 163.3 0	.04 0.03
392.5 16 - 277 0.236 1.300 146.9 0	.15 0.16
421.5 10 - 295 0.203 1.192 136.0 0	.26 0.23
452.1 18 - 277 0.179 1.129 130.2 0	.04 0.04
500.2 23 - 277 0.155 1.030 128.4 0	.01 0.01
534.9 37 - 278 0.140 0.919 109.5 0	.02 0.02

Table 5. Optimized parameters for each set of isothermal viscosity data fit to Equation 5.

The parameters D and E from Table 5 are fit to quadratic functions of temperature, Equations 9 and 10, respectively, to allow for calculating the viscosity at any temperature from 295 to 535 K. Note that parameter D is correlated to inverse temperature. The initial fit of these two parameters over the entire experimental temperature range exhibit minima at a temperature near 400 K that translated to very poor fits. Hence, a modified approach is used where D and E are fit in two different temperature ranges of 295 to 393 K and 393 to 535 K. The 393 K isotherm serves as a convenient break point for this two temperature ranges as it is roughly 9 K greater than the normal boiling point of toluene.

$$D = \sum_{i=0}^{2} d_{i} (K/T)^{i}$$
(9)

$$E / MPa = \sum_{i=0}^{2} e_i (T / K)^i$$
(10)

Equation 11 uses three parameters, A_{η} , B_{η} , and C_{η} , for correlating the temperature variation of the reference viscosities, η_0 , listed in Table 4. Here, again, data in then same two temperature ranges are used for the fit. With an initial estimate for C_{η} , a linear, least squares fit of Equation 11 provides a value for B_{η} from the slope and for A_{η} from the intercept. Optimized values for A_{η} , B_{η} , and C_{η} are obtained by minimizing the *AAD* in each temperature range.

$$\ln \eta_0 = \ln A_\eta + \left(\frac{B_\eta}{T - C_\eta}\right) \tag{11}$$

Finally, for each temperature range, re-optimized values for A_{η} , B_{η} , C_{η} , d_0 , d_1 , d_2 , e_0 , e_1 , and e_2 are obtained simultaneously using a non-linear optimization routine that minimizes the *AAD* between calculated and smoothed experimental viscosities. Figure 8 summarizes the method to correlate toluene viscosity data to Equation 8. Table 6 lists parameter values from this re-optimization along with values for the *AAD*, *SD*, D_{max} , and *bias*. The temperature variation of *D* and *E* is similar to that reported in the literature ^{19, 22, 23, 29}. The *AAD* in each temperature range is less than 0.4%, which is much lower than the estimated experimental uncertainty of \pm 2%. Figure 9 shows four data points having the largest percent deviations of slightly more than 1.0% occur in the temperature range of 296 to 393 K. A fifth data point with $D_{max} = 3.94\%$ is off scale in Figure 9. The very low values for the *bias* shown in Table 6 establish that the deviations are evenly distributed about zero.

T range /K	296 - 393	T range /K	393 - 535
$10^3 A_{\eta}$ /mPa s	3.0468	$10^2 A_{\eta}$ /mPa s	4.7176
$10^{-3}B_{\eta}/{ m K}$	2.5661	$10^{-2}B_{\eta}/\mathrm{K}$	4.7407
$10^{-2}C_{\eta}/{ m K}$	-1.9691	$10^{-1}C_{\eta}/{ m K}$	9.8448
d_0	4.1582	$10d_0$	-8.9288
$10^{-3}d_{l}/K$	-3.5207	$10^{-3}d_l/K$	1.2282
$10^{-5}d_2/\mathrm{K}^2$	9.4327	$10^{-5} d_2/\mathrm{K}^2$	-1.3770
$10^{-3}e_0$ /MPa	2.1503	$10^{-2}e_0$ /MPa	2.5916
$e_1/(MPa/K)$	-8.6609	<i>10e</i> ₁ /(MPa/K)	-2.2697
$10^3 e_2/(MPa/K^2)$	9.0820	$10^5 e_2 / (MPa/K^2)$	-9.5633
AAD/%	0.33	AAD/%	0.30
SD/%	0.65	SD/%	0.26
D _{max} /%	3.94	D _{max} /%	0.84
bias/%	-0.09	bias/%	0.06

Table 6. Parameters obtained for the re-optimized fit of Equations 5 through 8 to experimental viscosities in two temperature ranges.



Figure 8. Flow chart showing the necessary steps to correlate the viscosity to the Tait relationship

as a function of temperature and pressure.



Figure 9. Comparison of smoothed experimental viscosities, η_{exp} , to viscosities calculated using Equation 8, η_{Eq8} . O - 295.9 K, \Box - 323.4 K, \triangle - 347.3 K, \diamondsuit - 392.5 K, ∇ - 421.5 K, + - 452.1 K, \triangle - 500.2 K, × - 534.9 K.

Table 7 compares literature sources for toluene viscosities with experimental viscosities from the present study calculated using Equation 11 with parameters from Table 6. Table 7 shows *AAD* values consistently lower than the \pm 2.0% estimated experimental uncertainty for the data reported in the present study, with the expection of the data of Dymond et al. ¹⁰ and Wilbur and Jonas ²⁵. The larger *AAD* for the comparison to data from Dymond et al. ¹⁰ may be a result of the modestly large experimental uncertainty of \pm 4% reported by these authors. In contrast, Wilbur and Jonas ²⁵ do not report an experimental uncertainty for the viscosity and, more imporantly, they report data for deuterated toluene, which is not expected to have precisely the same viscosity as toluene.

Year	Authors	<i>T</i> /K	p/MPa	Method	Accuracy/ ±%	AAD/%	D _{max} /%
2015	This Study	296-535	9-300	Rolling Ball	2	0.3	3.9
2011	Daridon et al. 40	293-332	0.1-80	Vibrating Quartz	5	1.3	3.1
2009	Baylaucq et al. ⁴¹	293-323	0.1-100	Falling Body	2	0.7	2.8
2005	Pensado et al. ²⁴	303-353	0.1-60	Rolling Ball	2	0.9	2.8
2004	Caudwell et al. ²¹	323-373	0.1-90	Vibrating Wire	2-5	1.6	3.2
2003	Avelino et al. ¹⁶	248-323	0.1-80	Vibrating Wire	2-3	0.7	1.8
2000	Harris ⁹	255-323	0.1-400	Falling Body	1	1.7	5.4
1997	Vieira dos Santos, Nieto de Castro ²³	298-348	0.1-207	Vibrating Quartz	0.5	1.3	2.7
1995	Dymond et al. ¹¹	298-348	0.1-492	Falling Body	4	1.5	4.5
1992	Olivera, Wakeham ¹⁷	303-348	0.1-252	Vibrating Wire	0.5	1.6	10.4
1991	Assael et al. ¹⁹	303-323	0.1-71	Vibrating Wire	0.5	0.6	1.3
1991	Dymond et al. ¹⁰	298-373	0.1-519	Falling Body	4	3.6	13.4
1982	Kashiwagi, Makita* ²²	298-348	0.1-110	Vibrating Quartz	2	0.8	2.5
1974	Wilbur, Jonas ²⁵ **	238-473	0.1-350	Rolling Ball	N/A	3.5	10.7

Table 7. Comparison of toluene literature viscosities and viscosities from this study calculated with Equation 8 using the best fit parameters from Table 5.

* Literature data are calculated using authors' reported Tait parameters

** Viscosity data reported for toluene-d8

Table 7 lists a comparison of viscosity data available in the literature with data from the present study calculated with the Tait expression, Equation 8, up to 400 MPa. It is important to note that data in the present study are limited to 300 MPa, and, therefore part of the comparison considers extrapolated viscosity values. Figure 10 shows 11 out of 13 sources have *AAD* values less than 1.7%. Five of the 11 sources have *AAD* values less than 1.0% and these five sources use four unique viscometric techniques.

Only 21 out of 378 data points used in this comparison exhibit a deviation greater than \pm 3%. Seven of the 21 points are reported by Olivera and Wakeham ¹⁷, with six of the seven at 303 K. Nine of the 21 points are reported by Harris ⁹ with six of these points at 298 K, and three points at 323 K and pressures from 375 to 400 MPa. Three of the 21 points are reported by Caudwell *et al.* ²¹, one by Daridon *et al.* ⁴⁰, and one by Dymond *et al.* ¹¹.

Collectively, the data of Kashiwagi and Makita ²² and Baylaucq et al. ⁴¹ show no obvious trends in the deviation although this collective data set does contain four points that deviate from ± 2.0 to 3.0%. The data reported by Pensado *et al.* ²⁴ and Vieria dos Santos and Nieto de Castro ²³ cluster consistently around zero deviation and are within the $\pm 2.0\%$ experimental uncertainty of the data from the present study. The results shown in Figure 10 and Table 7 validate the reliability and accuracy of the RBVD technique used here given that the reported high pressure viscosities are in close agreement with viscosities obtained using other viscometric techniques. In addition, the high-temperature, high-pressure viscosities reported in the present study extend the available toluene data base to temperatures as high as 535 K and pressures to 300 MPa.



Figure 10. Comparison of available literature data, η_{lit}, and viscosities from this study calculated with Equation 8 using the best fit parameters from Table 5, η_{Eq8}. Three of the points reported by Olivera and Wakeham ¹⁷ exhibit a deviation greater than ± 6%, and do not show up on this graph. O - Baylaucq et al. ⁴¹, □ - Avelino *et al.* ¹⁶, △ - Caudwell *et al.* ²¹, ◇ - Olivera and Wakeham ¹⁷, + - Dymond *et al.* ¹¹, □ - Daridon *et al.* ⁴⁰, × - Pensado *et al.* ²⁴, ⊿ - Harris ⁹, ▽ - Assael *et al.* ¹⁹, ● - Kashwagi and Makita²², ⊠ - Vieria dos Santos and Nieto de Castro ²³

3.3.2 Harris Correlation

Harris⁹ describes a viscosity correlation that improves on his earlier approach^{8, 42}that uses Dymond's reduced viscosity⁴³. The Harris correlation is given by Equation 12 that is derived using a Padé approximation and that utilizes a reference temperature, T_r , in a mapping function, Equation 13, for the reference volume, V_r '.

$$\sqrt{T} / \eta = (f_1 + f_2 V_r^{'} + f_3 V_r^{'2}) / (1 + f_4 V_r^{'})$$
(12)

$$V_{r} = V - g_{1}(T - T_{r}) - g_{2}(T - T_{r})^{2}$$
(13)

Initially the parameters in Equations 12 and 13 are fit to viscosities over the entire experimental range of densities using a non-linear optimization routine that minimizes the *AAD*. However, it is not possible to obtain an optimal fit over the entire data set of the present study. In contrast, Harris⁹ reports a very good fit of the correlation for toluene viscosities obtained in the density range of 840 to 1020 kg•m⁻³. The poor fit of the Harris correlation in the present case is likely a consequence of fitting the viscosity to a slightly larger density range of 700 - 950 kg•m⁻³ that starts at a lower value of 700 kg•m⁻³. Table 8 shows the results from an alternative approach of fitting the viscosities from the present study to Equation 12 in two ranges of density, where the break in density is chosen at 850 kg•m⁻³, close to the lower limit in density reported by Harris. Figure 11 shows very good agreement of smoothed experimental viscosities from the present study to viscosities from the present study to 2 with two sets of parameters. The percent deviation of the data with this approach scatters around the zero line resulting in a *bias* of less than 0.2%. The largest percent deviations do not exhibit any systematic trends, however, the deviations do increase

slightly at the highest densities shown here although the bulk of the data are still within $\pm 2\%$, the experimental uncertainty of the data.

Table 8. Parameters obtained for the application of the viscosity correlation, shown in Equation 9, fit to two density ranges. The viscosity data are obtained at temperatures from 296 to 535 K and pressure to ~300 MPa.

700 - 850	ρ range/(kg•m ⁻³)	850 - 950
	Equation 9	
-9.9599	$10^{-2} f_l / (K^{0.5} / (mPa s))$	8.7197
7.8502	$f_2/(K^{0.5}/(mPa \ s \ cm^3))$	-2.0831
2.3193	$10^{2} f_{3} / (\mathrm{K}^{0.5} / (\mathrm{mPa \ s \ cm^{6}}))$	1.2387
2.3664	10 ² <i>f</i> ₄ /(K ^{0.5} /(mPa s cm ⁹))	1.0486
	Equation 10	
-2.5135	$10^2 g_1 / (\text{cm}^3 / (\text{K mol}))$	-4.4886
-1.0197	$10^5 g_2/(\text{cm}^3/(\text{K}^2 \text{ mol}))$	3.6309
0.70	AAD/%	0.94
0.98	<i>SD</i> /%	0.88
4.64	D_{max} /%	4.97
0.18	bias/%	0.09
	700 - 850 -9.9599 7.8502 2.3193 2.3664 -2.5135 -1.0197 0.70 0.98 4.64 0.18	$700 - 850$ ρ range/(kg·m ⁻³)Equation 9-9.9599 $10^{-2}f_{I}/(K^{0.5}/(mPa s))$ 7.8502 $f_{2}/(K^{0.5}/(mPa s cm^3))$ 2.3193 $10^{2}f_{3}/(K^{0.5}/(mPa s cm^{6}))$ 2.3664 $10^{2}f_{4}/(K^{0.5}/(mPa s cm^{9}))$ Equation 10Equation 10-2.5135 $10^{2}g_{I}/(cm^{3}/(K mol))$ -1.0197 $10^{5}g_{2}/(cm^{3}/(K^{2} mol))$ 0.70 $AAD/\%$ 0.98 $SD/\%$ 4.64 $D_{max}/\%$ 0.18 $bias/\%$



Figure 11. Comparison of smoothed experimental viscosities, η_{exp} , obtained in this study from 296 to 535 K, to viscosities calculated using Equation 9, η_{Eq9} . Three points, between ± 4.0 to 5.0%, are off scale and not shown here.

Experimental toluene viscosity data are well correlated with the empirical Tait and Harris equations and both correlations can be used for the reliable interpolation of toluene viscosity. However, the error in the predicted viscosity is unknown when these correlations are applied at temperatures and pressures beyond those used when fitting experimental data. In addition, there is no theoretical guidance available for predicting the coefficients for each correlation. In the following section toluene viscosity is modeled with the Free Volume Theory (FVT) coupled with the PC-SAFT EoS to overcome the limitations of the previously described correlation approach.

3.3.3 Free Volume Theory

Typically, viscosity data are modeled as a sum of two terms shown in Equation 14. The first term, η_0 , is the dilute gas viscosity calculated from the kinetic theory of gases at very low pressures ^{44, 45} and the second term, $\Delta \eta$, is calculated here using FVT ⁴⁶ model as shown in Equation 15 and described in more detail elsewhere ^{46, 47}.

$$\eta = \eta_0 + \Delta \eta \tag{14}$$

$$\Delta \eta = \frac{\rho L \left(\alpha \rho + \frac{pM}{\rho} \right)}{\sqrt{3RTM}} \exp \left[B \left(\frac{\alpha \rho + \frac{pM}{\rho}}{RT} \right)^{3/2} \right]$$
(15)

In Equation 15 ρ is density (kg•m⁻³) obtained either directly from experimental data or calculated using the PC-SAFT EoS, *M* (kg•mol⁻¹) is the molecular weight, *T* (K) is absolute temperature, *p* (MPa) is pressure, and *R*, the universal gas constant, is equal to 8.3145 J•mol⁻¹•K⁻¹. Table 9 lists values for the FVT parameters *L* (Å), α (m⁵•mol⁻¹•s⁻²), and *B* (dimensionless) obtained by minimizing the AAD, Equation 2, between experimental viscosities and calculated viscosities obtained with Equation 14. Experimental Densities are obtained from NIST while predicted densities are calculated with the PC-SAFT equation using pure component parameters obtained from fitting toluene vapor pressure data ³⁰ (Low-P) or from fitting density data at high-temperatures and high-pressures ⁴⁸ (HTHP). The variation of the FVT parameters is fairly modest regardless of the source for the density. More importantly, a reasonable fit of the viscosities

obtained from 296 to 535 K and pressures to ~ 300 MPa is obtained with constant values for L, α , and B. However, note that D_{max} values are quite large and, although not shown here, the maximum deviations appear at temperatures in excess of 500 K and pressures less than 120 MPa.

Table 9. FVT model parameters *L*, α , and *B* for toluene obtained from fitting viscosity data obtained in this study from 296 to 535 K and pressures to ~ 300 MPa. Toluene densities are obtained from NIST ³⁶ or are calculated with the PC-SAFT equation using pure component parameters obtained from fitting toluene vapor pressure data ³⁰ (Low-P) or from fitting density data at high-temperatures and high-pressures ⁴⁸ (HTHP). Listed also are the average absolute deviation, *AAD*, standard deviation, *SD*, and maximum deviation, *D_{max}* obtained using the different sources for density.

Density Source	L/Å	$\alpha/(m^5 \bullet mol^{-1}s^{-2})$	$\mathbf{B} \bullet 10^3$	AAD/%	SD/%	D _{max} /%
NIST ³⁶	0.7934	81.99	7.3340	2.71	2.80	14.1
PC-SAFT						
Low-P parameters ³⁰	0.6956	92.89	6.2382	2.41	2.67	14.0
HTHP parameters ⁴⁸	0.7987	81.48	7.2745	2.82	2.91	14.8

In an earlier study Burgess *et al.* ⁴⁷ calculate toluene FVT parameters by fitting the FVT equation to high-pressure viscosity data reported by Dymond *et al.* ¹⁰ available only to 373 K. Burgess reports an *AAD* of ~2.0% from the fit of viscosity and with the PC-SAFT EoS with Low-P parameters for density calculations. Burgess also reports an *AAD* of ~2.6% from the fit of viscosity and the PC-SAFT EoS with HTHP parameters for density calculations. Here toluene viscosities are predicted over the larger 296 to 535 K temperature range reported in the present

study using the two sets of FVT parameters published by Burgess *et al.* ⁴⁷ with the PC-SAFT EoS and appropriate parameters. The results from these calculations, listed in Table 10, show a modest increase in the *AAD* and *SD* suggesting that FVT parameters fitted over a limited temperature range can then be used with a suitable EoS to obtain viscosity predictions at much higher temperatures. As an example, Figure 12 shows the deviation plot obtained between the experimental data reported here and FVT predictions with Burgess *et al.* ⁴⁷ parameters coupled with the PC-SAFT EoS using HTHP parameters. Note the large deviations especially at pressures below ~100 MPa and temperatures in excess of 500 K. Similar trends are also observed when using constant FVT parameters with any density source to predict the viscosity data between 296 and 535 K.

Table 10. Comparison of the average absolute deviation, *AAD*, standard deviation, *SD*, and maximum deviation, D_{max} , for viscosities from 296 to 535 K. The two sets of FVT *L*, α , and *B* parameters reported by Burgess *et al.*⁴⁷ are used with the PC-SAFT equation with both Low-P and HTHP pure component parameters

PC-SAFT Parameters	L/Å	$\alpha/(\mathrm{m}^{5} \cdot \mathrm{mol}^{-1}\mathrm{s}^{-2})$	$B \cdot 10^3$	AAD/%	SD/%	D _{max} /%
Low-P	0.7904	81.72	7.4175	3.51	2.90	13.6
HTHP	0.8360	75.74	8.1256	3.10	3.24	16.2



Figure 12. Comparison of experimental viscosities (η_{exp}) from this study with predictive Free
Volume Theory calculations (η_{FVT}) using Toluene parameters reported by Burgess *et al.*⁴⁷ coupled with the PC-SAFT EoS calculated density using HTHP parameters. O 295.9 K, □ - 323.5 K, △ - 347.4 K, ◇ - 392.5 K, □ - 421.5 K, ⊞ - 451.8 K, ▽ - 500.3 K, ⊿ - 534.9 K.

Final sets of calculations are performed to ascertain the effect of temperature on each FVT parameter. In this approach density data reported by NIST ³⁶ are used when optimizing *L*, *a*, and *B* for each isotherm. The initial results show that *L* remains fairly constant which is not surprising since *L* is a characteristic length parameter related to the size of the molecule⁴⁹ and is only expected to vary from compound to compound. However, with increasing temperature *a* increases and *B* decreases, which are correlated according to Equations 16 and 17. As a final step the constants *L*, *a*₀, *a*₁, *a*₂, *b*₀, *b*₁, *b*₂ (coefficients for Equations 16 and 17) are optimized by fitting the entire viscosity data set. Table 11 lists the values for the coefficients for Equations 16 and 17 while Table 12 summarizes the performance of the temperature-dependent FVT model using density data reported by NIST. ³⁶ It is readily apparent that the fit of the FVT is significantly improved when

temperature-dependent parameters are used. Note that the maximum deviation has been reduced by a factor of about four compared to the values shown in Table 9 and Table 10. Figure 13 shows the improved toluene viscosity deviation plot obtained with the FVT predictions using temperature-dependent parameters. Note the percent deviations in Figure 13 are now within \pm 5 rather than \pm 20 shown in Figure 12, indicating a significant improvement in the predictions. It is interesting to note that Allal *et al.*⁴⁶ also obtained similar improvements in viscosity predictions for methane and propane using a pressure and temperature corrective factor for $\Delta \eta$. Nevertheless, the challenge remains to predict the temperature dependence of the FVT model and/or its parameters from first principles.

$$\alpha / (m^5 \bullet mol^{-1} s \bullet s^{-2}) = \sum_{i=0}^{2} a_i (T / K)^i$$
(16)

$$B = \sum_{i=0}^{2} b_i (T / K)^i$$
(17)

Table 11. Values for coefficients in Equations 13 and 14.

<i>i</i> =	0	1	2
a_i	9.3281 • 10 ¹	$-1.7014 \cdot 10^{-1}$	$3.9607 \cdot 10^{-4}$
b_i	1.2947 • 10 ⁻²	-8.4687 • 10 ⁻⁶	-1.4334 • 10 ⁻⁸

Table 12. Average absolute deviation, *AAD*, standard deviation, *SD*, and maximum deviation, D_{max} , obtained with temperature-dependent, FVT parameters and with density data reported by NIST.³⁶ *L* is a constant value of 0.6723.

T/K	AAD/%	SD/%	D _{max} /%
295.9	0.43	0.44	1.19
323.5	1.59	0.93	3.40
347.4	1.06	0.78	2.62
392.5	1.39	1.12	3.88
421.5	0.71	0.79	2.99
451.8	0.42	0.33	0.91
500.3	0.95	0.93	3.75
534.9	0.46	0.71	2.61
Overall	0.90	0.90	3.88



Figure 13. Comparison of experimental viscosities (η_{exp}) from this study with Free Volume Theory calculations (η_{FVT}) using temperature-dependent parameters coupled with toluene density data reported by NIST.³⁶ O - 295.9 K, \Box - 323.5 K, \triangle - 347.4 K, \diamondsuit - 392.5 K, \Box - 421.5 K, \boxplus - 451.8 K, \bigtriangledown - 500.3 K, \triangle - 534.9 K.

3.3.4 Superposition of viscosity data and insight to intermolecular forces

Roland, Bair, and Casalini⁵⁰ demonstrate how to superpose the viscosity for various fluids including van der Waals, H-bonded, and ionic liquids by the relationship,

$$\eta(T,V) = f(TV^{\gamma}) \tag{18}$$

where V (cm³·g⁻¹) is the specific volume and γ is a constant relating to the magnitude of intermolecular forces for a given fluid. This specific relationship provides a simplification of the Leonard-Jones potential function that only accounts for the repulsive potential. Roland, Bair, and Casalini found that the value of γ decreases as intermolecular interactions increase from mean-field van der Waals interactions to very strong ionic interactions. The lower values for γ seen in ionic interactions are attributed to the dominance of attractive intermolecular forces and not necessarily to a reduction in repulsive forces.

Similarly to approach given by Paredes *et al.*⁵¹, viscosity data are it to second order polynomials as a function of TV^{γ} ,

$$\eta = a \left(\frac{1}{TV^{\gamma}}\right)^2 + b \left(\frac{1}{TV^{\gamma}}\right) + c \tag{19}$$

Where the coefficients for equation 19 a (mPa•s (K•cm^{3 γ})²), b (mPa•s (K•cm^{3 γ})), and c (mPa•s) for $\gamma = 11.5$ are listed in Table 13 A nonlinear optimization tool is used to minimize the *AAD* while searching for a value of γ . Figure 14 shows the relationship between the viscosity and the quantity,

1000/(TV^{γ}), where $\gamma = 11.5$. The second order relationship between η and the quantity, 1000/(TV^{γ}) yields an *AAD* of 2.94%.

Table 13. Coefficients for equation 19, as second order polynomial relationship between the experimental viscosity, η_{exp} and $1000/TV^{\gamma}$.



Figure 14. Superposition of experimental toluene viscosity data obtained in this study with the relationship between smoothed viscosity data, η , and the quantity 1000/(TV^{γ}), where $\gamma = 11.5$. The two quantities, η and 1000/(TV^{γ}), are related through a second order polynomial.

Figure 15 show the comparison of the experimental toluene viscosity data obtained in this thesis against equation 19. The greatest deviations occur at the temperature extremities of the data set and at low density. The cause of the higher deviations at lower densities occurs because this is

where attractive forces dominate. The constant γ as stated beforehand is related to the magnitude of the intermolecular interactions. It is well understood that an increase in temperature is inversely related to the strength of intermolecular interactions, which could lead to a shift in the constant γ .



Figure 15. Comparison of experimental viscosity, η_{exp} , against superposed polynomial fit, η_{fit} with density. Guide lines are drawn at ± 3% relative to the *AAD*. O - 295.9 K, \Box - 323.4 K, \triangle - 347.3 K, \Diamond - 392.5 K, ∇ - 421.5 K, + - 452.1 K, \triangle - 500.2, and × - 534.9 K.

Chapter 4 Conclusions and Future Studies

In this thesis, a study using a High-Temperature, High-Pressure RBVD measured toluene density, and viscosity to a maximum temperature and pressure of 535 K and 300 MPa. Correlational work is presented using a modified Tait equation, and a Padè approximate in conjunction with a single mapping of the isotherms devised by Harris⁹. Using a more theoretical approach the viscosity data was modeled using Free Volume Theory and a superposition of the viscosity based on an approximation using the repulsive Leonard-Jones term⁵⁰. It is seen that reliable data is obtained with the system as the *AAD* when compared to various literature sources using different techniques is within $\pm 2\%$.

In future studies, some modifications will be implemented to the RBVD apparatus. Firstly, separate pressure transducer will be employed with an error of \pm 10 psi for measurements at pressures below 10,000 psi. Secondly, the body of the viscometer will be modified in order to incorporate "mini window holders" that will not require the use of o-rings. Eliminating o-rings from the set-up will increase the working temperature range of the RVBD, and experimental runtime of the system.

Once the modifications are successfully implemented, viscosity data will be obtained for several erythritols, so-called biodegradable esters, to highlight the impact of molecular structure on viscosity at high pressures. Biodegradable esters are currently being considered as lubricants that are a necessity in many industrial applications. For example, lubricants are used extensively in the automotive industry to reduce wear, corrosion, and even to circulate and cool the engine⁵². Ideally lubricants remain contained within the engine, although oftentimes leaks occur and the

environment can be contaminated. In addition, extreme pressure and temperature conditions can be exhibited within an engine. Hence, generating a reliable and expansive database of viscosity and density data on biodegradable lubricants aides in identifying their suitability for potential applications, which can also have a positive impact on the environment.

Polyol esters are identified as a class of environmentally friendly, biodegradable lubricants whose architecture can be readily modified to suit a variety of different applications. Figure 16 shows the variation in the basic structures of two basic polyol esters where the first ester, a pentaerythritol, and the second ester, a dipentaerythritol. These esters have the inherit advantage of not containing a hydrogen atom on the β -carbon atom, thus reducing their susceptibility to oxidation ⁵³. In addition, the molecules can be customized through the variability of the number of ester groups, and the length of their respective side chains.



Figure 16. Basic structures of pentaerythritol (left) and dipentaerythritol esters (right).

Studies are scarce which examine the pressure-temperature dependence on viscosity and density for pentaerythritol lubricants. To date the density of pentaerythritol lubricants have only been studied to a maximum pressure of 45 MPa and 353 K⁵⁴⁻⁵⁷. Likewise, viscosity data are only available to 60 MPa and 353 K⁵⁸⁻⁶⁰ with a modest experimental uncertainty of $\pm 4\%$.

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