Isochoric (p,ρ,T) Measurements for Liquid Toluene from 180 K to 400 K at Pressures to 35 MPa[†]

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The (p,ρ,T) relationships were measured for a specially purified sample of toluene by applying an isochoric method with gravimetric determinations of the amount of substance. Temperatures ranged from 180 K to 400 K, while pressures were up to 35 MPa. Measurements were carried out on 20 compressed liquid isochores at a total of 311 state conditions. Saturated liquid densities were estimated by extrapolating each isochore to the vapor pressure, and determining the temperature and density at the intersection. Published (p,ρ,T) data are in good agreement with this study. For the (p,ρ,T) apparatus, the expanded uncertainty (at the 2σ level) of the temperature is ±0.03 K, and for pressure it is ±0.01% at $p > 3$ MPa and ±0.05% at $p < 3$ MPa. The principal source of uncertainty is the cell volume (28.5193 cm^3 at 0 K and 0 MPa) which has an estimated statistical uncertainty (at the 1σ level) of ±0.003 cm^3. When the sources of uncertainty are combined, the expanded uncertainty (at the 2σ level) of the density values is estimated to be ±0.05%.

Introduction

The present investigation of the (p,ρ,T) surface of toluene from 180 K to 400 K is part of a comprehensive program at the National Institute of Standards and Technology to determine the thermophysical properties of substances with technological significance to the United States Chemical Processing Industry (CPI). In the past decade, toluene has consistently ranked in the top 50 chemical commodities produced by the U.S. CPI. There is also considerable interest in toluene as a standard reference fluid for density, viscosity, and thermal conductivity. A previous study carried out at NIST (Straty et al. 1988) produced 296 measurements of density from 348.15 K to 673.15 K at a state-of-the-art uncertainty. That study covered liquid and gaseous states at temperatures up to and exceeding the critical point temperature (591.75 K) of toluene. Accurate values of (p,ρ,T) such as those of Straty et al. are essential to the development and testing of equations of state for this fluid.

In a comprehensive work on the equation of state of toluene, Goodwin (1989) reviewed the literature for the thermodynamic properties of this substance. Goodwin emphasized five studies of the (p,ρ,T) surface which were published between 1970 and 1988. Of these five references, none of the density studies extended to temperatures below 270 K. Though aware of this deficiency, Goodwin fitted the available data at temperatures above 270 K and some data generated with a corresponding states method at temperatures below 270 K. Heretofore, no published data of high accuracy were available to test Goodwin's equation of state below 270 K. Thus, the chief goal of this study is to provide accurate (p,ρ,T) measurements that overlap the existing data and extend to temperatures close to the triple point (178.15 K) of toluene.

For the years 1970−1995, ten published studies of toluene densities are summarized in Table 1. For publications after 1970, we found five references not used or cited by Goodwin. Of these data sources, only Albert et al. (1985) present densities with a stated uncertainty (at the 2σ level) of 0.1% or less. Unfortunately, the stated uncertainties of temperature (80 mK) and pressure (0.3 MPa) are slightly larger than desirable for development and testing of an accurate equation of state. Also, these data do not provide new information because there are abundant data in their temperature range, 298 K to 400 K. In some cases, data sources did not provide uncertainties and we had to estimate them. For example, some of the densities derived from sound velocities (Takagi and Teranishi, 1984; Muringer et al., 1985) were estimated to have an uncertainty of approximately (0.2 to 0.3)%, including the added uncertainty from the integration of a thermodynamic relation for sound velocity. In any case, calculation of densities from sound velocities requires the use of heat capacities and densities from external sources and leads to some questions about their actual uncertainties.

Experimental Section

The apparatus used in this work has been used for numerous studies of both pure fluids and mixtures. Since details of the apparatus are available in previous publications (Goodwin, 1961; Magee and Ely, 1988), they will be only briefly reviewed here. An isochoric technique was employed to measure the single-phase liquid densities in this study. In this method, a sample of fixed mass is confined in a container of nearly fixed volume. The volume of the container as a function of pressure and temperature is accurately known. The temperature is changed in selected increments, and the pressure is measured at each temperature, until the upper limit of either temperature (400 K) or pressure (35 MPa) is attained. When an isochore is completed, that is, after the upper temperature or pressure limit of the run has been reached, the sample is expanded into a lightweight stainless steel cylinder which is immersed in liquid nitrogen. When the (p,ρ,T) cell and its connecting capillary have been heated to about 400 K, the stainless steel cylinder is sealed, warmed to ambient temperature, and weighed. The density of the test fluid is then determined from a knowledge of the cell volume and of the mass difference of the stainless steel cylinder before and after trapping the sample. Allowances are made to

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S0021-9568(96)00062-3

Table 1. Selected (p,ρ,T) Measurements for Toluene in the Single Phase (l, Liquid; v, Vapor)

			range of data		uncertainties		
source	purity	no.	T/K	p/MPa	δT/mK	δp	$\delta\rho$
this work (l)	0.99974	311	180−400	0.5−35	30	$0.0001p$	0.0005ρ
Akhundov and Abdullaev (1970) (*l*)	0.9998	294	298−673	0.9−50	10	$0.0002p$	0.001ρ
Albert et al. (1985) (l)	0.999	19	298−400	0.5−20	80	0.3 MPa	0.001ρ
Dymond et al. (1988) (l)	0.99	63	298−373	0.1−459			0.002ρ
Dymond et al. (1991) (l)	0.999	40	298−373	0.1−519			0.002ρ
Kashiwagi et al. (1982) (l)	0.995	94	273−373	0.1−250	10	$0.001p$	0.001ρ
Marcos et al. (1983) (v)	0.999	46	423−573	0.09−0.8	100	$0.003p$	0.002ρ
Muringer et al. (1985) (*l*)		166	179−320	0.1−263	1	$0.0001p$	0.002ρ
Straty et al. (1988) (l & v)	0.99999	296	348−673	1.6−34.5	100	$0.0005p$	0.001ρ
Takagi and Teranishi (1984) (*l*)	0.996	26	293−303	0.1−160	30	0.3 MPa	0.003ρ
Watanabe et al. (1988) (v)	0.998	22	503−603	1.1−3.5	10	$0.001p$	0.005ρ

account for the noxious volumes in the system, such as those of the capillaries and the pressure gauge. A small adjustment to the sample mass was made to account for the change in atmospheric buoyant force acting on the steel cylinder. The density of the sample fluid is then the quotient of the mass and the volume of the cell at each pressure and temperature.

The sample cell is a cylindrical piece of electrolytic tough pitch copper containing a cavity with a volume of approximately 28.5 cm^3. It is suspended inside an evacuated cryostat from a thin-walled stainless steel tube used for reflux cooling. High-resistance wire wound tightly around the cell is used to heat the cell. The cell temperature is determined with a platinum resistance thermometer (calibrated at NIST relative to the IPTS-68, with temperatures converted to the ITS-90) embedded in a small well at the top of the cell. An ultrastable current source supplies the thermometer with a current of 2 mA and is equipped with relays capable of reversing the direction of current in the circuit. Voltages are measured for opposite directions of current flow and averaged in order to minimize errors caused by steady-state thermal and contact emfs. The temperatures were controlled and reproduced within 1 mK. The expanded uncertainty in the temperature ranged from 10 mK at 100 K to 30 mK at 400 K. Throughout this document, expanded uncertainty is a 2σ value (coverage factor of 2).

Pressures are measured by reading the period of vibration, averaged over 10 s, of an oscillating quartz crystal transducer which is connected to the sample cell through a fine diameter (0.2 mm i.d.) capillary. Since the frequency of the transducer varies with temperature, the transducer has been anchored in an insulated aluminum block controlled at (333.15 ± 0.05) K. The transducer has been calibrated with an oil-lubricated piston gauge with an expanded uncertainty of ±0.01%. Calibrations have demonstrated that the transducer is extremely stable over long times. Changes of less than 0.003% were observed over 1 year. The expanded uncertainty in the pressure measurements is approximately 0.01% for pressures greater than 3 MPa but increases to 0.05% at low pressures (1 MPa and lower) as a result of the transducer resolution, the fluctuations in the temperature of the pressure transducer, and the occasional hysteresis in the vibrational frequency of the quartz element.

A high-purity (HPLC grade) toluene sample was obtained for the measurements. The manufacturer's lot analysis quoted a purity of 0.9998 mol fraction. To verify this purity and decide whether any further purification was needed, a small quantity of toluene was analyzed by gas chromatography/mass spectrometry and Karl Fisher Coulombic titrimetry. We found the sample had low levels of benzene (mol fraction of 0.001), thiophene (mol fraction of 0.0007), and water (mol fraction of 0.000 042), making the purity as tested 0.9983. Thus, purification was carried out in the following sequence: two concentrated sulfuric acid extractions; two washings with sodium hydroxide solution; five washings with high-purity water; treatment with phosphorous pentoxide for 12 h; and distillation two times over phosphorous pentoxide. The purified toluene was stored in a thoroughly cleaned and dried stainless steel cylinder with a volume of 300 cm^3. The residual dissolved air was removed by three cycles of freezing and vacuum pumping of the vapor space to a pressure of approximately 10^{-5} Pa. Subsequent analysis showed that the impurity level had been reduced to approximately a mol fraction of 0.000 26. Thiophene and water were absent from the chromatogram/spectrum. The largest remaining impurity was benzene. Table 2 gives the analysis of the purified (mol fraction of 0.999 74) toluene sample used in this study.

Table 2. Analysis of Toluene Samples before and after Purification

	mol fraction	
compd	before	after
toluene	0.9982	0.999 74
benzene	0.001	0.000 2
thiophene	0.0007	0.000 00
water	0.000042	0.000 00
other	0.0001	0.000 06

Results and Discussion

Assessment of Uncertainties. For the (p,ρ,T) apparatus the uncertainty in temperature is ±0.03 K and is a combination of ice point (R_0) resistor drift, temperature gradients in the cell enclosure, the drift of the 10 Ω standard resistor used in the PRT circuit, and radiation from the head of the thermometer or from the lead wires to cooler surfaces in their vicinity.

The uncertainty in pressure is ±0.01% at $p > 3$ MPa and ±0.05% at $p < 3$ MPa. The higher uncertainty at $p <$ 3 MPa is due to the increasing contribution of the variation with temperature of the ratio of the periods of vibration in vacuum and at pressure (τ_0/τ) of the oscillating quartz crystal pressure transducer, given by

$$p = C[(t - Dt^2) + (1 - 2Dt)\delta t] \qquad (1)$$

where C and D are constants, t is defined by $\mathrm{t} = 1 - (\tau_0/\tau)^2$, τ is the period at pressure p, τ_0 is the period in vacuum, the fluctuation of the transducer temperature about its setpoint is $\delta T/\mathrm{K} = 333.15 - \mathrm{T/K}$, the corresponding fluctuation in the variable t is $\delta \mathrm{t} = -2(\tau_0/\tau^2)\delta\tau_0$, and $\delta\tau_0$ is the change in τ_0 due to δT given by $\delta\tau_0 = (\mathrm{d}\tau_0/\mathrm{d}T)\delta T$. The coefficients obtained by calibration are $(\mathrm{d}\tau_0/\mathrm{dt}) = 0.2113$ ns·K^{-1}, $C = -3.49269 \times 10^2$ MPa, and $D = 3.54846 \times 10^{-2}$. This procedure was developed to correct (to a first-order approximation) for the temperature dependence of the transducer period of oscillation. Its contribution to the

Table 3. Experimental (p,ρ,T) Data for Toluene: T, Temperature (ITS-90); p, Pressure; ρ, Density

T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}
180.000	0.5263	972.59	232.999	5.2546	925.08	281.998	2.9237	878.99	340.000	9.5758	831.51
180.999	2.6381	972.49	234.000	6.8115	924.99	283.000	4.1140	878.91	344.001	13.1522	831.22
182.000	4.7382	972.39	235.000	8.3618	924.90	283.999	5.2996	878.83	348.000	16.6989	830.92
182.999	6.8219	972.29	236.000	9.9089	924.81	286.001	7.6627	878.67	352.000	20.2147	830.62
183.999	8.9033	972.19	238.000	12.9835	924.64	288.149	10.1855	878.50	356.001	23.7034	830.32
185.000	10.9785	972.09	239.999	16.0409	924.47	289.999	12.3500	878.36	360.001	27.1618	830.02
186.000	13.0435	971.99	242.000	19.0839	924.30	292.001	14.6811	878.20	364.000	30.6022	829.72
187.000	15.0984	971.90	244.001	22.1083	924.12	293.149	16.0144	878.11	368.000	34.0087	829.42
188.000	17.1428	971.80	246.001	25.1076	923.95	293.999	16.9942	878.04	340.000	0.5441	822.69
189.001	19.1876	971.70	247.999	28.0914	923.78	295.999	19.3020	877.88	341.002	1.4127	822.62
190.000	21.2142	971.60	249.998	31.0600	923.61	298.000	21.5982	877.72	342.002	2.2784	822.55
191.999	25.2569	971.41	252.000	34.0166	923.44	300.002	23.8812	877.56	342.999	3.1377	822.48
194.001	29.2695	971.22	240.002	0.5329	916.01	304.001	28.4148	877.24	344.001	4.0043	822.40
196.000	33.2405	971.02	241.000	2.0189	915.92	308.001	32.9061	876.93	346.001	5.7215	822.26
189.999	0.5289	962.98	242.000	3.5012	915.84	290.001	0.5421	869.84	348.000	7.4324	822.11
191.000	2.5131	962.89	243.151	5.1999	915.74	290.999	1.6773	869.76	350.002	9.1384	821.96
192.000	4.4892	962.79	244.001	6.4520	915.67	292.000	2.8067	869.68	352.000	10.8373	821.82
193.000	6.4537	962.69	245.001	7.9192	915.58	293.150	4.1048	869.59	356.002	14.2201	821.52
194.000	8.4129	962.60	245.999	9.3753	915.50	293.999	5.0603	869.53	360.002	17.5766	821.23
195.001	10.3696	962.50	248.000	12.2906	915.33	295.998	7.3002	869.37	363.999	20.9087	820.93
195.999	12.3116	962.41	250.002	15.1934	915.16	298.000	9.5294	869.22	368.000	24.2193	820.64
197.000	14.2504	962.31	251.999	18.0705	914.99	299.999	11.7490	869.06	371.998	27.4967	820.34
197.999	16.1756	962.22	254.000	20.9314	914.82	302.000	13.9574	868.90	376.000	30.7616	820.04
200.000	20.0186	962.03	256.002	23.7795	914.65	303.999	16.1542	868.75	379.999	33.9983	819.74
202.001	23.8327	961.84	258.000	26.6138	914.48	305.999	18.3467	868.59	350.000	0.5393	812.93
203.999	27.6167	961.65	259.999	29.4165	914.31	308.002	20.5246	868.43	351.002	1.3585	812.86
206.000	31.3712	961.46	262.000	32.2225	914.14	312.000	24.8563	868.12	352.000	2.1814	812.79
208.000	35.0968	961.27	264.000	35.0072	913.97	316.000	29.1428	867.81	353.000	2.9964	812.71
199.999	0.5356	953.51	250.000	0.5522	906.81	320.002	33.4022	867.49	354.001	3.8139	812.64
200.999	2.4018	953.42	251.001	1.9583	906.73	299.999	0.5373	860.50	356.000	5.4413	812.50
202.000	4.2667	953.32	252.001	3.3611	906.64	300.999	1.6095	860.43	358.000	7.0612	812.35
202.999	6.1169	953.23	252.998	4.7549	906.56	301.999	2.6784	860.35	360.000	8.6768	812.21
204.002	7.9726	953.14	254.001	6.1508	906.48	302.999	3.7483	860.27	362.002	10.2885	812.06
205.000	9.8074	953.04	256.000	8.9196	906.31	303.999	4.8139	860.20	364.001	11.8929	811.92
206.000	11.6411	952.95	257.999	11.6802	906.14	306.001	6.9399	860.04	365.998	13.4929	811.77
207.001	13.4678	952.86	259.999	14.4260	905.98	308.001	9.0544	859.89	367.998	15.0872	811.63
207.998	15.2832	952.76	262.000	17.1534	905.81	309.999	11.1585	859.73	370.000	16.6771	811.48
208.999	17.1036	952.67	264.001	19.8717	905.64	311.998	13.2581	859.58	371.998	18.2597	811.34
209.999	18.9085	952.58	266.000	22.5742	905.48	313.150	14.4442	859.49	376.000	21.4096	811.05
212.000	22.5088	952.39	268.001	25.2601	905.31	320.001	21.5547	858.96	380.001	24.5395	810.75
214.000	26.0819	952.21	269.999	27.9315	905.14	324.001	25.6591	858.65	384.001	27.6475	810.46
216.000	29.6338	952.03	271.999	30.5873	904.98	328.000	29.7123	858.34	387.999	30.7336	810.16
218.001	33.1546	951.84	274.000	33.2303	904.81	332.000	33.7207	858.03	391.999	33.7935	809.87
210.000	0.5336	944.11	260.001	0.5329	897.56	310.001	0.5410	851.13	360.000	0.5483	803.10
211.000	2.2976	944.02	261.001	1.8638	897.48	311.000	1.5563	851.06	361.001	1.3268	803.03
212.000	4.0529	943.93	261.999	3.1888	897.40	312.000	2.5703	850.98	362.000	2.1020	802.96
213.000	5.8035	943.84	263.002	4.5147	897.31	313.150	3.7373	850.90	363.001	2.8754	802.89
214.001	7.5481	943.75	264.002	5.8357	897.23	316.001	6.6090	850.68	364.000	3.6473	802.82
214.999	9.2789	943.66	266.001	8.4649	897.07	318.001	8.6151	850.53	366.000	5.1901	802.67
216.000	11.0105	943.57	268.000	11.0800	896.90	320.000	10.6156	850.38	368.000	6.7214	802.53
216.999	12.7354	943.48	270.001	13.6816	896.74	324.000	14.5892	850.07	370.000	8.2539	802.39
218.000	14.4571	943.39	272.001	16.2669	896.58	327.999	18.5281	849.77	372.001	9.7796	802.24
218.999	16.1702	943.30	274.000	18.8399	896.41	331.999	22.4319	849.46	374.000	11.3001	802.10
219.999	17.8741	943.21	276.002	21.4054	896.25	336.000	26.3087	849.16	375.998	12.8155	801.96
222.001	21.2752	943.03	278.149	24.1399	896.07	340.001	30.1258	848.86	378.000	14.3288	801.81
224.000	24.6534	942.85	279.999	26.4839	895.92	343.998	33.9269	848.55	379.999	15.8351	801.67
226.000	28.0082	942.67	281.999	29.0076	895.76	319.998	0.5453	841.83	384.001	18.8368	801.38
228.000	31.3402	942.49	283.998	31.5099	895.60	321.002	1.5116	841.76	388.000	21.8160	801.09
229.998	34.6482	942.31	286.000	34.0091	895.43	322.000	2.4721	841.68	392.001	24.7770	800.80
220.000	0.5370	934.78	270.000	0.5321	888.35	323.001	3.4331	841.60	395.999	27.7104	800.51
221.000	2.2025	934.69	270.998	1.7920	888.27	324.000	4.3917	841.53	400.000	30.6349	800.22
221.999	3.8619	934.60	271.999	3.0518	888.19	326.002	6.3026	841.38	369.999	0.5417	793.09
223.000	5.5099	934.51	273.149	4.4950	888.10	328.000	8.2024	841.23	370.998	1.2779	793.02
224.001	7.1553	934.42	273.999	5.5578	888.03	330.001	10.1004	841.08	372.001	2.0092	792.95
225.002	8.7956	934.33	276.000	8.0502	887.87	333.149	13.0720	840.84	373.000	2.7443	792.88
226.001	10.4327	934.24	278.151	10.7130	887.70	336.000	15.7427	840.63	374.001	3.4733	792.80
227.001	12.0572	934.15	280.000	12.9919	887.55	339.999	19.4710	840.33	376.001	4.9310	792.66
227.999	13.6839	934.07	282.000	15.4483	887.39	344.001	23.1651	840.03	378.002	6.3854	792.52
229.001	15.3011	933.98	284.001	17.8928	887.23	348.002	26.8399	839.72	380.001	7.8327	792.38
230.000	16.9168	933.89	286.000	20.3228	887.07	352.002	30.4818	839.42	381.999	9.2780	792.24
232.000	20.1229	933.71	288.148	22.9203	886.89	355.998	34.0828	839.12	384.000	10.7195	792.10
234.002	23.3231	933.54	290.000	25.1447	886.74	329.999	0.5217	832.25	386.001	12.1567	791.96
236.001	26.4945	933.36	291.998	27.5413	886.58	331.002	1.4389	832.18	387.999	13.5905	791.81
238.000	29.6514	933.18	294.000	29.9284	886.42	331.999	2.3471	832.10	390.001	15.0156	791.67
240.001	32.7904	933.01	296.001	32.2948	886.26	333.001	3.2579	832.03	392.000	16.4395	791.53
230.000	0.5550	925.34	298.000	34.6466	886.10	334.000	4.1664	831.96	395.999	19.2717	791.24
231.000	2.1234	925.25	280.001	0.5389	879.15	336.000	5.9763	831.81	399.999	22.0903	790.96
232.000	3.6941	925.16	281.000	1.7329	879.07	338.002	7.7814	831.66			

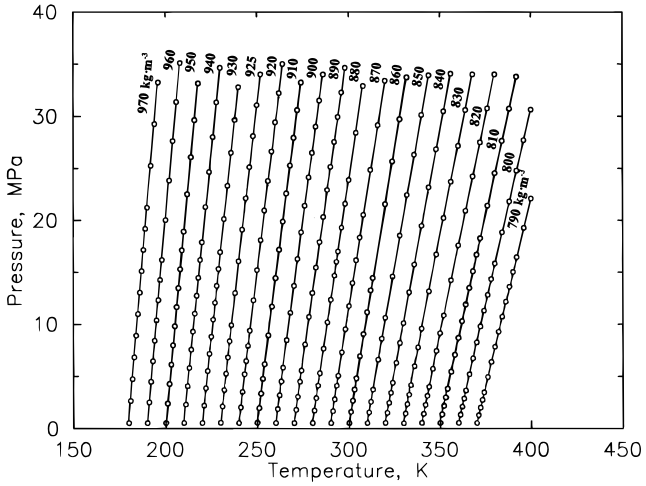

Figure 1. Range of (p,ρ,T) measurements for liquid toluene.

pressure derived from eq 1 becomes appreciable in the lower 5% of the full-scale (70 MPa) range of the instrument.

The uncertainty in the experimental values of density is due primarily to the uncertainties in the volume of the sample cell and in the determination of the amount of substance contained in the experimental volume. Before this study, methane gas was used to determine the cell volume (Magee et al., 1996). The mean ideal volume was determined to be 28.5193 cm^3 (calculated at 0 K and 0 MPa) with a statistical uncertainty (at the 1σ level) of ±0.003 . The results were confirmed by determinations with nitrogen gas. The effect of the presence of a mol fraction of 0.0002 of benzene impurity on the measurements is not pronounced. Since the molecular mass of benzene is approximately 15% lower than toluene, the mixture's molar mass is lowered by 0.003%. Mass densities are unaffected by this impurity. If molar densities were calculated from the results, then they would be 0.003% higher than we would report for 100% toluene. The sample mass determinations have an expanded uncertainty of $\pm 2 \times 10^{-3}$ g $\pm 2 \times 10^{-5}$ mol. By combining the uncertainty of the measured amount of sample with the uncertainty of the cell volume, we estimate that the values of density have an expanded uncertainty of ±0.05%.

Table 4. Saturated Liquid Density Values for Toluene Obtained from Extrapolation of Isochoric (p,ρ,T) Data to Vapor Pressure: T, Temperature (ITS-90); p_σ, Vapor Pressure Calculated from Goodwin (1989); ρ_{sat}, Saturated Liquid Density; ρ_{sat}(calc) from Eq 2; Dev = $100(\rho_{sat} - \rho_{sat}(calc))/\rho_{sat}(calc)$

		kg·m⁻³		
T/K	p_σ/kPa	ρ_{sat}	ρ_{sat}(calc)	dev
179.75	0.0001	972.62	972.59	0.003
189.73	0.0003	963.01	963.04	−0.003
199.71	0.001	953.54	953.55	−0.002
209.70	0.004	944.14	944.12	0.002
219.68	0.011	934.81	934.74	0.007
229.65	0.031	925.37	925.42	−0.005
239.64	0.076	916.04	916.11	−0.008
249.61	0.172	906.84	906.86	−0.002
259.60	0.365	897.58	897.60	−0.002
269.58	0.722	888.38	888.35	0.003
279.55	1.349	879.19	879.11	0.009
289.52	2.398	869.88	869.85	0.003
299.50	4.075	860.54	860.56	−0.002
309.48	6.651	851.17	851.21	−0.005
319.44	10.466	841.87	841.82	0.006
329.45	15.968	832.29	832.30	−0.002
339.40	23.614	822.73	822.74	−0.001
349.39	34.052	812.98	813.01	−0.004
359.36	47.916	803.14	803.16	−0.002

(p,ρ,T) Results and Comparison with an Equation of State. The experimental temperatures, pressures, and densities for liquid toluene are presented in Table 3. The original temperature measurements were made on the IPTS-68 scale and were converted to ITS-90 using a published table of conversions (Preston-Thomas, 1990). To illustrate the range of measurements, the isochoric data measured for liquid toluene are plotted in Figure 1.

Comparisons of the present isochoric (p,ρ,T) measurements with literature data have been facilitated by the equation of state of (Goodwin, 1989). The Goodwin correlation is based primarily on the results of the earlier NIST study (Straty et al. 1988), but also on selected data from other laboratories. Conversely, the Goodwin correlation is not based on the low-temperature (p,ρ,T) measurements of Muringer et al. (1985), also available before 1989. Figure 2 depicts deviations of the experimental densities reported here and other published data from the densities

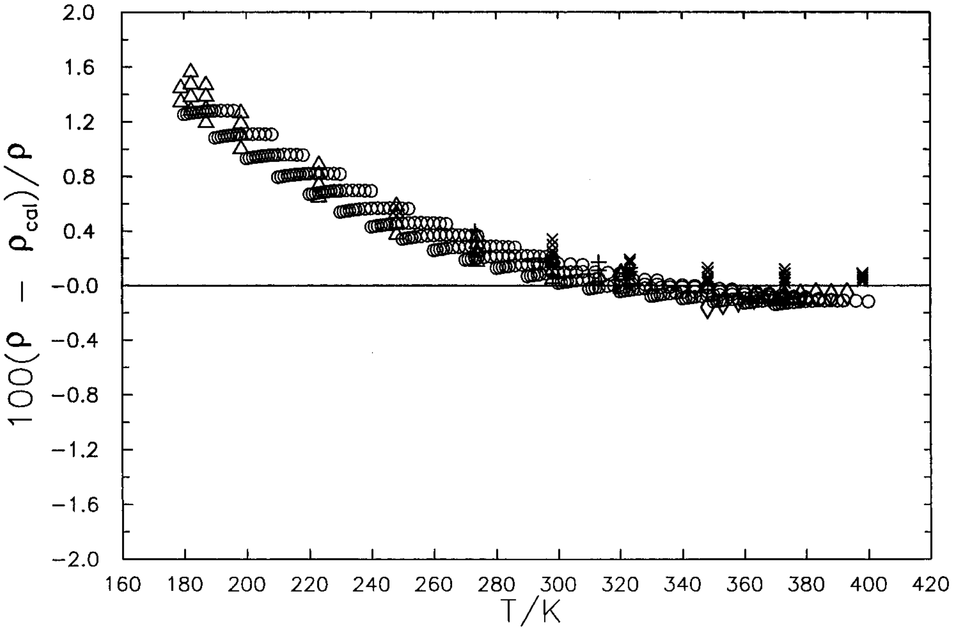

Figure 2. Percentage deviations of experimental liquid toluene densities obtained in this work [○], by Straty et al. (1988) [◇], by Kashiwagi et al. (1982) [+], by Akhundov and Abdullaev (1970) [×], and by Muringer et al., 1985) [△] from the values calculated with the equation of state of Goodwin (1989).

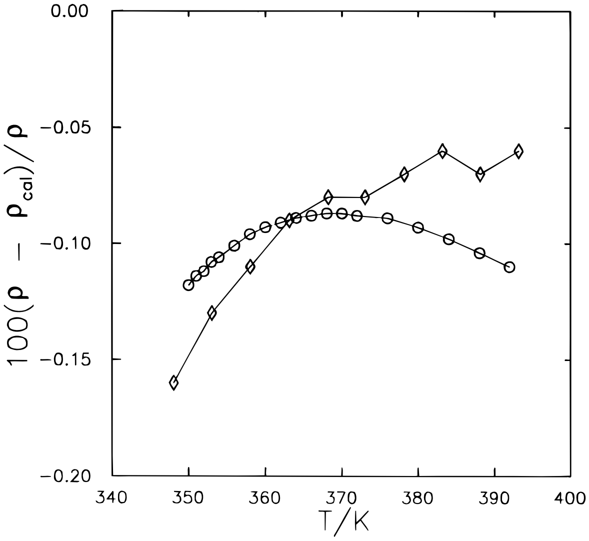

Figure 3. Percentage deviations of experimental liquid toluene densities on the 810 kg·m^{-3} isochore obtained in this work [○] and by Straty et al. (1988) [◇] from the values calculated with the equation of state of Goodwin (1989).

calculated using the Goodwin equation of state. The Goodwin equation of state should not be extrapolated below 270 K, since differences from the equation as large as 1.2% are observed. Figure 2 also shows that there is consistent agreement (±0.2%) for liquid toluene densities from Akhundov and Abdullaev (1970), Kashiwagi et al. (1982), and Muringer et al. (1985) with this study. It is now clear that Goodwin should have used the Muringer et al. data in the fitting process.

The agreement with Straty et al. (1988) is excellent. Both this study and Straty et al. made measurements on the 810 kg·m^{-3} isochore from about 350 to 400 K at pressures as high as 35 MPa. As Figure 3 shows, the densities from this study agree with Straty et al. within ±0.05%. This is a strong indication of the agreement of these two data sets over a wide range of temperatures and pressures. Because of the excellent agreement of these two data sets, an equation of state could be derived from the combined data of Straty et al. and this work. This combined data set would consist of more than 600 (p,ρ,T) states covering a temperature range from 180 to 673 K and a pressure range up to 35 MPa.

Densities of the Saturated Liquid. Saturated liquid densities derived in this study were obtained by extrapolating the isochoric data to their intersection with the vapor pressure equation presented by Goodwin (1989). The accuracy of the extrapolation depends primarily on the difference in the slope of the experimental isochore and the vapor pressure curve. At the high densities of this work, the expanded uncertainty of the temperature intersection is approximately ±0.01 K. This leads to about ±0.07% in the estimated density of the saturated liquid, including the estimated expanded uncertainty of the density measurement. The results of the saturated liquid density extrapolations are presented in Table 4.

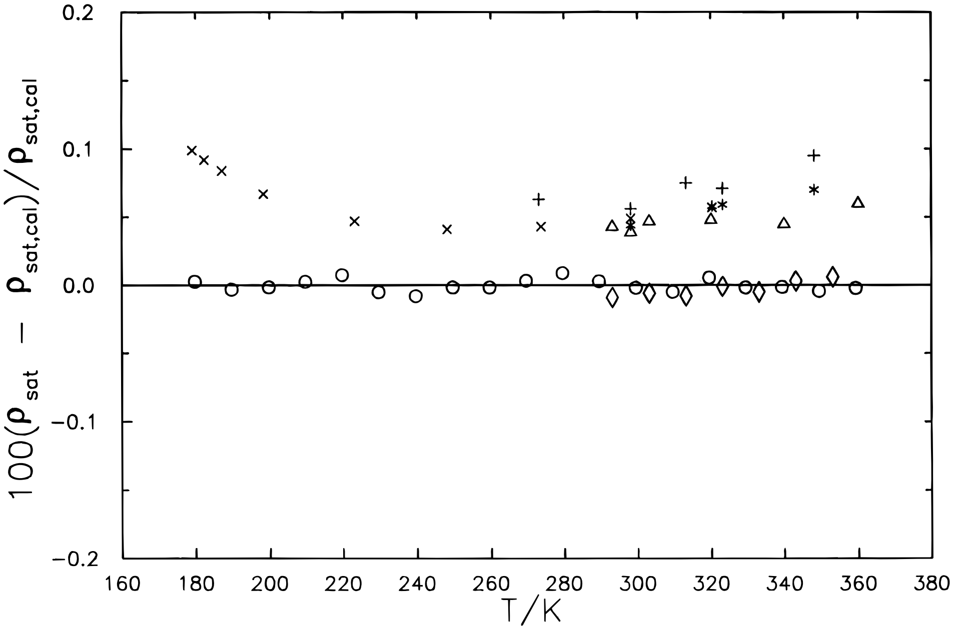

Figure 4. Percentage deviations of experimental saturated liquid densities for toluene obtained in this work [○], by Shraiber and Pechenyuk (1965) [◇], by Hales and Townsend (1972) [△], by Kashiwagi et al. (1982) [+], by Muringer et al. (1985) [×], and by Dymond et al. (1988) [*] from the values calculated with eq 2 fitted to results from this work.

Table 5. Summary of Saturated Liquid Density Measurements for Toluene and Root-Mean-Square (RMS) Deviation (%) of the Measured Densities from Those Calculated with Eq 2 for Temperatures in the Range 179 K to 360 K

source	purity	no.	range of data *T*/K	uncertainties δT/mK	$\delta\rho$	RMS (%)
this work[a]	0.99974	19	180−359	30	0.0005ρ	0.006
Dymond et al. (1988)[b]	0.99	6	298−373		0.002ρ	0.061
Hales and Townsend (1972)		14	293−490	30	0.00015ρ	0.048
Kashiwagi et al. (1982)[b]	0.995	6	273−373	10	0.001ρ	0.073
Muringer et al. (1985)[b]		9	179−320	1	0.002ρ	0.068
Shraiber and Pechenyuk (1965)		8	293−363		0.000025ρ	0.006

[a] Data used to fit eq 2. [b] Data evaluated at 0.1 MPa.

The following equation was fitted to saturated liquid densities in Table 4,

$$\rho/\rho_c = 1 + C_1\tau^{1/3} + C_2\tau^{2/3} + C_3\tau + C_4\tau^{4/3} \qquad (2)$$

where $\tau = 1 - T/T_c$, $T_c = 591.75$ K, $\rho_c = 292$ kg·m^{-3} as reported by Tsonopoulos and Ambrose (1995), and the coefficients are $C_1 = -2.692\,547\,2$, $C_2 = 18.959\,399\,8$, $C_3 = -24.949\,624\,6$, and $C_4 = 11.659\,077\,4$. The temperature range of validity for eq 2 is 180 K < T < 360 K. The ability of eq 2 to predict saturated liquid densities was tested by comparing with published high-quality experimental measurements which were not used in the fit. A pycnometer has been used (Shraiber and Pechenyuk, 1965) to measure liquid densities of toluene from 293.15 K to 363.15 K with an uncertainty of ±0.02 kg·m^{-3} (±0.0025%). Their measurements at temperatures between 293.15 K and 353.15 K agree with eq 2 within ±0.009%, with a root-mean-square deviation of 0.006%. Comparisons with this and other data sources are depicted in Figure 4, which shows the percent deviations $100(\rho_{exp} - \rho_{calc})/\rho_{calc}$ of experimental densities from densities calculated with eq 2. All of the published sources depicted in Figure 4 are in very good agreement. These deviations are as summarized in Table 5, which presents the root-mean-square deviation for each of the six published data sets compared with eq 2. All of the deviations are within the combined uncertainties of the data sets.

Conclusions. For toluene, we have reported 311 (p,ρ,T) state conditions and 19 saturated liquid densities. The uncertainty of pressure is ±0.01 to ±0.05%, that of density 0.05%, and that of temperature is ±0.03 K. We have reported a simple method for laboratory scale purification of toluene. For liquid densities in the overlapping temperature range, agreement with Straty et al. was ±0.05%. We recommend that a new equation of state be determined for toluene which is fitted primarily to data from this work and from Straty et al. at temperatures between 180 K and 673.15 K. For saturated liquid densities, agreement was 0.009% with published data reported by Shraiber and Pechenyuk, who reported an uncertainty of ±0.0025% at temperatures from 293.15 to 353.15 K. We recommend that toluene be used as a working reference material for liquid density measurements at temperatures between 293.15 and 353.15 K. At temperatures both above and below this range, the available data are also in very good agreement and can be used to check the performance of laboratory instruments used for density determinations.

Acknowledgment

The authors are grateful to Daniel Friend for technical assistance in programming the equation of state and many helpful discussions during this study. We thank W. M. Haynes for encouraging this study and many helpful discussions.

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Received for review February 12, 1996. Accepted May 1, 1996.⊗

JE960062Y

⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1996.