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Liquid Densities of Xylene Isomers and 2-Methylnaphthalene at Temperatures to 523 K and Pressures to 265 MPa: Experimental Determination and Equation of State Modeling

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ABSTRACT: Experimental density data for o-xylene, m-xylene, p-xylene, and 2-methylnaphthalene, are reported at pressures (P) to 265 MPa and temperatures (T) to 525 K using a variable-volume, high-pressure cell. The reported data agree to within ±0.4% of available literature data. o-Xylene has the largest densities and p-xylene has the smallest densities in the $P-T$ range investigated in this study although the 525 K isotherms for all three aromatics virtually superpose at high pressures. The aromatic densities are modeled using the Peng−Robinson (PR), high-temperature, high-pressure, volume-translated Peng−Robinson (HTHP VT-PR), and perturbed chain statistical associating fluid theory (PC-SAFT) equations of state (EoS). Generally, the PC-SAFT EoS gives the best predictions of the HTHP density data with mean absolute percent deviations (δ) within 1.0%, even though the pure-component parameters are fitted to low-pressure vapor pressure and saturated liquid density data. δ decreases to 0.4% for calculations with a new set of PC-SAFT parameters obtained from a fit of the HTHP experimental density data obtained in this study.

1. INTRODUCTION

High-temperature, high-pressure (HTHP) density data play an important role in the design and optimization of processes related to ultradeep reservoirs in the petroleum industry. HTHP density data are also used to test the performance capabilities of a equation of state (EoS) at extreme conditions. Our research group has previously reported HTHP density data and EoS modeling for short-chain and long-chain alkanes.[1−3] This study focuses on the experimental determination and EoS modeling of the density of several aromatic hydrocarbons including o-xylene, m-xylene, p-xylene, and 2-methylnaphthalene at the pressures to ∼265 MPa and the temperatures to ∼523.2 K. In this, and earlier studies,[1,2] a variable-volume, high-pressure cell technique is used to generate the HTHP experimental density data that are then modeled with the Peng−Robinson (PR) EoS,[4] the high-temperature, high-pressure, volume-translated Peng−Robinson (HTHP VT-PR) EoS,[5] and the perturbed-chain statistical associating fluid theory (PC-SAFT) EoS.[6]

2. EXPERIMENTAL SECTION

2.1. Materials. o-Xylene (99 wt % purity), m-xylene (99 wt % purity), p-xylene (99 wt % purity), and 2-methylnaphthalene (97 wt % purity) were purchased from Sigma-Aldrich and used as received.

2.2. Apparatus and Measurements. The high-pressure apparatus and technique used in this study has been described in detail[1,2,7] and is only briefly reviewed here. The system pressure

is measured with a pressure transducer (Viatran Corporation, model 245, 0−345 MPa) with a standard uncertainty of 0.07 MPa to pressures of 56 and 0.35 MPa for pressures from 56 to 275 MPa, and the system temperature is measured with a Type K thermocouple (Omega Corporation) with a standard uncertainty of 0.1 K calibrated against an immersion thermometer (Fisher Scientific, calibrated using methods traceable to NIST standards). The experimentally observed temperature variation for each reported isotherm is within ±0.10 K. The internal cell volume is determined with a linear variable differential transformer (LVDT, Schaevitz Corporation, model 1000 HR) calibrated using propane and n-decane density data provided by NIST.[8] Prior to loading, the cell is flushed three times with propane to remove residual air that does not readily dissolve in the hydrocarbons considered in study, whereas residual propane, which amounts to less than 0.2 wt % in the hydrocarbon of interest, readily dissolves in these hydrocarbons. Typically 6.0 to 7.0 g of hydrocarbon with a standard uncertainty of 0.0002 g are loaded into the cell, the system pressure and temperature are fixed, and the piston position is recorded to obtain the cell volume and, hence, a density data point. The data for a given isotherm are obtained at random pressures to minimize potential experimental artifacts in the measurements. The standard

Table 1. _o_-Xylene Density Data Obtained in This Study at 294.9, 325.0, 423.9, and 523.2 K and Pressures to 265 MPa. The Designation "Solidification" Signifies a Liquid−Solid Phase Transition

294.9 ± 0.1 K		325.0 ± 0.1 K		423.9 ± 0.1 K		523.2 ± 0.1 K	
P (MPa)	density (kg/m^3)	P (MPa)	density (kg/m^3)	P (MPa)	density (kg/m^3)	P (MPa)	density (kg/m^3)
4.0	882	3.6	853	4.1	768	6.5	665
7.5	886	7.1	857	7.2	773	9.2	676
10.5	888	10.3	860	10.6	778	12.8	684
14.3	891	14.4	864	14.1	782	12.8	685
21.2	895	17.6	866	17.7	786	20.2	702
28.3	900	21.2	869	21.0	789	27.9	718
35.8	904	27.5	873	28.0	796	28.4	718
42.6	907	34.9	878	35.1	803	35.1	730
49.5	911	41.6	883	41.9	809	35.7	730
56.5	915	48.8	886	48.8	815	44.6	744
69.6	921	55.6	891	55.6	821	45.6	744
83.2	928	68.7	898	69.6	831	54.7	757
103.8	936	82.9	905	82.9	841	69.1	773
124.2	944	103.5	915	103.9	854	88.8	791
138.9	950	124.9	924	124.3	866	114.6	811
152.4	955	138.9	930	138.9	874	144.4	831
172.6	961	154.5	936	153.3	881	178.0	850
204.1	972	172.9	943	172.9	891	204.6	864
solidification		208.4	955	207.7	906	233.5	853
		240.3	966	240.2	921	262.0	886
		263.2	975	265.4	931		

Table 2. _m_-Xylene Density Data Obtained in This Study at 295.7, 325.4, 422.4, and 522.9 K and Pressures to 269 MPa

295.7 ± 0.1 K		325.4 ± 0.1 K		422.4 ± 0.1 K		522.9 ± 0.1 K	
P (MPa)	density (kg/m^3)	P (MPa)	density (kg/m^3)	P (MPa)	density (kg/m^3)	P (MPa)	density (kg/m^3)
3.8	864	4.4	838	3.9	751	9.7	659
7.7	868	7.6	843	7.2	757	12.5	665
10.5	869	10.4	845	10.9	762	12.8	665
14.0	872	15.3	849	14.4	767	20.4	684
17.5	875	21.3	854	17.4	770	28.4	701
21.4	877	24.3	855	21.8	775	28.5	701
28.3	881	29.5	859	27.8	782	30.2	704
34.8	885	35.0	863	35.1	789	38.8	718
43.3	890	42.3	867	41.5	795	39.4	718
55.6	896	49.4	873	48.2	801	49.9	734
70.3	903	56.5	877	56.1	808	49.9	734
84.7	910	70.9	884	71.0	820	51.1	734
103.7	919	84.2	891	86.6	831	66.7	753
123.9	927	104.7	902	104.7	842	79.1	765
139.6	933	125.2	909	125.2	855	79.4	765
154.0	938	140.2	916	139.8	863	99.7	782
173.8	945	156.5	922	154.0	870	118.7	797
209.6	957	174.8	928	174.0	880	118.8	797
242.9	968	210.2	941	210.0	896	139.4	811
265.1	975	241.4	951	241.3	909	139.7	811
		268.9	959	264.3	919	164.7	826
						166.7	827
						191.4	839
						230.0	855
						262.7	868

uncertainties, u, are $u(T) = 0.20$ K, $u(P) = 0.07$ MPa below 56 and 0.35 MPa from 56 to 275 MPa, and the estimated accumulated (combined) expanded experimental uncertainty, U_c, obtained by multiplying the standard uncertainty by a coverage factor, is $U_c(\rho) = 0.75\% \cdot \rho$ (at coverage factor of 2 for an interval having a confidence level of approximately 95%) where ρ is a density data point.[9]

3. EXPERIMENTAL RESULTS

Tables 1 through 4 list the density data for _o_-xylene, _m_-xylene, _p_-xylene, and 2-methylnaphthalene obtained in this study at pressures to ~265 MPa and temperatures to ~525 K. Given that 2-methylnaphthalene is a solid at room temperature, liquid densities of 2-methylnaphthalene are reported staring at ~325 K,

Table 3. _p_-Xylene Density Data Obtained in This Study at 295.0, 325.7, 423.3, and 523.0 K and Pressures to 265 MPa. The Designation "Solidification" Signifies a Liquid−Solid Phase Transition

295.0 ± 0.1 K		325.7 ± 0.1 K		423.3 ± 0.1 K		523.0 ± 0.1 K	
P (MPa)	density (kg/m³)	P (MPa)	density (kg/m³)	P (MPa)	density (kg/m³)	P (MPa)	density (kg/m³)
3.8	858	4.0	833	3.9	749	7.8	643
7.3	863	7.2	837	7.2	753	8.1	645
11.1	866	10.6	840	10.6	759	14.0	665
15.1	869	14.3	843	14.3	763	14.6	665
18.0	871	17.6	846	17.3	767	19.7	679
20.8	873	21.3	849	21.2	772	19.8	679
24.3	875	28.0	854	27.8	779	27.5	695
solidification		34.5	858	34.8	786	36.0	709
		42.2	863	42.2	793	36.2	709
		49.1	867	49.2	800	36.4	709
		55.5	871	55.6	806	47.3	725
		61.8	876	69.2	816	48.1	725
		69.9	880	83.3	826	55.4	735
		83.1	887	103.4	840	55.8	735
		94.0	893	124.1	854	57.0	735
		104.1	898	138.6	861	70.1	751
		117.2	905	154.7	870	88.6	768
		solidification		173.4	878	89.2	767
				208.8	895	106.4	782
				240.9	908	125.5	796
				264.5	918	126.0	797
						152.3	814
						181.3	828
						210.1	843
						252.9	860

while the densities of _o_-xylene, _m_-xylene, and _p_-xylene are reported starting at ∼293 K. Note that a liquid−solid phase boundary is crossed for _o_-xylene, _p_-xylene, and 2-methylnaphthalene, termed a "solidification" in the data tables. Details are found elsewhere on the high-pressure solidification behavior for these aromatic hydrocarbons.[10]

The density data are fit to the modified Tait equation to provide a facile method to calculate densities at different temperatures and pressures.

$$\frac{\rho - \rho_0}{\rho} = C \log_{10} \frac{P + B}{P_0 + B} \tag{1}$$

where ρ is density in kg/m³, ρ_0 is density at $P_0 = 0.1$ MPa, P is pressure, in MPa, and B and C are fitted parameters. For a given hydrocarbon fluid, C is typically a temperature-independent constant, while ρ_0 and B are quadratic functions of temperature, given as[11]

$$\rho_0 = \sum_{i=0}^{2} a_i T^i \tag{2}$$

$$B = \sum_{i=0}^{2} b_i T^i \tag{3}$$

where a_i and b_i are fitted coefficients listed in Table 5 for _o_-xylene, _m_-xylene, _p_-xylene, and 2-methylnaphthalene. At high temperatures ρ_0 is a "pseudo"-liquid density since P_0 is not precisely equal to 0.1 MPa. The mean absolute percent deviation (δ) between experimental data obtained in this study, $\rho_{i,exp}$, and calculated values with the modified Tait equation, $\rho_{i,corr}$, for n data points is defined as

$$\delta\ (\%) = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{\rho_{i,exp} - \rho_{i,corr}}{\rho_{i,corr}} \right| \times 100 \tag{4}$$

The largest δ, 0.30%, is smaller than the estimated expanded uncertainty ($k = 2$), ±0.75%, of the experimental data. Calculated values of ρ_0 agree with ambient-pressure density data reported in the literature[11−20] to within ±0.10%.

Table 6 compares densities reported in this study with those available in the literature. The density data obtained in this study extend the current database to higher temperatures and/or higher pressures. Note that this table does not include references only reporting density data at atmospheric pressure.[12−16] It is worth noting that the _m_-xylene and _p_-xylene density data reported by Yokoyama et al.[21] are not consistent with other references. Their original publication reported _m_-xylene liquid density data at 298.15 K and pressures to 40 MPa and a solidification boundary at 298.15 K and 44 MPa. For _p_-xylene they reported liquid density data at the same temperature and pressures to 200 MPa without observing any solidification boundary. However, other references reported the solidification boundary for _m_-xylene at ∼300 K and a pressure greater than 300 MPa[22] and a solidification boundary for _p_-xylene at ∼300 K and a pressure of ∼44 MPa.[23,24] It is very likely that Yokoyama et al. switched labels for the data sets for _m_-xylene and _p_-xylene. In fact, Castro et al.[23] reported _p_-xylene solidification data that are in close agreement with the value reported here at 295 K and with an expanded solidification data set reported in a more detailed study by our group.[10]

Figures 1 through 4 show the percent deviation between available literature data and the densities calculated with the modified Tait equation fit to the data obtained in this study. Note the maximum temperature in these figures is 370 K except for the case of _m_-xylene since Caudwell et al.[11] reported _m_-xylene density data to 473 K. Figures 1 through 4 also do not include density data reported at atmospheric pressure[12−16] or data that

Table 4. 2-Methylnaphthalene Density Data Obtained in This Study at 326.7, 376.8, 421.3, and 523.8 K and Pressures to 265 MPa. The Designation "Solidification" Signifies a Liquid−Solid Phase Transition

326.7 ± 0.1 K		376.8 ± 0.1 K		421.3 ± 0.1 K		523.8 ± 0.1 K	
P (MPa)	density (kg/m³)	P (MPa)	density (kg/m³)	P (MPa)	density (kg/m³)	P (MPa)	density (kg/m³)
3.6	979	4.1	944	4.1	909	5.6	814
7.4	982	7.4	946	7.3	912	9.7	820
10.6	984	10.5	949	10.7	915	9.4	820
14.5	987	14.0	953	14.3	918	16.9	831
17.2	990	17.7	955	18.2	922	16.0	831
21.2	992	21.3	958	21.3	924	15.5	831
28.2	996	27.9	962	27.8	930	19.9	836
34.8	1000	35.0	967	35.1	935	25.1	843
42.1	1004	42.3	972	42.2	941	31.3	850
49.4	1009	49.2	977	49.0	946	34.9	854
55.9	1013	56.0	981	55.5	951	42.6	862
62.2	1016	69.5	989	69.0	960	42.9	862
69.3	1020	83.3	997	83.5	969	54.4	873
solidification		104.6	1009	104.1	980	61.2	880
		123.9	1018	124.5	992	63.5	882
		138.8	1025	139.3	999	80.3	895
		152.0	1031	153.6	1006	80.3	895
		173.6	1041	174.4	1016	98.7	909
		207.5	1055	208.5	1032	110.9	917
		240.1	1066	239.4	1044	123.0	925
		265.2	1076	262.9	1054	123.3	925
						145.8	938
						170.1	952
						170.0	952
						196.5	965
						225.0	978
						260.2	994

Table 5. Coefficients, Number of Data Points (n), and Mean Absolute Percent Deviation (δ) for the Best Fit of the Modified Tait Equation for o-Xylene, m-Xylene, p-Xylene, and 2-Methylnaphthalene (2-MNP) Density Data

coefficient	o-xylene	m-xylene	p-xylene	2-MNP
a_0 (kg m⁻³)	1051.1	1029.6	1029.4	1197.8
a_1 (kg m⁻³ K⁻¹)	−0.370	−0.319	−0.334	−0.576
$a_2 \times 10^4$ (kg m⁻³ K⁻²)	−7.337	−8.386	−8.242	−2.719
b_0 (MPa)	438.2	401.6	460.9	676.9
b_1 (MPa K⁻¹)	−1.443	−1.331	−1.597	−2.397
$b_2 \times 10^3$ (MPa K⁻²)	1.225	1.128	1.425	2.300
C	0.219	0.210	0.218	0.211
n	80	87	70	82
δ (%)	0.27	0.17	0.19	0.30

cover a very limited pressure range.[25−27] The largest percent deviation is less than 0.40% for all of the aromatics considered in this study, except for the deviation with the work of Skinner et al.[28] (not shown in the figures) who reported density data for o-xylene at 303.15 K and pressures to 200 MPa and p-xylene at the same temperature and pressures to 70 MPa. The percent deviation with the data reported by Skinner et al.[28] reaches a maximum of 0.80% for o-xylene and 1.20% for p-xylene. The reasons for these larger deviations are not readily apparent, especially given that the present data agree with o-xylene data from Taravillo et al.[29] and the p-xylene data from Castro et al.[23] to within ±0.2% and both groups reported experimental uncertainties within ±0.1%. Further, an inconsistency is noted for the p-xylene data of Takagi et al.,[30] who reported a density of

890.4 kg/m³ at 303.15 K and 40 MPa and an even smaller density of 885.1 kg/m³ at the same temperature but at 10 MPa higher pressure. The data for m-xylene and p-xylene at pressures other than 40 MPa reported by Takagi et al.[30] agree with data obtained in the present study and with other literature data to within ±0.1%. Therefore, the p-xylene density at 303.15 K and 40 MPa reported by Takagi et al.[30] is assumed to be in error and is excluded from comparison.

The trends in the xylene data are shown in Figure 5 where the lowest temperature, 293.2 K, and the highest temperature, 523.2 K, density isotherms have been calculated with the Tait equation. o-Xylene has the largest densities and p-xylene the smallest densities at near atmospheric pressure, which agree with the trend reported in the literature.[12] The ordering of the three density isotherms remains in the high-pressure region of the diagram at 293.2 K. However, at 523.2 K and high pressures, the three density isotherms become almost indistinguishable. In the next section calculations are presented with the PR, HTHP VT-PR, and the PC-SAFT EoS to demonstrate the ability of these equations to predict the values of the densities.

4. DENSITY PREDICTIONS

4.1. Equation of State Parameters. The PR EoS, HTHP VT-PR EoS, and PC-SAFT EoS are used in this study to predict the densities of o-xylene, m-xylene, p-xylene, and 2-methylnaphthalene. Only the parameters needed with these three equations are reported since details on these three equations can be found elsewhere.[4−6,31] Table 7 lists the critical temperatures, T_c, critical pressures, P_c, and acentric factor, ω, along with the molecular weight, M_w, of the aromatic compounds needed for the PR EoS

Table 6. Comparison of Data Obtained in This Study to Data Available in the Literature for *o*-Xylene, *m*-Xylene, *p*-Xylene, and 2-Methylnaphthalene

| literature	literature T range (K)	literature max P (MPa)	literature data points	T (K) and P (MPa) for density data obtained in this study that extend available literature data
o-Xylene				
Bridgman[35]	298	3920	12	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 275
Et-Tahir et al.[20]	298 to 363	40	45	293 K: P < 265 323 K: 40 < P < 265 423 K: P < 265 523 K: P < 275
Garg et al.[25]	318 to 373	10	72	293 K: P < 265 323 K: 10 < P < 265 423 K: P < 265 523 K: P < 275
Skinner et al.[28]	303	207	6	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 275
Takagi et al.[36]	303	180	19	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 265
Taravillo et al.[29]	257 to 298	108	139	293 K: 108 < P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 275
Yang et al.[27]	313 to 473	2	50	293 K: P < 265 323 K: 2 < P < 265 423 K: 2 < P < 265 523 K: P < 275
m-Xylene				
Bridgman[35]	298	3920	19	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 275
Caudwell et al.[11]	298 to 473	200	75	293 K: P < 265 323 K: 200 < P < 265 423 K: 200 < P < 265 523 K: P < 275
Chang et al.[17,18]	298 to 413	30	63	293 K: P < 265 323 K: 30 < P < 265 423 K: P < 265 523 K: P < 275
Et-Tahir et al.[20]	298 to 363	40	45	293 K: P < 265 323 K: 40 < P < 265 423 K: P < 265 523 K: P < 275
Garg et al.[25]	318 to 373	10	72	293 K: P < 265 323 K: 10 < P < 265 423 K: P < 265 523 K: P < 275
Takagi et al.[30]	303	200	21	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 265
Taravillo et al.[37]	226 to 299	110	182	293 K: 110 < P < 265
				323 K: P < 265 423 K: P < 265 523 K: P < 275
Yokoyama et al.[21]*	298	200	42	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 275
p-Xylene				
Bridgman[35,38]	298	3920	9	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 265
Castro et al.[23]	288 to 303	43	37	293 K: 43 < P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 265
Et-Tahir et al.[20]	313 to 363	40	36	293 K: P < 265 323 K: 40 < P < 265 423 K: P < 265 523 K: P < 275
Fang et al.[26]	313 to 473	3	39	293 K: P < 265 323 K: 3 < P < 265 423 K: 3 < P < 265 523 K: P < 265
Garg et al.[25]	318 to 373	10	72	293 K: P < 265 323 K: 10 < P < 265 423 K: P < 265 523 K: P < 275
Skinner et al.[28]	303	69	4	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 275
Takagi et al.[30]	303	50	6	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 265
p-Xylene (continued)				
Yokoyama et al.[21]	283 to 298	40	5	293 K: 200 < P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 275
Yang et al.[27]	313 to 473	2	50	293 K: P < 265 323 K: 2 < P < 265 423 K: 2 < P < 265 523 K: P < 275
2-Methylnaphthalene				
Bridgman[35]	298	3920	9	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 275
Ebina et al.[19]	333 to 343	140	26	293 K: P < 265 323 K: P < 265 423 K: P < 265 523 K: P < 275
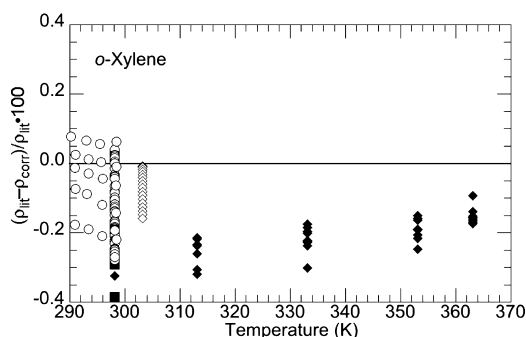
Figure 1. Percent deviation for *o*-xylene densities obtained with the Tait equation fit to data obtained in this study, $\rho_{i,corr}$, and literature data, $\rho_{i,lit}$, of Bridgman[35] (■), Et-Tahir et al.[20] (♦), Takagi et al.[36] (◇), and Taravillo et al.[29] (○).
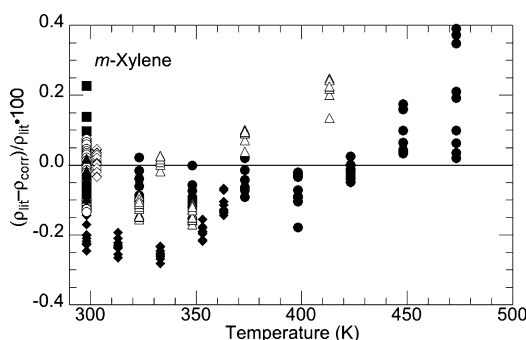
Figure 2. Percent deviation for *m*-xylene densities obtained with the Tait equation fit to data obtained in this study, $\rho_{i,corr}$, and literature data, $\rho_{i,lit}$, of Bridgman[35] (■), Caudwell et al.[11] (●), Chang et al.[17,18] (△), Et-Tahir et al.[20] (♦), Takagi et al.[30] (◇), Taravillo et al.[37] (○), and Yokoyama et al.[21] (▲).
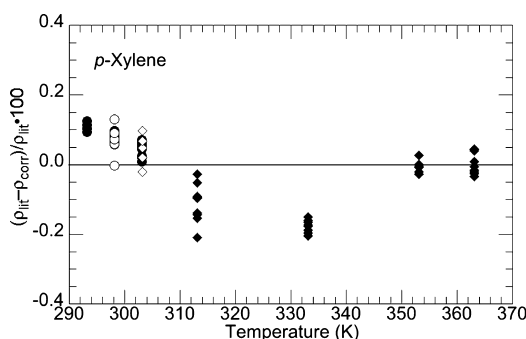
Figure 3. Percent deviation for *p*-xylene densities obtained with the Tait equation fit to data obtained in this study, $\rho_{i,corr}$, and literature data, $\rho_{i,lit}$, of Castro et al.[23] (●), Et-Tahir et al.[20] (♦), Takagi et al.[30] (◇), and Yokoyama et al.[21] (○).

and the HTHP VT-PR EoS. Table 8 lists the number of segments, m, temperature-independent segment diameter, σ, and interaction energy, ε/k_B, for each compound needed for the PC-SAFT EoS. In this instance the PC-SAFT pure-component parameters are either obtained from the literature,[6,32] Table 8a, or from a fit of the high-pressure density data reported here, Table 8b.

4.2. Density Predictions. Figure 6 shows density calculations for *m*-xylene at pressures to 265 MPa and temperatures to 523.2 K that are representative of the performance of the PR, HTHP VT-PR, and PC-SAFT EoS for each of the aromatic hydrocarbons considered in this study. The fit of each equation is
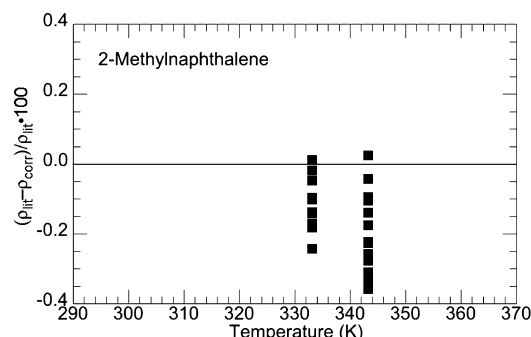

Figure 4. Percent deviation for 2-methylnaphthalene densities obtained with the Tait equation fit to data obtained in this study, $\rho_{i,corr}$, and literature data, $\rho_{i,lit}$, of Ebina et al.[19] (■).

Table 7. Molecular Weight, M_w, Critical Temperature, T_c, Critical Pressure, P_c, and Acentric Factor, ω, for *o*-Xylene, *m*-Xylene, *p*-Xylene, and 2-Methylnaphthalene (2-MNP) Obtained from Reid et al.[39]

compound	M_w	T_c (K)	P_c (MPa)	ω
o-xylene	106.2	630.2	3.7	0.314
m-xylene	106.2	617.0	3.5	0.331
p-xylene	106.2	616.2	3.5	0.324
2-MNP	142.2	761.0	3.5	0.382

Table 8. Molecular Weight, M_w, Number of Segments, m, Temperature-Independent Segment Diameter, σ, and Interaction Energy, ε/k_B, for *o*-Xylene, *m*-Xylene, *p*-Xylene Obtained from (a) Gross and Sadowski[6] and 2-Methylnaphthalene (2-MNP) from Tihic et al.[32] and from (b) a Fit of the Density Data Obtained in This Study

	(a)		
compound	M_w	m	σ (Å)	ε/k_B (K)
o-xylene	106.2	3.1362	3.7600	291.05
m-xylene	106.2	3.1861	3.7563	283.98
p-xylene	106.2	3.1723	3.7781	283.77
2-MNP	142.2	3.3234	3.9533	347.55
	(b)		
compound	M_w	m	σ (Å)	ε/k_B (K)
o-xylene	106.2	4.6648	3.2765	254.25
m-xylene	106.2	4.6772	3.2909	251.42
p-xylene	106.2	4.8463	3.2492	244.69
2-MNP	142.2	5.9772	3.2045	267.34

quantified by calculating the δ, shown in Table 9, for each aromatic hydrocarbon. Here the δ is defined as

$$\delta\ (\%) = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{\rho_{i,pred} - \rho_{i,exp}}{\rho_{i,exp}} \right| \times 100 \tag{5}$$

where $\rho_{i,exp}$ is the density obtained and $\rho_{i,pred}$ is the density calculated with an EoS. The PR EoS isotherms shown in Figure 6a and the δ values listed in Table 9 demonstrate clearly that the PR EoS does a poor job modeling compressed liquid densities, which is consistent with results in previously reported studies.[1,33,34] Further, for all the aromatic compounds considered in this study, the predicted density isotherms with the PR EoS tend to converge at extreme pressures, which has also been previously reported.[1,2] In contrast with the PR EoS results, Figure 6b shows that the HTHP VT-PR EoS provides a better fit
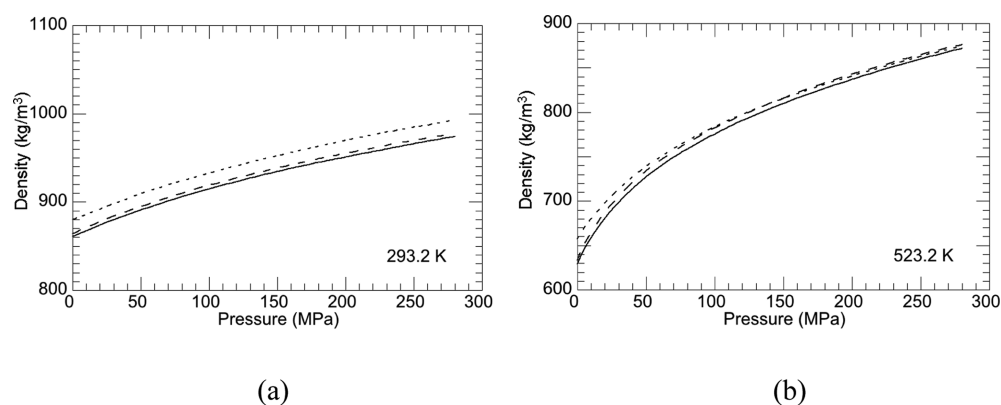
Figure 5. Variation of the densities of o-xylene (···), m-xylene (---), and p-xylene (———) calculated with the modified Tait equation at (a) 293.2 K and (b) 523.2 K. The density scales are different for each isotherm, but the differences between the maximum and the minimum densities, 300 kg/m³, are equal for easy comparison.
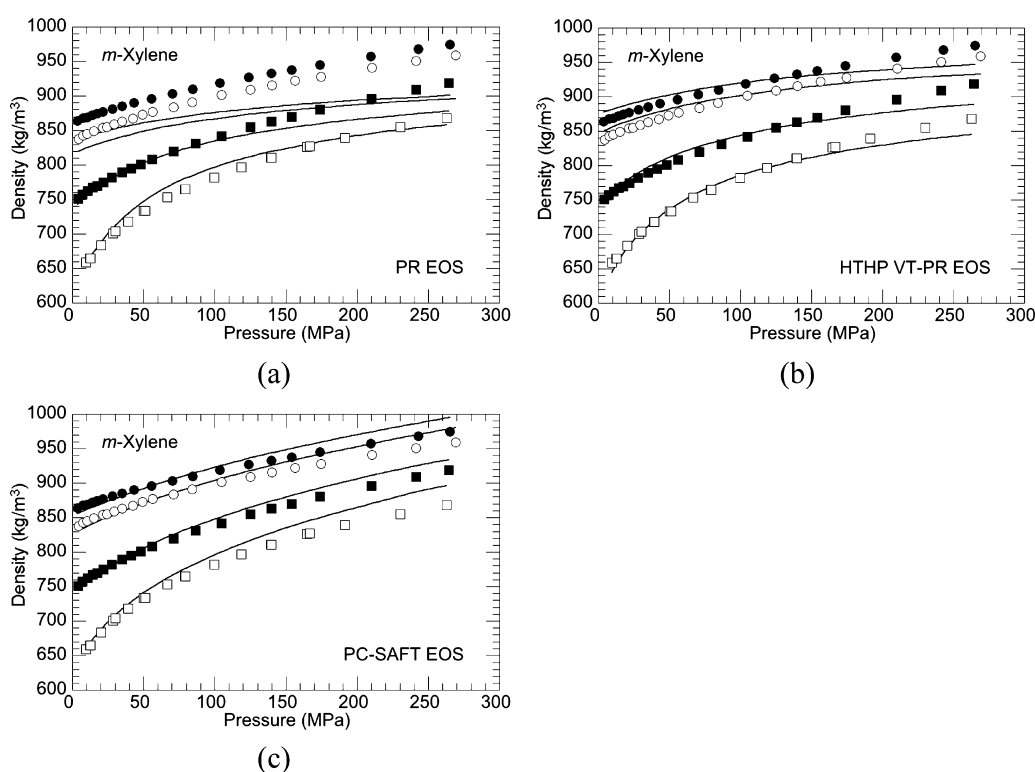

Figure 6. Comparison of m-xylene density data (symbols) obtained in this study with calculated densities (lines) with (a) PR EoS, (b) HTHP VT-PR EoS, (c) PC-SAFT EoS at temperatures of 295.7 K (●), 325.4 K (○), 422.4 K (■), and 522.9 K (□).

Table 9. Mean Absolute Percent Deviation (δ) and Standard Deviation (λ) for the PR, HTHP VT-PR, PC-SAFT EoS with Parameters from Gross and Sadowski[6] and Tihic et al.,[32] and PC-SAFT with Parameters from a Fit of the Density Data in This Study (HTHP PC-SAFT) for o-Xylene, m-Xylene, p-Xylene, 2-Methylnaphthalene (2-MNP), and all the Four Compounds (Overall)

	PR		HTHP VT-PR		PC-SAFT		HTHP PC-SAFT	
compound	δ (%)	λ (%)	δ (%)	λ (%)	δ (%)	λ (%)	δ (%)	λ (%)
o-xylene	2.00	1.27	1.62	0.81	0.85	0.57	0.24	0.20
m-xylene	2.49	1.84	1.04	0.71	1.03	0.70	0.22	0.24
p-xylene	2.05	1.22	0.87	0.76	0.95	0.63	0.22	0.24
2-MNP	4.53	2.57	2.23	0.90	0.98	0.81	0.36	0.26
overall	2.79	2.10	1.46	0.96	0.95	0.69	0.26	0.24

of the density isotherms especially at extreme pressures. However, the HTHP VT-PR EoS consistently underestimates the densities at pressures greater than 200 MPa for all of the aromatic density isotherms.
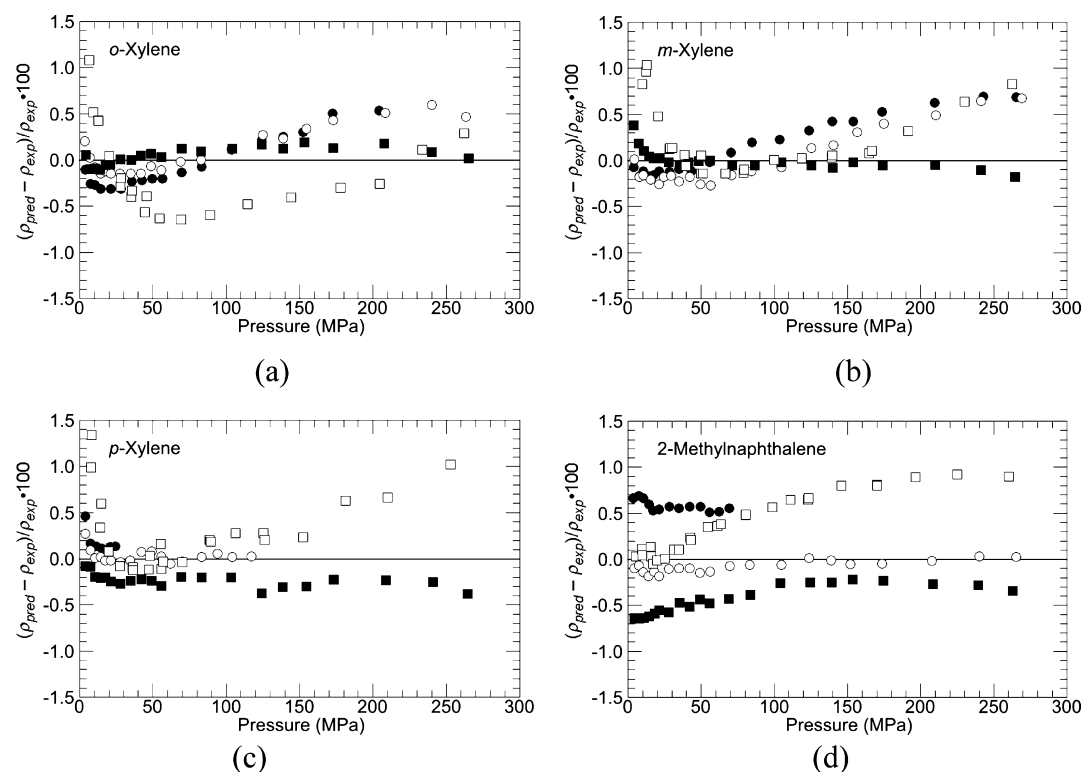
Figure 7. Percent deviation between density data obtained in this study and calculated results using HTHP PC-SAFT parameters optimized by fitting data reported in this study for (a) o-xylene, (b) m-xylene, (c) p-xylene, and (d) 2-methylnaphthalene at ~293.2 K (●), ~323.2 K (○), ~423.2 K (■), and ~523.2 K (□).

Figure 6c shows a comparison of experimental and predicted density isotherms using the PC-SAFT EoS with pure-component parameters obtained from the literature.[6,32] The δ for PC-SAFT EoS are smaller than those for the HTHP VT-PR EoS, although the PC-SAFT EoS overestimates the density at high temperatures and pressures, as is also found in previous studies.[1−3] Nevertheless, the PC-SAFT EoS provides reasonable predictions for compressed liquid densities at high pressures even though the literature values for the pure-component parameters used here were obtained by simultaneously fitting subcritical vapor pressure and liquid density data.[6,32]

4.3. HTHP PC-SAFT Parameterization. Alternative PC-SAFT pure-component parameters, found in Table 8b for o-xylene, m-xylene, p-xylene, and 2-methylnaphthalene, are obtained by fitting the PC-SAFT EoS to the HTHP density data reported in this study. These parameters complement those reported by Burgess et al.[31] who derived new sets of pure-component HTHP PC-SAFT parameters for normal alkanes. The δ values listed in Table 9 are within 0.4% for all four aromatic hydrocarbons when using the HTHP PC-SAFT parameters. Figure 7 shows deviation graphs for experimental and HTHP PC-SAFT calculated densities. In these instances, the maximum percent deviation is generally within ±1.0% for all four aromatic compounds.

5. CONCLUSION

This study extends the current density database for o-xylene, m-xylene, p-xylene, and 2-methylnaphthalene to temperatures of 523 K and pressures of 265 MPa. The density data agree with available literature data to within ±0.4%. The PR EoS, HTHP VT-PR EoS, and PC-SAFT EoS are used to model the densities of the studied aromatic compounds. The HTHP VT-PR EoS gives better predictions than PR EoS, but it should be noted that

HTHP VT-PR EoS has more parameters. When using pure-component parameters from the literature,[6,32] the PC-SAFT EoS provides good density predictions with mean absolute percent deviation (δ) within 1.0%, although it overpredicts the densities at extreme temperatures and pressures. Therefore, new sets of PC-SAFT parameters are determined for o-xylene, m-xylene, p-xylene, and 2-methylnaphthalene by fitting to the density data obtained in this study with δ within 0.4%.

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Notes

The authors declare no competing financial interest.

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dx.doi.org/10.1021/ie400805y | *Ind. Eng. Chem. Res.* 2013, 52, 11732−11740