

Effect of Isomeric Structures of Branched Cyclic Hydrocarbons on Densities and Equation of State Predictions at Elevated Temperatures and Pressures

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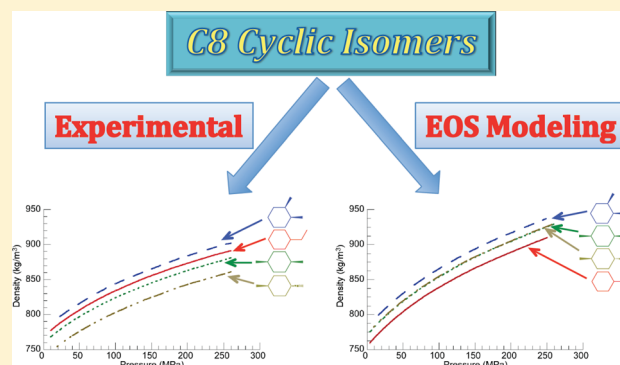
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S Supporting Information

ABSTRACT: The *cis* and *trans* conformation of a branched cyclic hydrocarbon affects the packing and, hence, the density, exhibited by that compound. Reported here are density data for branched cyclohexane (C6) compounds including methylcyclohexane, ethylcyclohexane (ethylC6), *cis*-1,2-dimethylcyclohexane (*cis*-1,2), *cis*-1,4-dimethylcyclohexane (*cis*-1,4), and *trans*-1,4-dimethylcyclohexane (*trans*-1,4) determined at temperatures up to 525 K and pressures up to 275 MPa. Of the four branched C6 isomers, *cis*-1,2 exhibits the largest densities and the smallest densities are exhibited by *trans*-1,4. The densities are modeled with the Peng–Robinson (PR) equation of state (EoS), the high-temperature, high-pressure, volume-translated (HTHP VT) PREoS, and the perturbed chain, statistical associating fluid theory (PC-SAFT) EoS. Model calculations highlight the capability of these equations to account for the different densities observed for the four isomers investigated in this study. The HTHP VT-PREoS provides modest improvements over the PREoS, but neither cubic EoS is capable of accounting for the effect of isomer structural differences on the observed densities. The PC-SAFT EoS, with pure component parameters from the literature or from a group contribution method, provides improved density predictions relative to those obtained with the PREoS or HTHP VT-PREoS. However, the PC-SAFT EoS, with either set of parameters, also cannot fully account for the effect of the C6 isomer structure on the resultant density.



1. INTRODUCTION

Hydrocarbon pressure–volume–temperature (PVT) data are indispensable for the design and optimization of processes related to the recovery and purification of oil. In fact, accessing ultradeep petroleum reservoirs requires fluid-property information, including density data, up to temperatures of 523 K and pressures in excess of 240 MPa.¹ In modeling studies, high-temperature, high-pressure (HTHP) density data provide a database for testing contemporary equations of state (EoS)^{1,2} and improving or establishing a specific EoS suitable for use at high temperatures and pressures.^{3,4} HTHP density data are also used to estimate hydrocarbon viscosities in a given pressure and temperature range.⁵ The present study reports experimental density data up to 525 K and pressures up to 275 MPa for several branched cyclic hydrocarbons including methylcyclohexane (methylC6) and four branched C6 cyclic isomers,

ethylcyclohexane (ethylC6), *cis*-1,2-dimethylcyclohexane (*cis*-1,2), *cis*-1,4-dimethylcyclohexane (*cis*-1,4), and *trans*-1,4-dimethylcyclohexane (*trans*-1,4). These data complement previously published HTHP data for short-chain and long-chain alkanes.^{1,2}

The density data are modeled using the Peng–Robinson (PR) EoS,⁶ the high-temperature, high-pressure, volume-translated PR (HTHP VT-PR) EoS,³ and the perturbed-chain, statistical associating fluid theory (PC-SAFT) EoS.⁷ Although the PREoS is computationally facile, it typically does not accurately predict liquid-like densities encountered at high pressures nor does it provide accurate density predictions for a

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compound with a large acentric factor.^{1,2,8} The performance of the PREoS can be improved by modifying the temperature dependence of the attractive energy term, $a(T)$,^{8,9} or by introducing a volume-translation (VT), correction term.^{10–13} In the present work, the HTHP VT-PREoS, recently proposed by Baled et al.,³ is used to model the experimental density data.

Compared with cubic equations, statistical associating fluid theory (SAFT) equations, for example, the PC-SAFT EoS, have a more molecularly based theoretical foundation, although they still require three independent parameters for nonassociating fluids and two more parameters for associating fluids, all of which are obtained by fitting experimental data.⁷ As an alternative, group contribution (GC) methods can be used to estimate these parameters when experimental data are not available.¹⁴ For example, Tihic et al.¹⁵ developed a GC method with both first-order (FOG) and second-order group (SOG) contribution values for calculating PC-SAFT pure-component parameters. In the present work, the PC-SAFT EoS, with pure-component parameters from the literature⁷ or from Tihic's GC method,¹⁵ is used to model the experimental density data. The calculated densities obtained from the SAFT approach are compared and contrasted with the results obtained using the PR and HTHP VT-PREoS equations.

2. EXPERIMENTAL SECTION

2.1. Materials. Methylcyclohexane (99.9 wt % purity), ethylcyclohexane (99.5 wt % purity), *cis*-1,2-dimethylcyclohexane (98.6 wt % purity), *cis*-1,4-dimethylcyclohexane (99.5 wt % purity), and *trans*-1,4-dimethylcyclohexane (98.2 wt % purity) were purchased from Sigma-Aldrich. All of the chemicals were used as received.

2.2. Apparatus and Measurements. The high-pressure apparatus and measurement techniques used in this study are described in detail elsewhere,^{1,2,16} and only highlights are provided here. The system pressure is measured with a pressure transducer (Viатran Corporation, model 245, 0–345 MPa) accurate to ± 0.07 MPa up to pressures of 56 MPa and to ± 0.35 MPa for pressures from 56 to 275 MPa, and the system temperature is measured with a type-k thermocouple (Omega Corporation), accurate to ± 0.05 K, calibrated against an immersion thermometer (Fisher Scientific, precision to ± 0.1 K, accurate to better than ± 0.1 K, recalibrated using methods traceable to NIST standards). The experimentally observed temperature variation for each reported isotherm is within ± 0.1 K. The internal cell volume is determined using a linear variable differential transformer (LVDT, Schaevitz Corporation, model 1000 HR) to track the location of a piston in the high-pressure cell. The LVDT is calibrated using NIST propane and *n*-decane density data.¹⁷

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, $(6.0\text{--}7.0) \pm 0.0002$ g of hydrocarbon 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. For any given isotherm, data are obtained at random pressures to minimize any potential experimental artifacts in the measurements. The standard 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) experimental uncertainty, $U_c = U_c(\rho) = 0.75\% \cdot \rho$ (at $k = 2$ for

an interval having a confidence level of approximately 95%) where ρ is a density data point.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Experimental density data are listed in Tables S1–S5 in the Supporting Information for methylcC6, ethylcC6, *cis*-1,2, 1,4, and *trans*-1,4 at temperatures up to 525 K and pressures up to 277 MPa, respectively. Note that a liquid–solid phase transition is observed for *cis*-1,2 and *trans*-1,4 at 294.9 K at high pressures. A detailed description of the solidification behavior for the cyclic hydrocarbons is described elsewhere.¹⁸

The density data are fit to the modified Tait equation, eq 1, to provide a means to calculate densities at conditions other than those experimentally investigated in this study.

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

where ρ is the density, in kg/m³, ρ_0 is the density at $P_0 = 0.1$ MPa, P is the 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 temperatures, given as¹⁹

$$\rho_0 = \sum_{i=0}^2 a_i T^i \quad (2)$$

$$B = \sum_{i=0}^2 b_i T^i \quad (3)$$

where a_i and b_i are fitted coefficients listed in Table 1. The calculated ambient-pressure density using eq 2 is within $\pm 0.3\%$

Table 1. Coefficients, Number of Data Points (n), and Mean Absolute Percent Deviation (MAPD) for the Best Fit of the Modified Tait Equation to methylcC6, ethylcC6, *cis*-1,2, *cis*-1,4, and *trans*-1,4 Density Data

coefficients	methylcC6	ethylcC6	<i>cis</i> -1,2	<i>cis</i> -1,4	<i>trans</i> -1,4
a_0 (kg m ⁻³)	915.6	885.0	903.5	975.9	846.8
a_1 (kg m ⁻³ K ⁻¹)	−0.182	0.058	0.001	−0.427	0.147
$a_2 \times 10^3$ (kg m ⁻³ K ⁻²)	−1.077	−1.296	−1.199	−0.753	−1.496
b_0 (MPa)	381.3	338.3	355.3	342.0	399.4
b_1 (MPa K ⁻¹)	−1.393	−1.149	−1.178	−1.156	−1.428
$b_2 \times 10^3$ (MPa K ⁻²)	1.294	0.993	0.996	0.986	1.295
C	0.210	0.206	0.217	0.208	0.217
n	79	74	74	84	80
MAPD (%)	0.30	0.17	0.14	0.14	0.17

of reported literature values.^{20–25} Note that at high temperatures, such as 525 K, ρ_0 for the cyclic hydrocarbons is a “pseudo” liquid density, since P_0 is not precisely equal to 0.1 MPa. In Table 1, the MAPD refers to the mean absolute percent deviation between experimental data obtained in this study, $\rho_{i,\text{exp}}$, and calculated values with the modified Tait equation, $\rho_{i,\text{corr}}$ for n data points.

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

The largest MAPD, 0.29%, is less than the estimated, expanded uncertainty ($k = 2$), $\pm 0.75\%$, of the experimental data.

Table 2. Comparison of the Data Obtained in This Study to That Available in the Literature

literature	literature temperature range (K)	literature maximum pressure (MPa)	literature data points	temperatures (K) and pressures (MPa) for density data obtained in this study that differ from available literature data
Methylcyclohexane				
Baylaucq et al. ³⁰	303–343	100	18	293 K: $P < 265$ 323 K: $100 < P < 265$ 423 K: $P < 265$ 523 K: $P < 275$
Brazier et al. ²⁶	303	450	10	293 K: $P < 265$ 323 K: $P < 265$ 423 K: $P < 265$ 523 K: $P < 275$
Bridgman ^{27,28}	298–348	4900	32	293 K: $P < 265$ 423 K: $P < 265$ 523 K: $P < 275$
Gouel ³¹	293–392	40	90	293 K: $40 < P < 265$ 323 K: $40 < P < 265$ 423 K: $P < 265$ 523 K: $P < 275$
Jonas et al. ²⁹	203–298	500	31	293 K: $P < 265$ 423 K: $P < 265$ 523 K: $P < 275$
Laesecke et al. ²¹	270–470	40	154	293 K: $40 < P < 265$ 323 K: $40 < P < 265$ 423 K: $40 < P < 265$ 523 K: $P < 275$
Et-Tahir et al. ³²	298–363	40	45	293 K: $40 < P < 265$ 323 K: $40 < P < 265$ 423 K: $P < 265$ 523 K: $P < 275$
Takagi et al. ³³	283–343	21	128	293 K: $21 < P < 265$ 323 K: $21 < P < 265$ 423 K: $P < 265$ 523 K: $P < 275$
Zeberg-Mikkelsen et al. ^{34,35}	283–353	100	101	293 K: $100 < P < 265$ 323 K: $100 < P < 265$ 423 K: $P < 265$ 523 K: $P < 275$
Ethylcyclohexane				
Voss et al. ³⁶	327–440	10	24	293 K: $P < 265$ 323 K: $P < 265$ 423 K: $10 < P < 265$ 523 K: $P < 265$
<i>cis</i> -1,2-Dimethylcyclohexane				
Voss et al. ³⁶	325–461	10	21	293 K: $P < 265$ 323 K: $P < 265$ 423 K: $10 < P < 265$ 523 K: $P < 265$
<i>cis</i> -1,4-Dimethylcyclohexane, <i>trans</i> -1,4-Dimethylcyclohexane				
Data at $P > 0.1$ MPa are not reported in the literature				293 K: $P < 265$ 323 K: $P < 265$ 423 K: $P < 265$ 523 K: $P < 265$

Table 2 compares densities reported in this study with those available in the literature. The table does not include references only reporting densities at atmosphere pressure.^{20,22–25} To the best of our knowledge, density data have not been reported for ethylcC6 and *cis*-1,2 at temperatures above 462 K and pressures above 10 MPa and for *cis*-1,4 and *trans*-1,4 other than at ambient pressure. There are several reports on the density of

methylcC6^{26–29} at extreme pressures, although none of these studies report data at temperatures greater than 348 K.

Only the densities of methylcC6 obtained in this study are compared with sufficient literature data given the lack of high-pressure density data available for ethylcC6, *cis*-1,2, *cis*-1,4, and *trans*-1,4. The MAPD here is defined as

$$\text{MAPD} = \frac{1}{n} \sum_{i=1}^n \left| \frac{\rho_{i,\text{lit}} - \rho_{i,\text{corr}}}{\rho_{i,\text{lit}}} \right| \times 100\% \quad (5)$$

where $\rho_{i,\text{lit}}$ and $\rho_{i,\text{corr}}$ are the density reported in the literature and the density calculated with the modified Tait equation, respectively. The MAPD is less than 0.4% in the temperature and pressure range determined in this study except for the data of Bridgman²⁸ where the MAPD is as high as 0.8%. However, Bridgman did not use a temperature control system²⁸ to precisely maintain 298 K, making any comparison problematic. In another study, Bridgman²⁷ reported data at 348 K with temperature control, but the pressures are outside the range determined in the present study. Figure 1 shows the percent

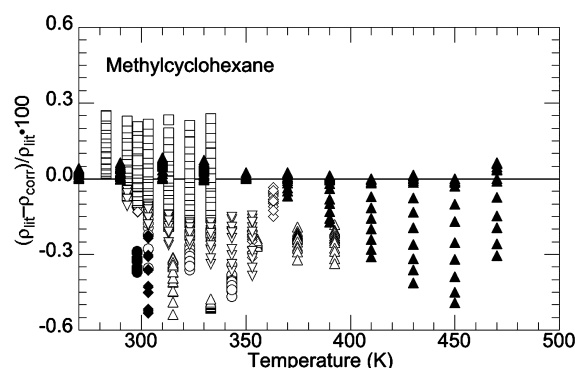


Figure 1. Percent deviation between the data obtained in this study, $\rho_{i,\text{corr}}$ and literature data, $\rho_{i,\text{lit}}$ of Baylaucq et al.³⁰ (○), Brazier and Freeman²⁶ (◆), Goulet³¹ (△), Jonas et al.²⁹ (●), Et-Tahir et al.³² (◇), Takagi et al.³³ (□), Zeberg-Mikkelsen et al.^{34,35} (▽), and Laesecke et al.²¹ (▲).

deviation between available methylcC6 data and the densities calculated with the modified Tait equation. The percent deviation of all the data fall within $\pm 0.6\%$, which is smaller than the estimated expanded uncertainty of the data reported in the present study, and the percent deviation scatters around the zero baseline in the pressure and temperature ranges available for comparison. It should be noted that the data of Bridgman^{27,28} are not included nor are any atmospheric density data shown in this figure.^{20,22–24}

Figure 2 shows the densities of the four branched cyclic C6 isomers calculated with the modified Tait equation at the lowest, 293 K, and highest, 523 K, temperatures. *cis*-1,2 has the

largest densities and *trans*-1,4 has the smallest densities over the entire temperature and pressure range investigated in this study. This trend is also observed for the other two isotherms, 323 and 423 K, and the trend agrees with that observed for ambient-pressure densities at 273, 293, and 313 K reported in the literature.²⁰ We conjecture that this density difference is due to the packing of the methylcC6 at high pressures, given that there likely is very little difference between the strength of intermolecular attraction energies for these isomers. One goal of the EoS modeling is to determine if it is possible to mimic the trends observed for the densities of the four C6 cyclic isomers.

4. DENSITY PREDICTIONS

4.1. Equations and Parameters. The PREoS, HTHP VT-PREoS, and PC-SAFT EoS are used to predict the densities of methylcC6, ethylcC6, *cis*-1,2, *cis*-1,4, and *trans*-1,4. Details on the three EoS are found elsewhere^{3,4,6,7} and are not given in this article. Table 3 lists the critical properties needed to use PREoS and HTHP VT-PREoS.

Table 3. Pure-Component Parameters³⁷ of methylcC6, ethylcC6, *cis*-1,2, *cis*-1,4, and *trans*-1,4, where T_c , P_c , and ω are the Critical Temperature, Critical Pressure, and Acentric Factor, Respectively

compound	molecular weight	T_c (K)	P_c (MPa)	ω
methylcC6	98.2	572	3.5	0.233
ethylcC6	112.2	609	3.0	0.243
<i>cis</i> -1,2	112.2	606	3.0	0.236
<i>cis</i> -1,4	112.2	598	3.0	0.234
<i>trans</i> -1,4	112.2	590	3.0	0.242

The PC-SAFT EoS^{7,38} is an expansion of the residual, molar Helmholtz free energy. For nonassociating fluids, the pure component number of segments, m , temperature-independent segment diameter, σ , and interaction energy, ϵ/k , are needed to model thermodynamic properties.¹⁴

PC-SAFT modeling is performed with pure component parameters determined from different types of experimental data. The first set of parameters is obtained, directly or indirectly, from a simultaneous fit of the PC-SAFT equation to vapor pressure and subcritical density data. The parameters for methylcC6 and ethylcC6, listed in Table 4, are taken directly from literature sources.⁷ The parameters for *cis*-1,2, *cis*-1,4, and *trans*-1,4 are estimated using the GC method described by

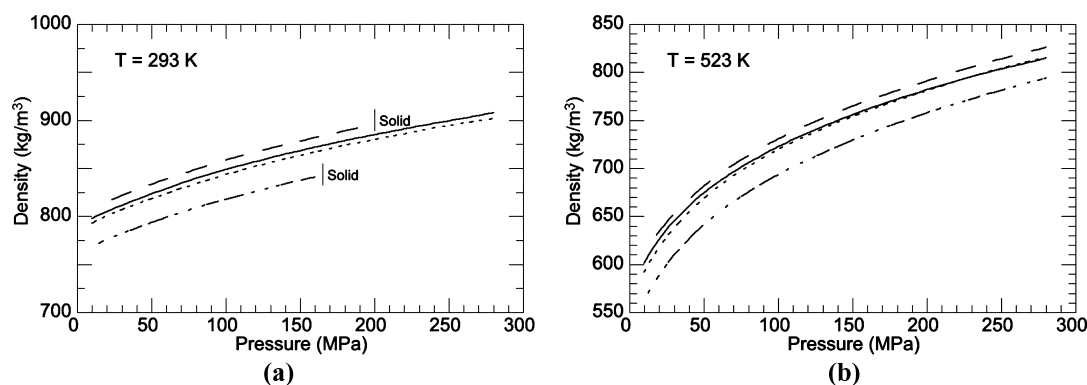


Figure 2. Densities of *cis*-1,2 (---), ethylcC6 (—), *cis*-1,4 (···), and *trans*-1,4 (— · —) calculated with the modified Tait equation at (a) 293 K and (b) 523 K.

Table 4. PC-SAFT Parameters, m , σ , and ϵ/k_B , for methylc6 and ethylc6 from Gross and Sadowski⁷

compound	M_w	m	σ (Å)	ϵ/k_B (K)
Methylc6	98.2	2.6637	3.9993	282.33
Ethylc6	112.2	2.8256	4.1039	294.04

Tihic et al.¹⁵ who analyzed available pure-component PC-SAFT parameters also determined by simultaneously fitting vapor pressure and subcritical density data. The first application of the GC method only uses first-order group (FOG) values, shown in Table 5. Note that the three dimethylcyclohexane isomers have the same types and number of FOGs and, hence, the calculated PC-SAFT parameters are identical. The second application of the GC method uses both FOGs and second-order group (SOG) values listed in Table 5. In this instance, the SOG, $-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-$, only appears in *cis*-1,2. Table 6 shows that the *cis*-1,2 pure-component parameters calculated with the second GC method are different from the parameters for either *cis*- or *trans*-1,4. Unfortunately, *cis*-1,4 and *trans*-1,4 have the same FOG and SOG values and, hence, the same PC-SAFT EoS parameters.

4.2. Density Predictions. Table 7 lists the MAPD and standard deviation (SD) for each EoS for each cyclic hydrocarbon. Both the PREoS and the HTHP VT-PREoS tend to underestimate the densities with increasing pressure for ethylc6 and the three cyclohexane isomers. For methylc6, both equations overestimate the densities at low to moderately high pressures. At pressures in excess of ~ 100 MPa, the HTHP VT-PREoS provides a better representation of the densities compared to that obtained with the PREoS, especially at elevated temperatures. It is not surprising that there is only a modest improvement in the density predictions for the four C6 isomers, since the volume-translation term is only a function of molecular weight, critical temperature, and acentric factor, which, as shown in Table 3, are virtually identical for these four isomers. Nevertheless, the HTHP VT-PREoS approach proposed by Baled et al.³ offers a facile method that improves the performance of the PREoS for estimating hydrocarbon densities when experimental data are not available.

Another issue of importance for any EoS is whether the equation can capture the effect of isomer structure on density as observed in the present study for ethylc6, *cis*-1,4, *cis*-1,2, and *trans*-1,4. Both the PREoS and the HTHP VT-PREoS predict the density isotherm order, from highest to lowest densities, as ethylc6, *cis*-1,4, *cis*-1,2, and *trans*-1,4. However, the experimental ordering is *cis*-1,2, ethylc6, *cis*-1,4, and *trans*-1,4. It is apparent that neither the PREoS nor the HTHP VT-PREoS are capable of accounting for the effect of isomer structural differences on the observed densities.

Table 6. PC-SAFT Parameters for *cis*-1,2, *cis*-1,4, and *trans*-1,4 Calculated Using the GC Method Proposed by Tihic et al.¹⁵

approach	compound	M_w	m	σ (Å)	ϵ/k_B (K)
first-order GC method only	<i>cis</i> -1,2	112.2	2.9137	4.0503	276.10
	<i>cis</i> -1,4	112.2	2.9137	4.0503	276.10
	<i>trans</i> -1,4	112.2	2.9137	4.0503	276.10
first-order plus second-order GC method	<i>cis</i> -1,2	112.2	2.6406	4.1597	308.82
	<i>cis</i> -1,4	112.2	2.6869	4.1535	306.03
	<i>trans</i> -1,4	112.2	2.6869	4.1535	306.03

Figure 3 shows a comparison of density isotherms calculated with the PC-SAFT EoS using pure-component parameters from the literature, Table 4, and parameters calculated with GC equations only using FOGs reported by Tihic et al.,¹⁵ Table 6. The MAPD values obtained with the PC-SAFT EoS shown in Table 7 are approximately 14–40% lower than the MAPD values obtained with the PREoS for four out of five of the cyclohexanes. MAPD values with the PC-SAFT EoS are also lower than those obtained with the HTHP VT-PREoS, except for the case of *trans*-1,4. The pure-component parameters listed in Table 6 show that first-order GC cannot capture the effect of the structural differences on the density for *cis*-1,2, *cis*-1,4, and *trans*-1,4. Although the calculated pure-component parameters for the *cis*-1,2 isomer differ from those for *cis*-1,4- and *trans*-1,4 isomers when using both FOG and SOG values, the MAPD values in Table 7 indicate a worse fit is obtained for these three isomers compared to fits using only FOG values to calculate pure-component parameters. It should also be noted that the tendency of the PC-SAFT EoS to overestimate cyclohexane densities in the high-pressure region, regardless of the origin of the pure-component parameters, agrees with results published previously for short- and long-chain alkanes under HTHP conditions.^{1,2}

As mentioned previously, it is important to determine if the EoS can capture the effect of isomer structure on density for ethylc6, *cis*-1,2, *cis*-1,4, and *trans*-1,4. Figure 4 shows a comparison of the calculated densities for the four isomers at a single temperature of 323 K using the PC-SAFT EoS and experimental densities correlated by the modified Tait equation. Note that ethylc6 densities (Figure 4b and c) are predicted with pure-component parameters reported by Gross and Sadowski,⁷ while the densities for the three other isomers are predicted using the GC approach of Tihic et al.³⁹ with FOG values only (Figure 4b) and with FOG and SOG values (Figure 4c). It is not surprising that the four isotherms superpose in

Table 5. First-Order Group (FOG) and Second-Order Group (SOG) Values from Tihic et al.¹⁵ for Each Functional Group in Dimethylcyclohexanes

type	group	no. of groups	m	$m\sigma^3$ (Å ³)	$m\epsilon/k_B$ (K)
FOG	$-\text{CH}_2$	4	0.3843	24.340	102.32
	$-\text{CH}_3$	2	0.6444	34.170	129.39
	$-\text{CH}<$	2	0.0438	13.954	68.21
SOG	$-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-^a$	1	−0.0463	−2.465	−6.81
	ring of six carbons	1	0.0642	−0.637	29.25
	string in cyclic	2	−0.1455	−0.220	−5.72

^a $-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-$ only appears in *cis*-1,2.

Table 7. MAPD and Standard Deviation (SD) Values for the PREoS, HTHP VT-PREoS, PC-SAFT EoS, and PC-SAFT EoS Combined with the GC Method of Tihic et al. for methylcC6, ethylcC6, *cis*-1,2, *cis*-1,4, and *trans*-1,4^a

compound	PR		HTHP VT-PR		PC-SAFT	
	MAPD (%)	SD (%)	MAPD (%)	SD (%)	G-S	
methylcC6	4.86	2.47	3.95	1.52	2.14	1.46
ethylcC6	3.42	2.05	2.35	1.49	1.50	1.05

compound	PR		HTHP VT-PR		PC-SAFT			
	MAPD (%)	SD (%)	MAPD (%)	SD (%)	Tihic GC 1st		Tihic GC 2nd	
<i>cis</i> -1,2	5.32	2.56	4.97	1.36	1.78	1.15	3.16	1.56
<i>cis</i> -1,4	2.91	1.98	2.02	1.51	1.99	1.38	4.32	1.44
<i>trans</i> -1,4	3.95	2.12	3.43	1.53	4.41	1.60	7.34	1.77

^aG-S means pure-component parameters from Gross and Sadowski,⁷ Tihic GC 1st means the GC method of Tihic et al.,¹⁵ using first-order GC parameters, and Tihic GC 2nd means the same GC method but using both first- and second-order GC parameters.

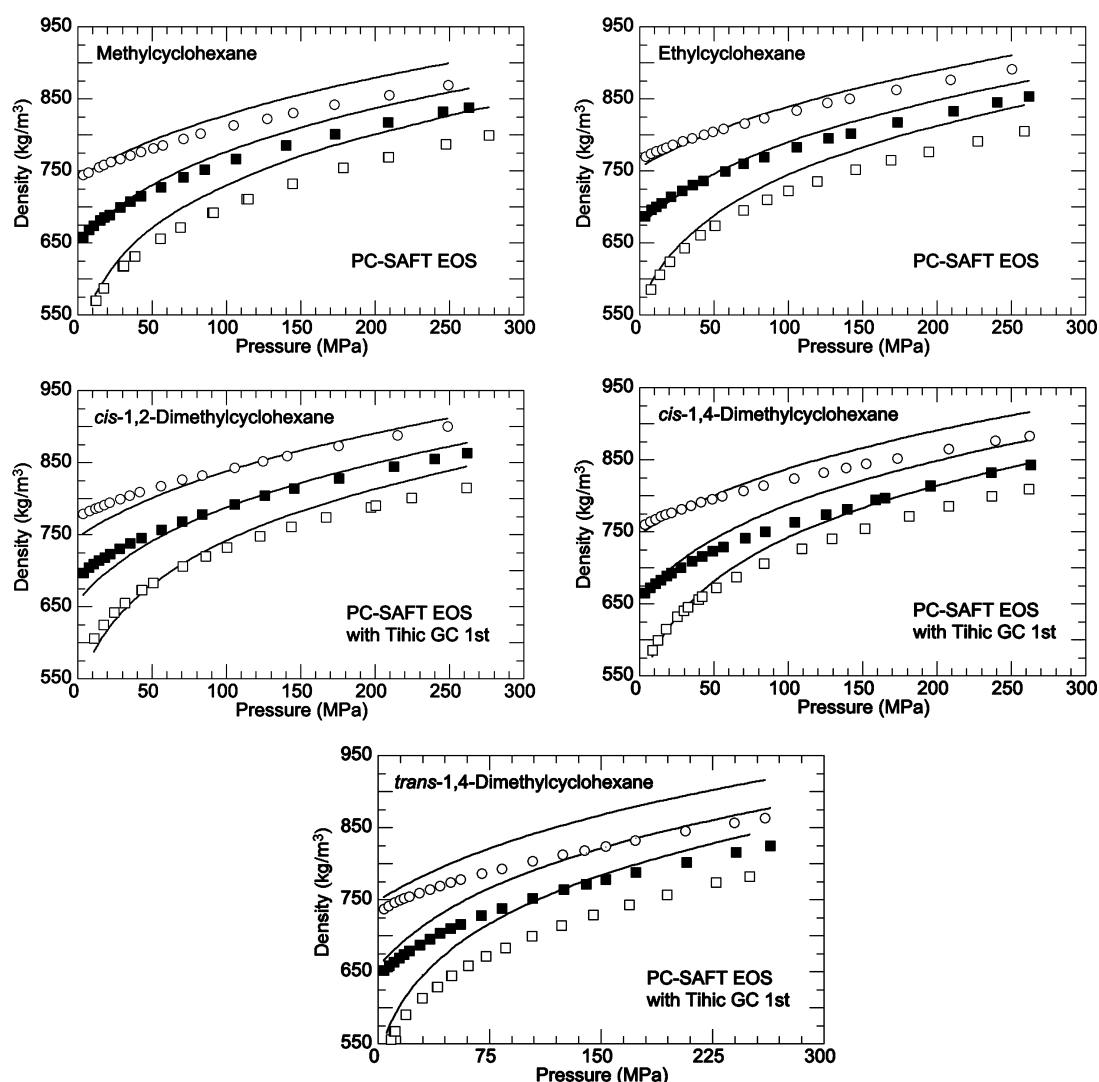


Figure 3. Comparison of select experimental cyclohexane density data—(○) 324.3 K, (■) 423.4 K, (□) 522.5 K—with calculated densities (lines) using the PC-SAFT EoS with parameters reported by Gross and Sadowski,⁷ Table 4, and parameters calculated using the GC method reported by Tihic et al.,¹⁵ with first-order groups only, Table 6.

Figure 4b given that the three dimethylcyclohexane isomers have identical pure-component parameters.

Figure 4c shows that the GC approach by Tihic et al., with both FOG and SOG values, does correctly predict a larger

density for *cis*-1,2 compared to either *cis*-1,4 or *trans*-1,4 at the same temperature and pressure. However, the density differences between *cis*-1,4 and *trans*-1,4 are not predicted. More importantly, the predicted ethylcC6 densities in Figure 4c are

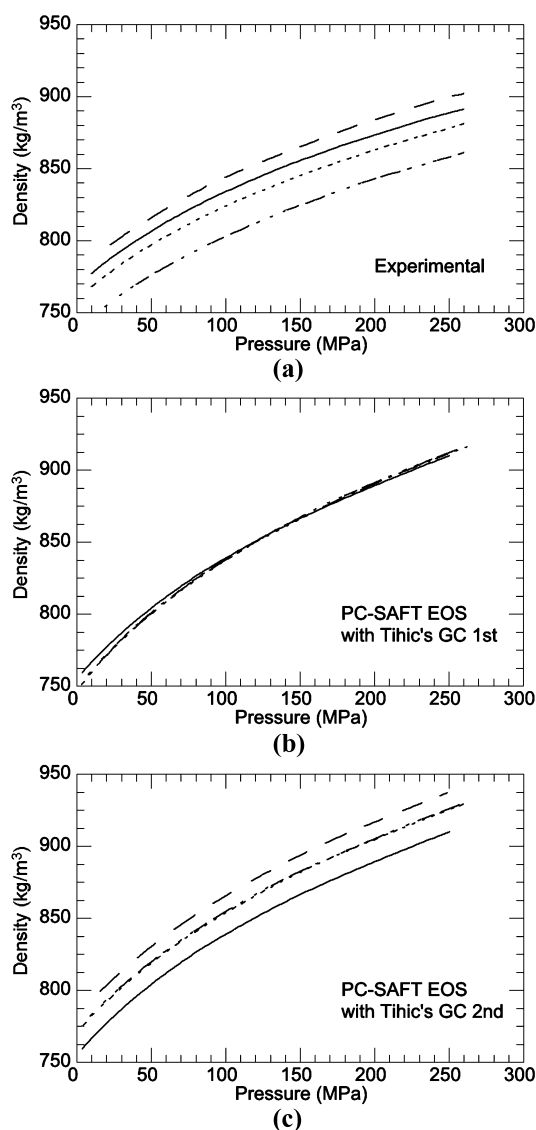


Figure 4. Comparison of calculated densities at 323 K for ethylcC6 (—), *cis*-1,2 (---), *cis*-1,4 (···), and *trans*-1,4 (— · —) using (a) a modified Tait equation and the PC-SAFT EoS (b) with Tihic et al.'s first-order GC parameters only and (c) with Tihic et al.'s first- and second-order GC parameters. The isotherms in part b for ethylcC6, *cis*-1,2, *cis*-1,4, and *trans*-1,4 superpose. The isotherms in part c for *cis*-1,4 and *trans*-1,4 also superpose.

lower than those for the other three isomers, which does not agree with experimental trends. It might argue that, since the densities of ethylcC6 are predicted with the PC-SAFT parameters reported by Gross and Sadowski⁷ instead of using parameters calculated with the GC method, the results are not directly comparable. However, when the same GC method is used with the PC-SAFT EoS to predict the densities of ethylcC6 (not shown here), the results are virtually identical to those found using Gross and Sadowski's reported PC-SAFT parameters and the predicted ethylcC6 densities are still the smallest among the four isomers. These observations should not be surprising, since the GC parameters reported by Tihic et al. are determined using available PC-SAFT parameters from Gross and Sadowski⁷ as well as previous work of Tihic et al.³⁹

At present, to the best of our knowledge, it is not possible to predict the density differences between *cis*-1,2 and *cis*-1,4 using

the GC method. The current limited database for PC-SAFT parameters for numerous compounds is the main reason retarding the development of more SOG GC parameters. Therefore, this study reports the PC-SAFT parameters of *cis*-1,2, *cis*-1,4, and *trans*-1,4 in the following section for further studies.

4.3. Parameterization of PC-SAFT Pure-Component Parameters. As previously mentioned, the PC-SAFT parameters for *cis*-1,2, *cis*-1,4, and *trans*-1,4 are not reported in the literature. In this section, pure-component parameters are obtained by fitting the PC-SAFT EoS to two different experimental sets of data. One data set combines density data obtained in this study and vapor pressure data obtained from the literature.⁴⁰ The other data set only uses the HTHP density data obtained in this study. Table 8 lists the PC-SAFT

Table 8. PC-SAFT Parameters for *cis*-1,2, *cis*-1,4, and *trans*-1,4 Obtained by Two Different Methods^a

(A) Simultaneous Fit of Density Data Obtained in This Study and Literature Vapor Pressure Data ⁴⁰					
compound	<i>m</i>	σ (Å)	ϵ/k_B (K)	MAPD (%)	
				p^{sat}	ρ
<i>cis</i> -1,2	3.2607	3.8866	269.63	0.16	1.22
<i>cis</i> -1,4	3.1505	3.9655	270.33	0.08	1.35
<i>trans</i> -1,4	3.2658	3.9451	260.59	0.15	1.35

(B) Fit of Density Data Obtained in This Study					
compound	<i>m</i>	σ (Å)	ϵ/k_B (K)	MAPD (%)	
				ρ	
<i>cis</i> -1,2	5.3041	3.2818	235.96	0.26	
<i>cis</i> -1,4	5.1519	3.3413	235.71	0.51	
<i>trans</i> -1,4	5.6068	3.2617	220.93	0.23	

^a p^{sat} and ρ represent the vapor pressure and the liquid density, respectively. Each isomer has a molecular weight of 112.2. Vapor pressure data are reported in a temperature range from 313 to 403 K and a pressure range from 0.01 to 0.1 MPa. Density data are reported in a temperature range from 293 to 523 K and a pressure range from 3 to 275 MPa.

parameters obtained with these two approaches for *cis*-1,2, *cis*-1,4, and *trans*-1,4 and the MAPD between experimental and calculated data. Figure 5 shows the percent deviation between density data obtained in this study and calculated values with each set of optimized PC-SAFT parameters. When using parameters fit to vapor pressure and density data, the PC-SAFT EoS tends to underestimate densities at pressures below 20 MPa and overestimate them at pressures above 120 MPa for all three isomers. Nevertheless, the PC-SAFT EoS does provide reasonable density predictions throughout the entire pressure range. In addition, the parameters obtained from a fit of vapor pressure and density data are expected to give reasonable results for phase equilibrium predictions.^{4,41} When using parameters fit exclusively to HTHP density data, the PC-SAFT EoS tends to provide better predictions at extreme temperatures and pressures. Not surprisingly, MAPD values are now within $\pm 0.5\%$ and the maximum deviation is generally within $\pm 1.0\%$. However, it is worth noting that the PC-SAFT EoS may not perform well when predicting phase equilibrium data when using pure-component parameters optimized to HTHP density data.^{4,14,41}

Comparing the parameters obtained by the above two fitting methods, the values of *m* obtained by the simultaneous fit of density data and vapor pressure data are always smaller than the

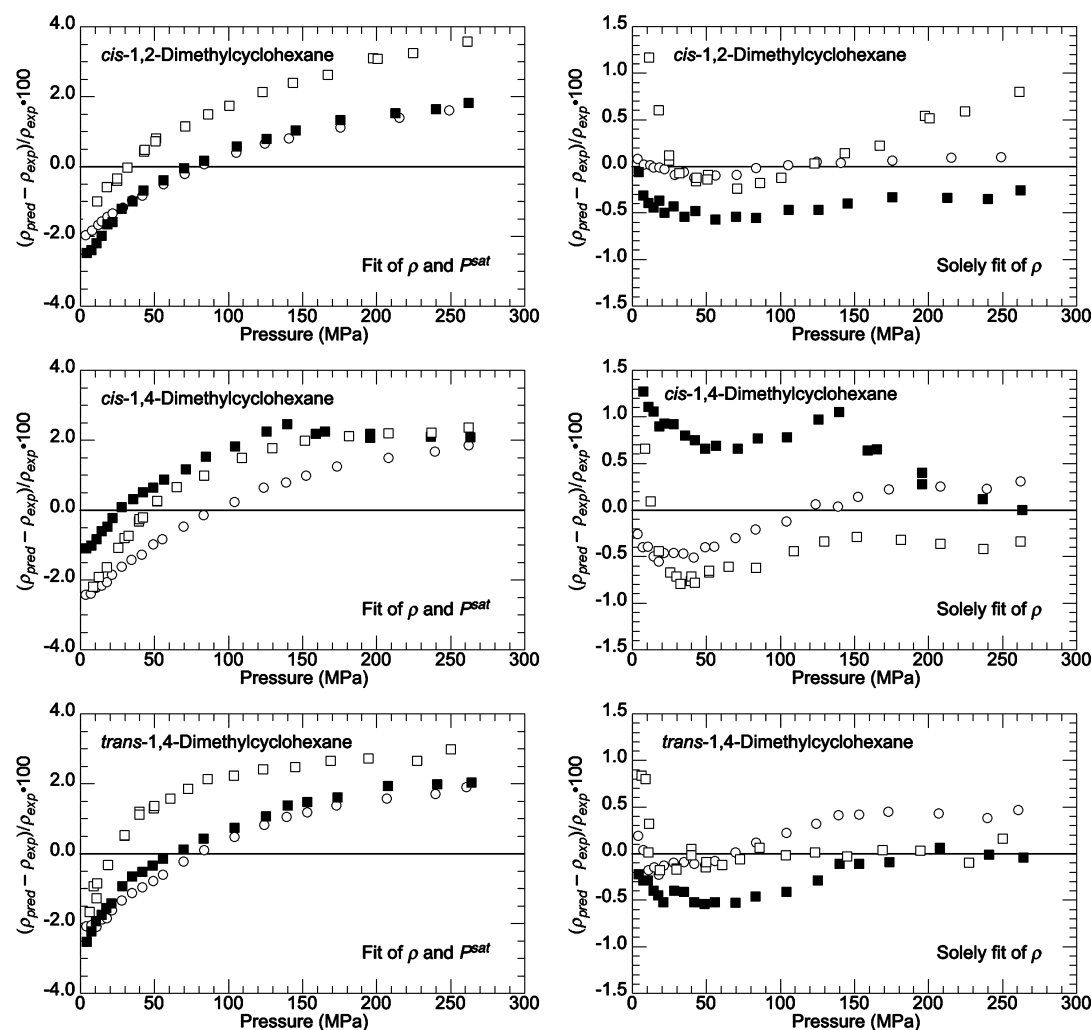


Figure 5. Percent deviation between density data obtained in this study and calculated density using the PC-SAFT EoS with pure component parameters optimized by simultaneously fitting experimental density data and vapor pressure data⁴⁰ (fit of ρ and P^{sat}) and by only fitting experimental density data (solely fit of ρ) at 323 K (○), 423 K (■), and 523 K (□). The deviation curve for the 293 K isotherm is not included to avoid cluttering the graph.

values from the fit of density data, while the values of σ and ε/k_B are larger for the simultaneous fit of density data and vapor pressure data. This trend is also found when comparing the pure-component parameters obtained by Gross and Sadowski⁷ and Tihic et al.³⁹ with the HTHP parameters obtained by Burgess et al.⁴ For example, for cyclooctane, a different dimethylcyclohexane isomer, m , σ (Å), and ε/k_B (K) are 2.8856, 4.0117, and 307.03, respectively, when obtained by simultaneously fitting density and vapor pressure data³⁹ and 5.9785, 3.1395, and 250.05, respectively, when obtained by solely fitting HTHP density data.⁴

5. CONCLUSIONS

This study reports the density data for methylcC6, ethylcycC6, *cis*-1,2, *cis*-1,4, and *trans*-1,4 at temperatures up to 525 K and pressures up to 277 MPa, extending the current database for cyclic hydrocarbons. The MAPD for data obtained in the present study is within 0.4% of available literature data for methylcC6, the only compound with published data under the conditions investigated in this study. The structural differences of the four C6 cyclic isomers are reflected in the ordering of the density data at high temperatures and pressures. Compared

with the PREoS and the HTHP VT-PREoS, the PC-SAFT equation of state provided more accurate calculated densities for the cyclic compounds. Nevertheless, even the PC-SAFT EoS cannot fully account for the effect of C6 isomer structure on the resultant density. Further work is in progress to improve the performance of the PC-SAFT EoS when using group contribution parameters and calculating fluid properties under extreme conditions.

■ ASSOCIATED CONTENT

Supporting Information

Tables S1–S5 listing the experimental density data for methylcyclohexane, ethylcyclohexane, *cis*-1,2-dimethylcyclohexane, *cis*-1,4-dimethylcyclohexane, and *trans*-1,4-dimethylcyclohexane at temperatures up to 525 K and pressures up to 277 MPa, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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