A Systematic Study of Cubic Equations of State with van der Waals Mixing Rules and Different Combining Rules in Predicting the Densities of LNG and Natural Gas Model Systems

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Abstract

Cubic equations (EoSs) of state are successfully used in petroleum and natural gas industry. In order to extend these equations to mixtures, van der Waals mixing rules with Lorentz-Berthelot (LB) combining rules are often employed; however, the accuracies of these EoSs in predicting the liquid densities of hydrocarbon mixtures are not adequate. The main objective of this study was comparing 13 EoSs coupled with 10 combining rules in predicting the densities of hydrocarbon mixtures. Binary and ternary liquid mixtures, LNG mixtures and synthetic natural gas mixtures comprising 752 data points were collected and used in this study. Results revealed that for predicting the liquid densities of binary and ternary mixtures, the Schmidt and Wenzel (SW) EoS coupled with Hudson-McCoubrey (HMC) or LB combining rules are the best among the others. The SW EoS coupled with the LB combining rules were also the best in predicting the densities of the LNG mixtures. Additionally, the LB combining rules are the best in predicting natural gas mixtures densities using the Patel and Teja (PT), SW and Patel-Teja-Valderrama (PTV) EoSs. In general, it was found that the Redlich-Kwong (RK) family EoSs, SW and Trebble-Bishnoi-Salim (TBS) EoSs are best coupled with the LB combining rules. However, the Peng and Robinson (PR) family EoSs with Halgren (HHG) combining rules were in better agreement with experimental data. The Waldman-Hagler (WH) combining rules lacked predictability when coupled with the most EoSs.

Keywords: Density; natural gas, hydrocarbon, equation of state, combining rules.

1. Introduction

In natural gas and petroleum engineering, cubic equations of state (EoSs) are important in equilibrium calculations. Often the accuracy of the EoSs in equilibrium calculations are not identical and comparisons are made to find the best EoS among the others. For instance, Nasrifar et al. [1] compared 15 EoSs in predicting lean and rich natural gas dew points. They found that the dew points of lean synthetic natural gases are predicted best by the Redlich-Kwong (RK) family EoSs [2] and the Schmidt and Wenzel (SW) EoS [3] whereas the three-parameter EoSs like Patel-Teja (PT) [4], Patel-Teja-Valderrama (PTV) [5] and Guo-Du (GD) [6,7] are the best in predicting the dew points of rich natural gases.

Equally important is the application of EoSs in predicting the pressure-volume-temperature (PVT) and the thermodynamic properties of hydrocarbon fluids. Coats and Smarts [8] conducted a study where the Peng-Robinson (PR) [9] and Zdudkevitch-Joffe-Redlich-Kwong (ZRK) EoSs [10] were applied to correlate and predict fluid phase properties. The results showed that the agreement between laboratory properties, such as gas oil ratio and stock tank oil gravity, and the EoS calculated values was generally good to excellent. However, both EoSs gave generally poor agreement with any set of laboratory PVT data. Ahmed [11] compared eight cubic EoSs in predicting the volumetric and phase equilibria of gas condensate systems. He found that the SW EoS exhibits a superior predictive capability for volumetric properties of gas-condensate systems. The PT and SW EoSs were found to give reliable gas density predictions and in terms of vapor-liquid equilibrium (VLE) calculations, the PR, PT, and SW EoSs all performed equally well. Nasrifar and Bolland [12] compared 10 EoSs including a proposed EoS to predict thermodynamic properties such as saturated liquid density of LNG mixtures, compressibility factors, speeds of sound, isobaric heat capacity and Joule–Thomson coefficient of natural gas mixtures. Their results indicated that the saturated liquid density of the LNG mixtures was predicted best by the modified Nasrifar-Moshfeghian (MN) [13] and Mohsenia-Madarres-Mansoori (3M) EoSs [14] and the accuracy of the proposed EoS was between the Redlich-Kwong-Soave (RKS) [15] and PR family EoSs. For predicting the compressibility factor and speeds of sound of natural gas mixtures, the proposed EoS was found to be the most accurate EoS among the others; however, the accuracy of the proposed EoS in predicting the isobaric heat capacity and Joule–Thomson coefficient was found comparable to the RKS EoS or one of its variants.

EoSs are in plenty. The PVT of an EoS accounts for its accuracy and exact thermodynamic relations are often expressed in terms of the PVT of fluids [16]. Accurate PVT relation for an EoS then leads to accurate thermodynamic property calculation. For instance, the RK EoS or one of its variants describes well the PVT of natural gas mixtures. For hydrocarbon mixtures with heavy fractions, however, the PR EoS is somewhat more accurate, especially in predicting
liquid density. These EoSs are still subject of research to improve their accuracies [17, 18].

Dealing with mixtures, mixing rules also play a vital role. For hydrocarbon mixtures, van der Waals mixing rules are invariably used in equilibrium calculations [19].

Lennard-Jones potential is frequently used to describe the interaction between molecules. Because of its simplicity, it has been applied in many molecular simulations for thermodynamic properties of simple fluids. This model can be expressed by:

\[ u_{ij} = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \]  

where \( \varepsilon \) and \( \sigma \) are the energy and size parameters and \( r \) is the distance between the molecules. For unlike pairs of molecules we need to introduce proper combining rules for size and energy parameters. One of the oldest and the most used combining rules for these parameters have been proposed by Lorentz [20] and Berthelot [21]. Lorentz combining rule for size parameter (\( \sigma \)) which is correct for hard sphere potential models is an arithmetic average of the size parameters of two unlike molecules read as

\[ \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \]  

For the energy parameter, the geometric average of two unlike molecules has been proposed by Berthelot as follows

\[ \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \]  

These two equations known as Lorentz-Berthelot (LB) combining rules have been widely used in molecular dynamics simulations. Based on LB combining rules, almost all cubic equations of state followed the same rules for calculation of the energy (aij) and size parameter (bij) for unlike pairs of components in a multicomponent mixture, read as

\[ a_{ij} = \sqrt{a_i a_j} \] \[ b_{ij} = \frac{b_i + b_j}{2} \]  

In spite of successful application of the above mentioned rules for the volumetric and phase equilibrium calculations for multicomponent mixtures, serious deficiencies have been observed in many molecular simulations for various mixtures properties using these simple rules [22-25].

In engineering, the inadequacy of LB combining rules has been corrected by using binary interaction parameters. The binary interaction parameters are often optimized using VLE calculations for binary mixtures and matching with experimental values [26]. The idea in this work is to circumvent or obscure the use of binary interaction parameters by employing more appropriate combining rules with theoretical basis.

In a word, the impetus in this work is improving the accuracy of cubic EoSs in describing the PVT of hydrocarbon systems. This study attempts to extend the comparisons made by Ahmed [11] to more EoSs. Further, this study evaluates theoretical combining rules. The subject of this work is furthermore extended to LNGs, some synthetic natural gases and some middle range hydrocarbon mixtures. This study would be comparative in nature. Van der Waals mixing rules are used for all EoSs. Ten combining rules available in literature are combined with seven well-known PVT relations to predict the densities of natural gas mixtures. The best pairs are introduced and reported. No binary interaction parameter would be used.

2. Equations of State (EoS)

Thirteen different EoSs and their variants were used in this study. The two-parameter Redlich-Kwong-Soave (RKS) [15] and their variants RKT [27] and RKSS [28] were used. The two-parameter Peng-Robinson (PR76) [9], Robinson and Peng (PR78) [29] and their variants PRT [30] and PRG [31] were used. The three-parameter Patel-Teja (PT) [4] and its variant by Valderrama (PTV) [5] were used. The three-parameter Schmidt and Wenzel (SW) [3], Guo and Du (GU) [6] and Mosen-Nia et al. (MMM) [14] were used. Salim and Trebble (TBS) [32] was a four-parameter EoS that was also used in this study. The PVT of the EoSs are provided in Figure 1.

![Figure 1. The PVT relationships for EoSs used in this study.](image)

3. Mixing Rules

EoSs require mixing rules to describe mixture properties. For hydrocarbon systems, van der Waals mixing rules are often used:

\[ a = \sum x_i a_{ij} \] \[ a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \] \[ b = \sum x_i b_{ij} \] \[ w = \sum x_i w_j \]

where \( x \) is the mole fraction, \( a \) is the attractive parameter, \( b \) is the co-volume parameter and \( w \) can be \( c \) or \( d \). The parameter \( k_{ij} \) is the binary interaction parameter, which is set to zero in this work. This parameter is used to correct attractive parameter combining rule expressed by Eq. (7). Eq. (5) is used for calculating \( b_{ij} \). Eq. (7) and Eq.(5) are the LB combining rules for EoS calculations. Combining rules target the energy and the size parameters \( a \) and \( b \) in the van der Waals mixing rules (Eqs. 6 and 8). Eq. (9), which is a linear mixing rule, would be applied to \( c \) and \( d \) of the three-parameter and four-parameter EoSs. LB combining rules are the oldest and the most common ones used in practice but due to its inaccurate prediction of properties, other combining rules have also been proposed. Therefore, comparisons with different combining rules would be employed – that is, Lorentz-
The equation has a physical property called polarizability \( \alpha \) which "quantifies the distortion of the overall charge distribution of an atom, group or molecule by an electric field." Values of polarizability of some components that commonly exist in petroleum fluids are presented in Table 1. Lorentz rule was proposed to be used for the repulsive parameter \( b \) as given by Eq. (5).

### Table 1. Polarizability and ionization potential values for some pure components used in this study [42].

<table>
<thead>
<tr>
<th>Component</th>
<th>( I ) (Joule)</th>
<th>( A ) (10^{-24} \text{ cm}^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>3.93934 x 10^{-18}</td>
<td>0.204956</td>
</tr>
<tr>
<td>O2</td>
<td>1.93378 x 10^{-18}</td>
<td>1.5812</td>
</tr>
<tr>
<td>CO2</td>
<td>2.05668 x 10^{-18}</td>
<td>2.911</td>
</tr>
<tr>
<td>N2</td>
<td>2.49632 x 10^{-18}</td>
<td>1.7403</td>
</tr>
<tr>
<td>C1</td>
<td>2.02034 x 10^{-18}</td>
<td>2.593</td>
</tr>
<tr>
<td>C2</td>
<td>1.85212 x 10^{-18}</td>
<td>4.47</td>
</tr>
<tr>
<td>C3</td>
<td>1.75438 x 10^{-18}</td>
<td>6.29</td>
</tr>
<tr>
<td>i-C4</td>
<td>1.6935 x 10^{-18}</td>
<td>8.14</td>
</tr>
<tr>
<td>n-C4</td>
<td>1.68709 x 10^{-18}</td>
<td>8.2</td>
</tr>
<tr>
<td>i-C5</td>
<td>1.65345 x 10^{-18}</td>
<td>-</td>
</tr>
<tr>
<td>n-C5</td>
<td>1.64704 x 10^{-18}</td>
<td>9.99</td>
</tr>
<tr>
<td>n-C6</td>
<td>1.623 x 10^{-18}</td>
<td>11.9</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>1.57814 x 10^{-18}</td>
<td>-</td>
</tr>
<tr>
<td>n-C7</td>
<td>1.59096 x 10^{-18}</td>
<td>13.7</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.41434 x 10^{-18}</td>
<td>11.8</td>
</tr>
<tr>
<td>n-C8</td>
<td>1.57013 x 10^{-18}</td>
<td>15.9</td>
</tr>
</tbody>
</table>

### 3.4 Sikora (S)

In both the energy and the repulsive parameters in Sikora’s combining rules [36], “repulsion” is considered via deformation energies of the electron clouds and resulting unsymmetric collision diameters, which occur at small distances between overlapping atoms or molecules. Accordingly, \( a_{ij} \) and \( b_{ij} \) read:

\[
a_{ij}^S = 2^{15} \frac{I_{ai}I_{aj}}{I_{ai+aj}} \sqrt{\frac{a_{ii}a_{jj}}{a_{ij}\alpha_{ij}}} \tag{13}
\]

\[
b_{ij}^S = 2^{13} \frac{b_{ij}}{b_{ii} + b_{jj}} \tag{14}
\]

### 3.5 Smith-Kong (SK)

Smith [37] developed a combining rule considering the repulsive interaction of simple molecules. His combining rule includes the atomic distortion theory for repulsion (Eq. 16). Kong [38] used a same approach for the energy parameter ‘a’ (Eq. 15):

\[
a_{ij}^{SK} = 2^{33} \frac{a_{ij}a_{ii}^2a_{jj}b_{ij}^2}{(a_{ii}b_{ij}^2)^\frac{1}{13} + (a_{jj}b_{ij}^2)^\frac{1}{13}} \tag{15}
\]

\[
b_{ij}^{SK} = 2^{13} \frac{b_{ij}}{b_{ii} + b_{jj}} \tag{16}
\]

### 3.6 Halgren (HHG)

Halgren [39] proposed cubic mean for the repulsive parameter \( b \) after doing experiments on noble gas mixtures because it described the van der Waals minimum energy distances very well. For the energy parameter \( a \), a combination of the geometric and harmonic mean was applied to yield good descriptions of the experimental noble gas values:

\[
a_{ij}^{HHG} = \frac{4a_{ii}a_{jj}}{\sqrt{a_{ii}^2 + a_{jj}^2}} \tag{17}
\]

\[
b_{ij}^{HHG} = \frac{b_{ii}^3 + b_{jj}^3}{b_{ii}^3 + b_{jj}^3} \tag{18}
\]

### 3.7 Waldman-Hagler (WH)

Waldman and Hagler [40] proposed the combining rules for the energy parameter \( a \) and repulsive parameter \( b \) based on graphical analysis on noble gas mixtures:

\[
a_{ij}^{WH} = \frac{2b_{ii}^2b_{jj}^3}{b_{ii}^6 + b_{jj}^6} \sqrt{a_{ii}\alpha_{jj}} \tag{19}
\]

\[
b_{ij}^{WH} = \left[ \frac{b_{ii}^6 + b_{jj}^6}{2} \right]^\frac{1}{6} \tag{20}
\]

### 3.8 Al-Matar (M1 and M2)

Al-Matar and Rockstraw [41] proposed two combining rules by applying mathematical methods on noble gas mixtures. M1 is the first combining rule, which was proposed by considering that the energy and repulsive parameters \( a \) and \( b \) of the pure components are equally weighted:

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In the second combining rule, (M2), weighting matrices are used and they are found by fitting them to noble gas mixtures. Weighting matrices account for uneven contributions of the energy and repulsive parameters a and b of the pure components to the unlike quantities:

\[ a_{ij}^{M2} = \frac{3b_{ij}^3b_{jj}^3}{2L_{ij}^2} \sum_{L=0}^{L_{ij}} \left( \frac{0.25(b_{ij}^3 + b_{jj}^3)}{b_{ij}^3 + b_{jj}^3} \right)^{6-2L} \]  

\[ b_{ij}^{M1} = \frac{1}{2} \sum_{L=0}^{L_{ij}} \left( \frac{0.25(b_{ij}^3 + b_{jj}^3)}{b_{ij}^3 + b_{jj}^3} \right)^{6-2L} \]  

4. Results and Discussion

A data bank comprised of two binary mixtures, one ternary mixture, five liquefied natural gas (LNG) mixtures and seven synthetic natural gas mixtures was collected. In Table 2 the number of points, the temperature, pressure and density ranges of the binary and ternary mixtures are given. The ranges for temperature are limited to the applications of the mixtures in gas industry. In Tables 3 and 4 the ranges and compositions of LNGs are provided, respectively. One can find the ranges and compositions of the seven synthetic natural gas mixtures in Tables 5 and 6.

The combining rules were based on their effect on predicting densities using the equations of state. The percent average absolute deviation (%AAD) of the predicted densities from experimental values are expressed by:

\[ \%\text{AAD} = \frac{100}{NP} \sum_{i} \left| \frac{\rho_{i}^{\text{exp}} - \rho_{i}^{\text{calc}}}{\rho_{i}^{\text{exp}}} \right| \]  

### Table 2. Binary and ternary mixtures used in this study [43].

<table>
<thead>
<tr>
<th>Binary/Ternary System</th>
<th>No. of data points</th>
<th>Temperature Range (K)</th>
<th>Pressure Range (MPa)</th>
<th>Density Range (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C₅ + n-C₆</td>
<td>105</td>
<td>298.15 – 348.15</td>
<td>0.1 - 40</td>
<td>572.51 - 686.15</td>
</tr>
<tr>
<td>n-C₆ + n-C₇</td>
<td>90</td>
<td>298.15 – 348.15</td>
<td>0.1 - 40</td>
<td>610.77 – 708.48</td>
</tr>
<tr>
<td>n-C₅ + n-C₆ + n-C₇</td>
<td>120</td>
<td>298.15 – 348.15</td>
<td>0.1 - 40</td>
<td>583.77 – 702.63</td>
</tr>
</tbody>
</table>

### Table 3. LNG mixtures used in this study [44].

<table>
<thead>
<tr>
<th>LNG Mixture</th>
<th>Data points</th>
<th>Temperature Range (K)</th>
<th>Pressure Range (MPa)</th>
<th>Density Range (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNG 1</td>
<td>31</td>
<td>105 – 135</td>
<td>0.47938 – 8.74337</td>
<td>451.578 – 498.2</td>
</tr>
<tr>
<td>LNG 2</td>
<td>35</td>
<td>105 – 135</td>
<td>0.18628 – 8.90791</td>
<td>436.468 – 484.597</td>
</tr>
<tr>
<td>LNG 3</td>
<td>28</td>
<td>105 – 135</td>
<td>0.18832 – 8.37252</td>
<td>437.71 – 485.11</td>
</tr>
<tr>
<td>LNG 4</td>
<td>28</td>
<td>105 – 135</td>
<td>0.18805 – 8.65236</td>
<td>436.262 – 484.274</td>
</tr>
<tr>
<td>LNG 5</td>
<td>28</td>
<td>105 – 135</td>
<td>0.18718 – 6.83937</td>
<td>395.82 – 446.529</td>
</tr>
</tbody>
</table>

### Table 4. Composition of the LNG mixtures [44].

<table>
<thead>
<tr>
<th>Component</th>
<th>LNG 1</th>
<th>LNG 2</th>
<th>LNG 3</th>
<th>LNG 4</th>
<th>LNG 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N₂</td>
<td>0.6953</td>
<td>0.3504</td>
<td>0.5854</td>
<td>0.3435</td>
<td>0.1933</td>
</tr>
<tr>
<td>C₁</td>
<td>81.5626</td>
<td>87.8854</td>
<td>84.6362</td>
<td>87.9716</td>
<td>97.8989</td>
</tr>
<tr>
<td>C₂</td>
<td>13.3744</td>
<td>7.2738</td>
<td>12.8</td>
<td>7.24</td>
<td>0.999</td>
</tr>
<tr>
<td>C₃</td>
<td>3.6793</td>
<td>2.9527</td>
<td>1.499</td>
<td>2.9</td>
<td>0.4971</td>
</tr>
<tr>
<td>i-C₄</td>
<td>0</td>
<td>0</td>
<td>0.2199</td>
<td>0.6428</td>
<td>0.1771</td>
</tr>
<tr>
<td>n-C₅</td>
<td>0.6884</td>
<td>1.5647</td>
<td>0.2093</td>
<td>0.6917</td>
<td>0.2092</td>
</tr>
<tr>
<td>i-C₅</td>
<td>0</td>
<td>0.0201</td>
<td>0.11</td>
<td>0.0183</td>
<td></td>
</tr>
<tr>
<td>n-C₅</td>
<td>0</td>
<td>0</td>
<td>0.0301</td>
<td>0.1004</td>
<td>0.0162</td>
</tr>
</tbody>
</table>

### Table 5. Synthetic natural gases used in comparisons [45-47].

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Data points</th>
<th>Temperature Range (K)</th>
<th>Pressure Range (MPa)</th>
<th>Density Range (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix 1</td>
<td>41</td>
<td>250 - 450</td>
<td>0.586 - 37.3445</td>
<td>3.739 - 328.877</td>
</tr>
<tr>
<td>Mix 2</td>
<td>33</td>
<td>250 - 450</td>
<td>0.596 - 36.749</td>
<td>3.877 - 338.88</td>
</tr>
<tr>
<td>Mix 3</td>
<td>30</td>
<td>270 - 340</td>
<td>3.447 - 34.474</td>
<td>23.264 - 298.051</td>
</tr>
<tr>
<td>Mix 4</td>
<td>28</td>
<td>253.15 - 323.15</td>
<td>0.992 - 15.008</td>
<td>6.106 - 177.978</td>
</tr>
<tr>
<td>Mix 5</td>
<td>28</td>
<td>253.15 - 323.15</td>
<td>1 - 15.023</td>
<td>6.746 - 211.811</td>
</tr>
<tr>
<td>Mix 6</td>
<td>59</td>
<td>250 - 450</td>
<td>10 - 65</td>
<td>52.7 - 396.94</td>
</tr>
<tr>
<td>Mix 7</td>
<td>59</td>
<td>250 - 450</td>
<td>10 - 65</td>
<td>50.35 - 377.03</td>
</tr>
</tbody>
</table>
Table 6. Composition of the synthetic natural gases [45-47].

<table>
<thead>
<tr>
<th>Component</th>
<th>Mix 1</th>
<th>Mix 2</th>
<th>Mix 3</th>
<th>Mix 4</th>
<th>Mix 5</th>
<th>Mix 6</th>
<th>Mix 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.015</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.111</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.707</td>
<td>0</td>
<td>0.403</td>
<td>0.066</td>
<td>0.647</td>
<td>2.331</td>
<td>0</td>
</tr>
<tr>
<td>N₂</td>
<td>1.699</td>
<td>0</td>
<td>2.031</td>
<td>0.841</td>
<td>1.474</td>
<td>3.496</td>
<td>0</td>
</tr>
<tr>
<td>C₁</td>
<td>89.99</td>
<td>90.001</td>
<td>90.991</td>
<td>98.352</td>
<td>90.362</td>
<td>84.99</td>
<td>90.26</td>
</tr>
<tr>
<td>C₂</td>
<td>3.15</td>
<td>4.565</td>
<td>2.949</td>
<td>0.511</td>
<td>5.708</td>
<td>5.529</td>
<td>5.828</td>
</tr>
<tr>
<td>C₃</td>
<td>1.583</td>
<td>2.243</td>
<td>1.513</td>
<td>0.153</td>
<td>1.124</td>
<td>2.008</td>
<td>2.106</td>
</tr>
<tr>
<td>i-C₄</td>
<td>0.781</td>
<td>1.14</td>
<td>0.755</td>
<td>0.021</td>
<td>0.301</td>
<td>0.401</td>
<td>0.412</td>
</tr>
<tr>
<td>n-C₄</td>
<td>0.790</td>
<td>1.151</td>
<td>0.755</td>
<td>0.031</td>
<td>0.169</td>
<td>0.585</td>
<td>0.641</td>
</tr>
<tr>
<td>i-C₅</td>
<td>0.150</td>
<td>0.450</td>
<td>0.299</td>
<td>0.008</td>
<td>0.059</td>
<td>0.169</td>
<td>0.214</td>
</tr>
<tr>
<td>n-C₅</td>
<td>0.150</td>
<td>0.450</td>
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Table 7. %AAD for the RK family EoSs in predicting the liquid density of the binary and ternary mixtures using different combining rules.

**RKSS**

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**RKT**

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**RK**

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<th>n-C₆ + n-C₇</th>
<th>%AAD</th>
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<tr>
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</table>
Table 7 provides %AAD in predicting the liquid density of the binary/ternary systems using the RK family EoSs including RKS, RKT and RKSS. Results indicate that for these symmetric systems the LB combining rules are the best among the others when coupled with RK family EoSs. The next best combining rules were FH and HMC, respectively. The %AAD was found to be around 9.6% for this family EoSs with LB combining rules.

When the combining rules were applied to the PR family EoSs in predicting the same liquid mixtures, the results were not coherent. Shown in Fig. 2, WH outperforms the other combining rules when used with the PR family EoSs in predicting the liquid density of n-C5 + n-C6 mixtures. Clearly, the LB combining rules undermine the PR family EoSs among the others. For n-C6 + n-C7 mixtures, HHG was found the best and for the ternary mixture n-C5 + n-C6 + n-C7, the combining rules S were found to be superior.

It was found that the three-parameter EoSs used in this work are more accurate than the two-parameter EoSs in predicting the densities of the liquid mixtures. One reason is that the EoSs are based on a mean field theory. They largely deviate in predicting liquid density near the critical point (reduced temperatures from 0.9 to 1). The ability of two-parameter EoS is often improved by incorporating a third parameter, which is normally a function of the true compressibility factor of fluids. In this way, the ability of the three-parameter EoS is partially augmented. The other reason is that the third parameter, which is similar to molar co-volume b, translates the EoS volume towards experimental value. In Fig. 3 one can see the accuracies of PT and PTV EoS with different combining rules. WH is the best combining rules. However, no particular conclusion can be drawn concerning the combining rules. Only the LB combining rules are not adequate for these EoSs when applied to the binary and ternary mixtures.

Figure 2. %AAD of the PR Family EoSs in predicting the liquid densities of the n-C5 + n-C6 binary mixtures using different combining rules.

Figure 3. %AAD of the PT and PTV EoSs in predicting the liquid densities of the binary mixtures n-C5 + n-C6 and n-C6 + n-C7 using different combining rules.
The ability of the best combining rules with the EoSs in predicting the densities of LNG mixtures are provided in Table 9. Again, the LB combining rules are the best with RK family and TBS EoSs. LB is also superior with the SW and MMM EoSs. For PR family, however, the K combining rules are the best. Compared to LB combing rules, the K combining rules improve greatly the ability of the PR family. While the %AAD is about 2.3% for the PR family with K combining rules, use of LB deteriorates the %AAD to 11.5%. For the rest, other combining rules have privilege as shown in Table 9.

Table 8. The best pairs of EoS/combining rules in predicting the liquid densities of the binary and ternary mixtures.

<table>
<thead>
<tr>
<th>EoS</th>
<th>Combining rules</th>
<th>%AAD</th>
</tr>
</thead>
<tbody>
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<td>RKS</td>
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</tr>
<tr>
<td>RKT</td>
<td>LB</td>
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</tr>
<tr>
<td>RKSS</td>
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</tr>
<tr>
<td>PR78</td>
<td>HHG</td>
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<tr>
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<td>HHG</td>
<td>1.18 (1.70)</td>
</tr>
<tr>
<td>PRT</td>
<td>HHG</td>
<td>1.18 (1.72)</td>
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<td>PT</td>
<td>HHG</td>
<td>0.87 (1.47)</td>
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<tr>
<td>GD</td>
<td>HHG</td>
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<tr>
<td>MMM</td>
<td>WH</td>
<td>5.58 (8.29)</td>
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<tr>
<td>TBS</td>
<td>LB</td>
<td>2.13</td>
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</table>

*The number in the parenthesis indicates the %AAD by LB combining rules

Given in Table 8 are the %AADs in predicting the liquid densities of the binary and ternary mixtures for the best combinations of the EoSs with combining rules. Clearly, the LB combining rules are the best with the RK family EoSs (RKS, RKT, RKSS) and the TBS EoS. For the rest, the LB combining rules has no priority. Clearly, use of the other combining rules, in particular HHG greatly improves the prediction ability of PR family EoSs (PR76, PR78, PRT, PRG) for these binary and ternary mixtures.

Table 9. The best pairs of EoS/combining rules in predicting the liquid densities of the LNG mixtures.

<table>
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<th>EoS</th>
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<th>%AAD</th>
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<tr>
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</tr>
<tr>
<td>PR78</td>
<td>K</td>
<td>2.28 (11.48)</td>
</tr>
<tr>
<td>PRG</td>
<td>K</td>
<td>2.26 (11.62)</td>
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<td>PTV</td>
<td>HHG</td>
<td>1.82 (5.48)</td>
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<tr>
<td>SW</td>
<td>LB</td>
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<tr>
<td>GD</td>
<td>PH</td>
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<td>MMM</td>
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<tr>
<td>TBS</td>
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<td>1.69</td>
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</table>

*The number in the parenthesis indicates the %AAD by LB combining rules

The ability of the best combing rules with the EoSs in predicting the densities of LNG mixtures are provided in Table 9. Again, the LB combining rules are the best with RK family and TBS EoSs. LB is also superior with the SW and MMM EoSs. For PR family, however, the K combining rules are the best. Compared to LB combing rules, the K combining rules improve greatly the ability of the PR family. While the %AAD is about 2.3% for the PR family with K combining rules, use of LB deteriorates the %AAD to 11.5%. For the rest, other combining rules have privilege as shown in Table 9.

Table 10. The best pairs of EoS/combining rules for predicting the densities of the synthetic natural gas mixtures.

<table>
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<td>PR76</td>
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*The number in the parenthesis indicates the %AAD by LB combining rules

Shown in Fig. 4, the four-parameter TBS EoS with LB combining rules predict the liquid densities of binary and ternary mixtures with less %AAD. The FM and HMC closely follow the LB combining rules.

Figure 4. %AAD of the TBS EoS in predicting the liquid densities of the binary mixtures n-C5 + n-C6 and n-C5 + n-C7 and the ternary mixture n-C5 + n-C6 + n-C7 using different combining rules.

Comparisons made in Table 10 reveals that the LB and M1 are quite good for predicting the densities of synthetic natural gas mixtures for the most EoSs. Even when the M1 combining rules are the most accurate, LB combining rules are still close. Then, with the exception of PR family (PR76, PR78, PRT, PRG), LB combing rules are more appropriate for the other EoSs. For the PR family EoSs, however, HHG are more accurate.

Comparing Tables 8-10 makes it clear that for the RK family EoSs (RKS, RKT, RKSS), the SW and TBS equations of state, one can reliably use the LB combining rules. The PR family (PR76, PR78, PRG, PRT) are more accurate with HHG combining rules, however. Although for predicting the densities of LNG mixtures the K combining rules are the best, the use HHG provides an average %AAD of circa 5 %. It means that one can rely on HHG mixing rules for PR family mixing rules.
Gerimental data from Mu and ., n. Equnints from 15 Equations of State,” HHG combining rules were the best. For the PR family EoSs (PR76, PR78, PRT, PRG); however, EoSs (RKS, RKT, RKSS), the SW gas mixtures. The comparisons revealed that for RK family binaries, one ternary, five LNGs and seven synthetic natural

Conclusions

Thirteen EoSs have been coupled with ten combining rules in predicting the liquid and gas densities of two binaries, one ternary, five LNGs and seven synthetic natural gas mixtures. The comparisons revealed that for RK family EoSs (RKS, RKT, RKSS), the SW and TBS EoSs, the LB combining rules are the most accurate and should be preferred. For the PR family EoSs (PR76, PR78, PRT, PRG); however, it was found that HHG combining rules were the best.

List of symbols

- $\alpha$: Temperature-dependent term
- $\sigma$: Size parameter
- $\varepsilon$: Energy parameter

Subscripts

- $c$: Critical property
- $i$: Component number or index
- $LJ$: Lennard-Jones
- $r$: Reduced property

Greek letters

- $\alpha$: Size parameter
- $\varepsilon$: Energy parameter

Abbreviations

- AAD: Average absolute deviation
- EoS: Equation of state
- FH: Fender-Halsey combining rule
- GD: Guo and Du equation of state
- HHG: Halgren combining rule
- HMC: Hudson-McCoubrey combining rule
- K: Kohler combining rule

References


