LIQUID DENSITY OF PURE AND MULTICOMPONENT FLUIDS BY SCALED-VARIABLE-REDUCED-COORDINATE (SVRC) METHOD

Mahmood Moshfeghian, Ataolah Soltani Goharrizy, and I.N.H. Saber
Department of Chemical Engineering, Shiraz University
Shiraz, Iran.

ABSTRACT

The Scaled-Variable-Reduced-Coordinate (SVRC) method with a proposed set of mixing rules are applied to calculate the liquid density of several system of liquid mixture and satisfactory results are obtained. The ability and accuracy of the proposed method are compared with other widely used method such as Hankinson-Thomson method and Spencer and Danner modification of Rackett method. The results of SVRC method with the proposed mixing rule and comparison with other methods indicate that the proposed model is as good as the best available methods.

NOMENCLATURE

AAPD : The average absolute percent deviation
$k_{ij}$ : Binary interaction coefficient defined by eq. (22)
$l_{ij}$ : Binary interaction coefficient defined by eq. (23)
MW : Molecular weight
N : Number of data points
T : Temperature, K
$T_c$ : Critical point temperature, K
$T_t$ : Triple point temperature, K
V : Molar volume, m$^3$/mole
$V_c$ : Molar volume, m$^3$/mole, at the critical point
$V_t$ : Molar volume, m$^3$/mole, at the triple point
x : Mole fraction
$Z_c$ : Compressibility factor at the critical point
$\alpha$ : Scaling exponent
$\rho$ : Liquid density, kg/m$^3$, at given T
$\rho_c$ : Liquid density, kg/m$^3$, at the critical point
\[ \rho_t \] : Liquid density, kg/m\textsuperscript{3}, at the triple point

\[ \omega \] : Acentric factor

**INTRODUCTION**

The prediction of the physical properties of a fluid system is an essential part of any computer simulation package or in model development of any chemical engineering process. One of these physical properties is liquid density. Several correlations have been suggested in the literature for the prediction of liquid density [2-7, 11-15, 18-21, 23, 25-26, 28, 31]. Unfortunately, an evaluation of the popular equations of state such as Soave-Redlich-Kwong [27] and Peng-Robinson [22] has shown that their ability for predicting liquid density is not accurate enough. In addition, a direct calculation of liquid density is more desirable.

Spencer and Danner [28] have studied the capabilities of several correlations, and results of their evaluation are presented in Table 1. Even though the Ehrlich [5], Riedel [25] and Holmes [18] method give relatively acceptable results but since their errors are large in comparison with the Francis correlation and they are therefore not used in a further evaluation. Harmans [15] correlation is applicable

<table>
<thead>
<tr>
<th>Method</th>
<th>No. of Compounds Tested</th>
<th>No. of Points Tested</th>
<th>Average Absolute % Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyckman et al.</td>
<td>36</td>
<td>1597</td>
<td>4.22</td>
</tr>
<tr>
<td>Holmes</td>
<td>6</td>
<td>353</td>
<td>1.80</td>
</tr>
<tr>
<td>Gunn and Yamada</td>
<td>36</td>
<td>1597</td>
<td>0.59</td>
</tr>
<tr>
<td>Francis</td>
<td>36</td>
<td>1597</td>
<td>0.43</td>
</tr>
<tr>
<td>Harmans</td>
<td>11</td>
<td>824</td>
<td>0.68</td>
</tr>
<tr>
<td>Bradford and Thodos</td>
<td>36</td>
<td>1597</td>
<td>2.19</td>
</tr>
<tr>
<td>Riedel</td>
<td>9</td>
<td>641</td>
<td>1.16</td>
</tr>
<tr>
<td>Yen and Woods</td>
<td>24</td>
<td>1357</td>
<td>0.91</td>
</tr>
<tr>
<td>Harlacher</td>
<td>32</td>
<td>1473</td>
<td>0.81</td>
</tr>
<tr>
<td>Ehrlich</td>
<td>5</td>
<td>248</td>
<td>1.30</td>
</tr>
<tr>
<td>Narsimhan</td>
<td>32</td>
<td>1473</td>
<td>2.04</td>
</tr>
<tr>
<td>Rackett</td>
<td>36</td>
<td>1597</td>
<td>2.24</td>
</tr>
</tbody>
</table>
to hydrocarbons heavier than C7 only and therefore, because of this limitation, it is not considered further. Obviously, due to their large errors, the Bradford and Thodos [3], Lyckman [20] and Narsimham [21] correlations are also omitted.

The Rackett equation [23] is a very simple equation which requires only the critical temperature, $T_c$, critical volume, $V_c$, and critical compressibility, $Z_c$. In addition it is capable of predicting liquid density over the range from the triple point to the critical point. However, the large error of 2.24 is not tolerable; Spencer and Danner [28] therefore proposed a modification to this equation and increased its accuracy considerably. They replaced the critical compressibility factor, $Z_c$, by $Z_{RA}$ which was determined for each compound. Table 2 presents the comparison results for the Francis, Rackett and the Spencer and Danner modification of the Rackett equations and shows that the Spencer and Danner method gives excellent results for hydrocarbons but its accuracy is not as good as the Francis method. It should be noted that the Francis method requires four parameters whereas the Spencer and Danner Method requires only one parameter.

**Table 2: Capability of Three Liquid Density Correlations for Pure Compounds (Spencer and Danner, 1972)**

<table>
<thead>
<tr>
<th>Group of Compound</th>
<th>No. of Compounds Tested</th>
<th>No. of Points</th>
<th>Francis</th>
<th>Rackett</th>
<th>Spencer and Danner</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbons</td>
<td>37</td>
<td>1948</td>
<td>1.01</td>
<td>2.50</td>
<td>0.53</td>
</tr>
<tr>
<td>Organics</td>
<td>36</td>
<td>652</td>
<td>0.43</td>
<td>5.50</td>
<td>0.60</td>
</tr>
<tr>
<td>Inorganics</td>
<td>11</td>
<td>148</td>
<td>0.58</td>
<td>0.53</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Recently, Shaver et al. [26] have proposed a unified framework for the prediction of saturated properties using the Scaled-Variable-Reduced-Coordinate (SVRC) approach, specifically for the saturated liquid density of pure fluids. Because of its generality and relatively high precision it will be discussed in detail in the following section. Finally, a set of mixing rules will be proposed to extend their approach to systems of binary and multi-components mixtures.
THE SCALED-VARIABLE-REDUCED-COORDINATE APPROACH

Shaver et al. [26] proposed their Scaled-Variable-Reduced Coordinate model for saturated liquid density of pure fluids as:

$$\rho = \left[ \rho_c^\alpha - \Theta (\rho_c^\alpha - \rho_l^\alpha) \right]^{(1/\alpha)}$$  \hspace{1cm} (1)

where:

$$\Theta = \frac{(1 - A^\varepsilon^B)}{(1 - A)}$$  \hspace{1cm} (2)

$$\alpha = \alpha_c - (\alpha_c - \alpha_l) \left[ \frac{(1 - A^\varepsilon)}{(1 - A)} \right]$$  \hspace{1cm} (3)

$$\alpha_c = C_5 + C_6 \cdot T_t^{(C_7 + C_8 \cdot \omega)}$$  \hspace{1cm} (4)

$$\Delta \alpha = \alpha_c - \alpha_l = C_1 + C_2 \cdot T_t^{(C_3 + C_4 \cdot Z_e)}$$  \hspace{1cm} (5)

$$\varepsilon = \frac{(T_c - T)}{(T_c - T_l)}$$  \hspace{1cm} (6)

A, B, and C_1 through C_8 are the model parameters and were determined by Shaver et al. [26] from experimental data and their values are given in Table 3.
Table 3: The SVRC Model Parameters
(Robinson et al. 1988)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.325</td>
</tr>
<tr>
<td>C₁</td>
<td>3.63493</td>
</tr>
<tr>
<td>C₂</td>
<td>-3.73713</td>
</tr>
<tr>
<td>C₃</td>
<td>0.32786</td>
</tr>
<tr>
<td>C₄</td>
<td>-0.90951</td>
</tr>
<tr>
<td>C₅</td>
<td>+0.36141</td>
</tr>
<tr>
<td>C₆</td>
<td>+2.95802</td>
</tr>
<tr>
<td>C₇</td>
<td>+16.4993</td>
</tr>
<tr>
<td>C₈</td>
<td>-25.4640</td>
</tr>
</tbody>
</table>

EXTENSION OF THE SVRC MODEL TO MULTICOMPONENT SYSTEMS

In order to extend the SVRC model to multicomponent systems, several mixing rules were tested. For each set of mixing rules, liquid densities were predicted and compared with experimental data and the percent deviation for each data point was calculated. Then the average of the absolute percent deviations was calculated. The set of mixing rules giving the least average absolute deviation is the desired one. Based on our evaluation, we propose the following mixing rules.

\[ V_{cm} = \sum_{i}^{n} \sum_{j}^{n} x_i x_j V_{c_{ij}} \]  

(7)

\[ T_{cm} = \frac{1}{V_{cm}^{1/10}} \sum_{i}^{n} \sum_{j}^{n} x_i x_j V_{c_{ij}}^{1/10} T_{c_{ij}} \]  

(8)
\[
\rho_{c_{ij}} = \left( \frac{3\sqrt{\rho_{c_i}} + 3\sqrt{\rho_{c_j}}}{2} \right)^3
\]

(16)

\[
\rho_{l_{ij}} = \left( \frac{3\sqrt{\rho_{l_i}} + 3\sqrt{\rho_{l_j}}}{2} \right)^3
\]

(17)

\[
V_{c_{ij}} = \left( \frac{1}{8} \right) \left( 3\sqrt{V_{c_i}} + 3\sqrt{V_{c_j}} \right)^3
\]

(18)

\[
T'_{c_i} = \frac{T_{c_i}}{C} \cdot \frac{1}{1 + \frac{MW_i \cdot T}{C}}
\]

(19)

\[
C = \eta 2.6 \left( \frac{1}{\eta} \right)^{\left( \frac{1}{\eta} \right)}
\]

(20)

\[
\eta = \sum_{i}^{n} (0.11 - \omega_i) \cdot MW_i \left[ \frac{T_{c_i}}{T} \right]^4
\]

(21)

In the above equations, \( T_{c_i} \) represents the true critical temperature of component \( i \) and \( T'_{c_i} \) is the "effective" critical temperature; \( MW \) is molecular weight; \( V_c \) is critical volume, and \( x \) is mole fraction. If \( C \) in equation (19) is set equal to zero, the "effective" critical temperature, \( T'_{c_i} \), becomes equal to the true critical temperature. The binary interaction parameters \( k_{ij} \) and \( l_{ij} \) are defined by equations (22) and (23),
respectively. The subscript m stands for mixture, c for critical point and t for triple point.

\[
k_{ij} = 1 - \frac{8\left(\sqrt{V_{c_i}V_{c_j}}\right)}{\left(3\sqrt{V_{c_i}} + 3\sqrt{V_{c_j}}\right)^3}
\]

(22)

\[
l_{ij} = 1 - \frac{8\left(\sqrt{V_{t_i}V_{t_j}}\right)}{\left(3\sqrt{V_{t_i}} + 3\sqrt{V_{t_j}}\right)^3}
\]

(23)

The working equations for the calculation of the liquid density of a multi-components system are the same as those for the pure component with mixture properties as described above i.e.

\[
\rho_m = \left[\rho_{c_m}^{\alpha_m} - \Theta_m (\rho_{c_m}^{\alpha_m} - \rho_{t_m}^{\alpha_m})\right]^{\frac{1}{\alpha_m}}
\]

(24)

where:

\[
\Theta_m = \frac{(1 - A_{\varepsilon_m}^{\beta})}{(1 - A)}
\]

(25)

\[
\alpha_m = \alpha_{c_m} - (\alpha_{c_m} - \alpha_{t_m}) \left[\frac{(1 - A_{\varepsilon_m})}{(1 - A)}\right]
\]

(26)

\[
\alpha_{c_m} = C_5 + C_6 \cdot T_{t_m}^{(C_7 + C_8 \cdot \omega_m)}
\]

(27)
\[
\Delta \alpha_m = \alpha_c - \alpha_l = C_1 + C_2 \cdot T_m \cdot (C_3 + C_4 \cdot Z_m)
\]  

(28)

\[
\varepsilon_m = \frac{(T_c - T)}{(T_c - T_m)}
\]  

(29)

It should be noted that the values of A, B and C_1 through C_8 are the same as those presented in Table 3 for pure components. The average absolute percent deviation, AAPD, is calculated by equation (30).

\[
AAPD = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{\rho_{\text{EXP}} - \rho_{\text{CAL}}}{\rho_{\text{EXP}}} \right|
\]  

(30)

In the above equation, N is the number of data point tested and the subscripts EXP and CAL represent experimental and calculated values, respectively.

**RESULTS**

In order to compare the SVRC model with other accurate methods, a computer program and data base were prepared. Using the computer program, the liquid densities of several pure fluid were predicted by the SVRC of Shaver et al. [26], Hankinson-Thomson [13], and Spencer-Danner modification [28] of the Rackett equation and the calculated values were compared with the experimental data. A summary of the results of this comparison is presented in Table 4. In addition, Figs 1 through 5 also present graphical comparison of some of the selected pure fluids. These figures represent the typical accuracy obtained for pure fluids.

The analysis of Table 4 indicates that the SVRC method gives a smaller error for hydrocarbons than both the Hankinson-Thomson and Spencer-Danner methods. For water, however the Hankinson-Thomson gives more accurate results than the other two methods. As it is noticed from Table 4, the SVRC method gives overall best results.
Table 4: Ability of Three Methods in Prediction of Pure Fluid Densities

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>1</td>
<td>32</td>
<td>-280 -125</td>
<td>4.9</td>
<td>575</td>
<td>0.6622</td>
<td>1.2968</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>1</td>
<td>30</td>
<td>-200 70</td>
<td>0.3</td>
<td>563</td>
<td>1.2571</td>
<td>1.5940</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>1</td>
<td>29</td>
<td>-100 190</td>
<td>2.9</td>
<td>524</td>
<td>0.6981</td>
<td>0.9972</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>1</td>
<td>36</td>
<td>-150 290</td>
<td>0.1</td>
<td>477</td>
<td>0.6138</td>
<td>0.3472</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>1</td>
<td>28</td>
<td>-160 180</td>
<td>0.3</td>
<td>562</td>
<td>1.3921</td>
<td>0.3504</td>
</tr>
<tr>
<td>H₂</td>
<td>1</td>
<td>14</td>
<td>-435 -403</td>
<td>1.0</td>
<td>152</td>
<td>1.0958</td>
<td>6.1871</td>
</tr>
<tr>
<td>N₂</td>
<td>1</td>
<td>12</td>
<td>-346 -240</td>
<td>1.8</td>
<td>407</td>
<td>1.0447</td>
<td>0.4027</td>
</tr>
<tr>
<td>CO₂</td>
<td>1</td>
<td>31</td>
<td>-70 80</td>
<td>75.1</td>
<td>969</td>
<td>1.2233</td>
<td>0.3674</td>
</tr>
<tr>
<td>H₂O</td>
<td>1</td>
<td>29</td>
<td>33 500</td>
<td>0.1</td>
<td>680</td>
<td>4.0289</td>
<td>1.1007</td>
</tr>
<tr>
<td>NH₃</td>
<td>1</td>
<td>34</td>
<td>-108 260</td>
<td>0.9</td>
<td>1484</td>
<td>0.4441</td>
<td>1.1833</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>1</td>
<td>35</td>
<td>-144 -440</td>
<td>0.1</td>
<td>945</td>
<td>0.6951</td>
<td>2.0511</td>
</tr>
<tr>
<td>Ar</td>
<td>1</td>
<td>24</td>
<td>-309 -196</td>
<td>10.0</td>
<td>603</td>
<td>1.0316</td>
<td>0.2391</td>
</tr>
<tr>
<td>Ne</td>
<td>1</td>
<td>12</td>
<td>-416 -383</td>
<td>6.3</td>
<td>311</td>
<td>0.2731</td>
<td>0.5851</td>
</tr>
<tr>
<td>Average AAPD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.1123</td>
<td>1.2850</td>
</tr>
</tbody>
</table>
Fig. 1: Ability of three methods in predicting the liquid density of methane

Fig. 2: Ability of three methods in predicting the liquid density of nitrogen
Fig. 3: Ability of three methods in predicting the liquid density of methane carbon dioxide

Fig. 4: Ability of three methods in predicting the liquid density of ammonia
In order to test the capability of the proposed model, the liquid density of several multicomponent systems were predicted by the three methods and the predicted values were compared with literature data. A summary of the results of this comparison is presented in Table 5. As can be seen in Table 5, with the exception of carbon dioxide-butane and propane-butane system the Hankinson-Thomson and Spencer-Danner methods give better results compared to the method when the value of C in equation (19) is set to zero. The quality of SVRC method is improved considerably if C is calculated by eqs. (20-21). The overall analysis of Table 5 indicates that the accuracy of the proposed model is as good as other best available methods and can be used for industrial application.
Table 5: Ability of Three Methods for Prediction of Multicomponent Fluid Density

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₆ C₃H₈</td>
<td>9</td>
<td>22</td>
<td>50 60</td>
<td>2.76 4.14</td>
<td>2.715</td>
<td>2.159</td>
<td>1.690</td>
</tr>
<tr>
<td>CO₂ C₄H₈</td>
<td>24</td>
<td>3</td>
<td>160 160</td>
<td>10.00 10.0</td>
<td>3.420</td>
<td>8.759</td>
<td>13.210</td>
</tr>
<tr>
<td>C₃H₈ C₄H₁₀</td>
<td>9</td>
<td>15</td>
<td>50 140</td>
<td>0.60 1.72</td>
<td>0.243</td>
<td>0.504</td>
<td>0.400</td>
</tr>
<tr>
<td>C₂H₆ C₃H₈ C₄H₁₀</td>
<td>9</td>
<td>14</td>
<td>60 139</td>
<td>0.69 2.41</td>
<td>0.797</td>
<td>0.512</td>
<td>0.335</td>
</tr>
<tr>
<td>N₂ CH₄</td>
<td>16</td>
<td>8</td>
<td>-253 -244</td>
<td>0.841 1.013</td>
<td>1.163</td>
<td>0.771</td>
<td>0.783</td>
</tr>
<tr>
<td>Ar CH₄</td>
<td>30</td>
<td>4</td>
<td>-253 -226</td>
<td>0.88 1.57</td>
<td>2.098</td>
<td>1.148</td>
<td>1.085</td>
</tr>
<tr>
<td>Ar C₃H₆</td>
<td>16</td>
<td>8</td>
<td>-253 -226</td>
<td>0.59 1.47</td>
<td>10.67</td>
<td>5.081</td>
<td>4.225</td>
</tr>
<tr>
<td>Ar CH₄ C₂H₆</td>
<td>30</td>
<td>8</td>
<td>-253 -226</td>
<td>0.65 1.12</td>
<td>2.0987</td>
<td>0.745</td>
<td>0.543</td>
</tr>
<tr>
<td>N₂ CH₄ C₄H₁₀</td>
<td>16</td>
<td>4</td>
<td>-253 -226</td>
<td>0.65 1.12</td>
<td>3.248</td>
<td>0.479</td>
<td>0.199</td>
</tr>
<tr>
<td>CH₄ C₂H₆ C₃H₈ C₄H₁₀</td>
<td>17</td>
<td>5</td>
<td>-217 -253</td>
<td>0.118 0.43</td>
<td>6.650</td>
<td>0.094</td>
<td>0.331</td>
</tr>
<tr>
<td>N₂ CH₄ C₃H₆ C₃H₈ C₄H₁₀</td>
<td>16</td>
<td>4</td>
<td>-235 -253</td>
<td>0.221 0.479</td>
<td>4.566</td>
<td>0.201</td>
<td>0.129</td>
</tr>
<tr>
<td>Average AAPD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.33</td>
<td>1.85</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Average Absolute % Deviation
CONCLUSIONS

A set of mixing rules has been proposed for the SVRC method for the prediction of multicomponent densities. The SVRC along with this set of mixing rules has been evaluated for several binary and multicomponent mixtures. The comparison of calculated results with experimental data indicates that the accuracy of the proposed method is as good as the best available methods such as the Hankinson-Thomson method (COSTALD) or Spencer and Danner modification of the Rackett equation. It should be emphasized that no curve fitting of parameters was required nor were any additional parameters were incorporated in the model. Only the pure component parameters were required in this model. Since the method is so general, it can be recommended for design calculations.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Shiraz University Office of Vice-Chancellor for financial support of this research project under grant no. 69-EN-614-327.

REFERENCES


5. Ehrlich, P., 1967. Advances in thermophysical properties at extreme temperature and pressure, ASME.


30. **Vienrave, T. and Miller, R.C., 1982.** Excess volumes and compressibilities derived from dielectric constant measurements for liquid mixtures of Ar, CH₄, and C₂H₆ from 115 to 130 at pressure to 35 MPa, J. of Chemical Thermodynamics, 14, 361.