Correlation of Vapor-Liquid Equilibria and Saturated Densities of Binary Mixtures by the Generalized Scott-Fuller-Soave-Redlich-Kwong Equation of State

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A new cubic type of Scott-Fuller-Soave-Redlich-Kwong equation of state (SFSRK EOS) has been proposed to calculate both vapor-liquid equilibria and saturated densities of vapor and liquid phases. The parameters of the proposed EOS are given for each pure substance. In this study, the parameters were generalized, based on the critical properties and the acentric factor, for several components representative of LNG. Furthermore, by adopting the exponent type mixing rules for the parameters, both the vapor-liquid equilibria and the saturated densities of vapor and liquid phases for binary mixtures were correlated using the SFSRK EOS. The calculated results show a good correlation with observations, especially for the liquid phase densities.

1. Introduction

An equation of state (EOS) is useful to correlate thermodynamic properties and phase equilibria. Many equations of state have been proposed and can be classified into the van der Waals cubic EOS type such as the Soave-Redlich-Kwong (SRK) EOS¹¹, and the virial expansion EOS type such as the Benedict-Webb-Rubin (BWR) EOS. Both types of EOS have been used to calculate thermodynamic properties and phase equilibria such as vapor-liquid equilibria. The cubic EOS such as the SRK has been frequently adopted because only the critical properties and the acentric factor are required to obtain the constants. However, errors in the calculation of liquid phase densities are large although vapor-liquid equilibria can be well represented. Therefore, we previously proposed a new cubic type of Scott-Fuller-Soave-Redlich-Kwong (SFSRK) EOS¹²) which can be applied to calculate both vapor-liquid equilibria and saturated densities of vapor and liquid phases. The constants of the proposed EOS were given for each pure substance. In this study, we attempted to generalize the constants, using the critical properties and the acentric factor, for several fluid components representative of LNG and examined the correlation of the SFSRK EOS calculations with observed values.

2. Scott-Fuller-Soave-Redlich-Kwong Equation of State

Previously, the Scott-I type repulsion term⁰ was adopted and the attraction term of modified Soave-Redlich-Kwong EOS by Fuller⁵ was coupled with the repulsion term. The proposed EOS is given as follows.

\[ p = \frac{RT(2v + b)}{v(v - b)} - \frac{a}{v(v + cb)} \] (1)

where

\[ a = \Omega_a R^2 T_c^2 \alpha / p_c \] (2)
\[ b = \Omega_b R T_c / p_c \] (3)
\[ c = \frac{1}{\beta} \left[ \frac{\sqrt{\frac{1}{\beta}} + 4 - \beta}{4 - \beta} \frac{1}{4} + \frac{1}{8} \beta^2 - \frac{3}{2} \right] \] (4)

and related parameters are given as

\[ \Omega_a = \frac{\left(4 + 4\beta - \beta^2\right)(1 + c\beta)^2}{\beta(2 - \beta)^2(2 + c\beta)} \Omega_b \] (5)
\[ \Omega_b = \beta \left(4 \beta^2(2 + c\beta) - (4 + 4\beta - \beta^2)(1 + c\beta) \right) (2 - \beta)^2(2 + c\beta) \] (6)
\[ \alpha = \left[1 + q(1 - T_1^{1/2})\right]^2 \] (7)

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\[ q = \left( \frac{\beta}{0.345} \right)^{1/4} m \]  
\[ Z_e = \frac{(4 - \beta c)(2 + c_0 \beta c) - (4 + 4 \beta c - \beta c)}{(2 - \beta c)(2 + c_0 \beta c)} \]  
\[ \beta = \beta c + (\beta_0 - \beta c) \left[ 2 \left( 1 + \exp \left\{ \frac{\theta (T_c - 1)}{1 + \exp \{\theta (T_c - 1)\}} \right\} \right] \]  
\[ \beta_0 = b / v_c \quad (T = T_c) \]  
\[ \theta = 10.9356 + 0.0285 P \]  

As shown above, by using the critical properties \( T_c, p_c, \) and \( Z_c, \) the parachor \( P, \) and the parameters \( m \) and \( \beta_0 \) of the pure substance, the three constants \( a, b, \) and \( c \) can be evaluated. The following conditions should be adopted:

\[ a = a_c, \quad b = b_c, \quad c = c_c \quad (T > T_c) \]  

### 3. Generalized Parameters

To apply Eq. (1) to a variety of substances, the parameters \( m \) and \( \beta_0 \) should be generalized because \( T_c, p_c, \) and \( Z_c, \) can be given as the critical properties, \( P, \) can be estimated by a group-contribution method, and the parameter \( \beta_0 \) can be determined by solving Eqs. (4) and (9) using a given \( Z_c. \) Based on the parameter \( m \) determined previously for normal fluids, the following expression can be obtained.

\[ m = 0.283 + 1.33 \omega \quad (0 < \omega < 0.23) \]  
\[ \beta_0 \]  

The values of the physical properties and SFRSK parameters are listed in Table 1. The generalized results are also shown in Figs. 1 and 2. The average deviations for the parameters \( m \) and \( \beta_0 \) were 1.3% and 4.7%, respectively.

### 4. Mixing Rules

Suitable mixing rules for the three constants are required to calculate the thermodynamic properties of mixtures. The following exponent type mixing rule was adopted here because such a mixing rule seems to be more flexible and provides the conventional mixing rule by letting \( \beta_i = 1 \) and \( \beta_i = \beta_i = 1. \)

\[ a_m = \sum_i \sum_j x_i x_j a_{ij}, \quad a_{ij} = (1 - k_{ij})a_a a_j \]  
\[ b_m = \sum_i \sum_j x_i x_j b_{ij}, \quad b_{ij} = (1 - l_{ij}) \left( \frac{b_i + b_j}{2} \right) \]
\[
\begin{align*}
\text{Table 2 Correlations of the Results Using the SFSRK EOS for Vapor-Liquid Equilibria and Saturated Densities} \\
\begin{array}{|c|c|c|c|c|c|c|c|c|}
\hline
\text{Binary system} & \text{Temp.} & k_{12} & \beta_{12} & l_{12} & x & y & \rho^x & \rho^y \\
(1) + (2) & [K] & [-] & [-] & [-] & & & & \\
\hline
\text{CH}_4 + \text{C}_2\text{H}_6 & 294.26 & 0.040 & 1.00 & 0.00 & 4.8 & 2.1 & 3.4 & 8.0 \\
& & 0.074 & 1.00 & 0.03 & 2.2 & 2.2 & 3.0 & 7.3 \\
& & 0.074 & 1.00 & 0.03 & 2.2 & 2.2 & 3.0 & 7.3 \\
& 310.93 & 0.082 & 1.00 & 0.00 & 4.7 & 4.5 & 5.0 & 4.8 \\
& 0.119 & 1.00 & 0.06 & 2.8 & 4.0 & 3.1 & 4.9 \\
& 0.129 & 1.01 & 0.08 & 1.3 & 3.9 & 3.0 & 4.8 \\
& 327.59 & 0.108 & 1.00 & 0.00 & 5.1 & 4.1 & 4.0 & 3.0 \\
& 0.146 & 1.00 & 0.06 & 0.9 & 1.4 & 1.5 & 3.1 \\
& 0.146 & 0.99 & 0.04 & 0.4 & 1.4 & 2.2 & 2.8 \\
& 310.93 & 0.034 & 1.00 & 0.00 & 8.6 & 7.3 & 3.8 & 9.6 \\
& 0.062 & 1.00 & 0.04 & 5.1 & 5.5 & 4.2 & 9.9 \\
& 0.060 & 1.01 & 0.04 & 4.6 & 5.6 & 4.2 & 9.9 \\
& 344.26 & 0.084 & 1.00 & 0.00 & 6.0 & 2.7 & 4.2 & 5.5 \\
& 0.111 & 1.00 & 0.04 & 3.1 & 3.1 & 3.6 & 6.0 \\
& 0.116 & 1.01 & 0.05 & 2.7 & 3.2 & 3.6 & 6.1 \\
& 377.59 & 0.170 & 1.00 & 0.00 & 6.1 & 4.0 & 5.8 & 3.7 \\
& 0.189 & 1.00 & 0.04 & 2.8 & 5.3 & 4.0 & 3.5 \\
& 0.192 & 0.99 & 0.04 & 1.3 & 6.0 & 3.7 & 3.5 \\
& 310.93 & 0.037 & 1.00 & 0.00 & 8.0 & 6.2 & 3.7 & 9.1 \\
& 0.065 & 1.00 & 0.03 & 6.0 & 5.7 & 3.3 & 8.9 \\
& 0.082 & 1.02 & 0.07 & 3.3 & 6.5 & 3.7 & 9.3 \\
& 344.26 & 0.090 & 1.00 & 0.00 & 2.9 & 1.7 & 4.2 & 3.6 \\
& 0.097 & 1.00 & 0.01 & 2.3 & 1.9 & 3.9 & 3.7 \\
& 0.097 & 1.01 & 0.02 & 2.7 & 1.7 & 3.8 & 3.9 \\
& 377.59 & 0.172 & 1.00 & 0.00 & 4.4 & 6.0 & 4.0 & 1.1 \\
& 0.154 & 1.00 & -0.02 & 4.8 & 5.2 & 4.4 & 1.0 \\
& 0.158 & 0.98 & -0.04 & 3.8 & 5.3 & 4.5 & 0.8 \\
& 323.15 & 0.086 & 1.00 & 0.00 & 4.5 & 7.5 & 3.4 & 8.2 \\
& 0.145 & 1.00 & 0.02 & 2.0 & 7.6 & 4.3 & 8.7 \\
& 0.142 & 0.99 & 0.01 & 1.1 & 7.5 & 4.2 & 8.8 \\
& 273.15 & 0.163 & 1.00 & 0.00 & 2.1 & 4.3 & 3.4 & 5.3 \\
& 0.159 & 1.00 & -0.01 & 2.4 & 3.5 & 2.8 & 4.7 \\
& 0.159 & 1.00 & -0.01 & 2.4 & 3.5 & 2.8 & 4.7 \\
& 288.15 & 0.181 & 1.00 & 0.00 & 3.1 & 6.9 & 2.3 & 1.0 \\
& 0.195 & 1.00 & 0.02 & 3.1 & 6.6 & 2.9 & 1.2 \\
& 0.195 & 1.00 & 0.02 & 3.1 & 6.6 & 2.9 & 1.2 \\
& 253.15 & 0.087 & 1.00 & 0.00 & 4.2 & 11.5 & 3.3 & 7.3 \\
& 0.053 & 1.00 & -0.04 & 0.9 & 9.1 & 2.7 & 7.1 \\
& 0.053 & 1.00 & -0.04 & 0.9 & 9.1 & 2.7 & 7.1 \\
& 273.15 & 0.155 & 1.00 & 0.00 & 6.2 & 7.1 & 2.1 & 3.9 \\
& 0.077 & 1.00 & -0.08 & 1.8 & 1.6 & 2.1 & 3.9 \\
& 0.077 & 1.00 & -0.08 & 1.8 & 1.6 & 2.1 & 3.9 \\
& 288.15 & 0.179 & 1.00 & 0.00 & 6.5 & 7.1 & 3.1 & 3.4 \\
& 0.123 & 1.00 & -0.08 & 3.9 & 4.8 & 1.7 & 1.6 \\
& 0.102 & 1.01 & -0.09 & 2.7 & 4.9 & 1.5 & 1.5 \\
\hline
\end{array}
\end{align*}
\]

\(a) \text{Dev.} = \frac{1}{N} \sum \frac{|\text{calc.}^{(i)} - \text{exp.}^{(i)}|}{\text{exp.}^{(i)}} \times 100, N = \text{Number of datum points.}\)

\[d_m = \sum_{i} \sum_{j} x_i x_j d_{ij}, \quad d_{ij} = (1 - l_{ij}) \left( \frac{d_i + d_j}{2} \right) \tag{18}\]

\[\ln \frac{f_i}{p_{x_i}} = 2 \ln \left( \frac{2v_{x_i} - b_{x_i}}{2v - b_{x_i}} \right) + 2A_{i} \frac{R T d_m}{v + d_m} \ln \left( \frac{v}{v + d_m} \right) - \frac{a_m C_i}{RT d_m^2} \left( \ln \left( \frac{v}{v + d_m} \right) + \frac{d_m}{v + d_m} \right) - \ln Z \tag{20}\]

where

\[d_i = (cb)_i\]

On the basis of the standard thermodynamic procedure, the fugacity of the \(i\)-th component \(f_i\) which is needed for the calculation of the phase equilibria can be readily derived as follows from the EOS given by Eq. (1) with the mixing rules shown above.

\[A_{i} = 2 \left( \sum_{j} x_i b_{ij} \right) - b_{x_i} \quad (b_{ij} = b_{ji}, i \neq j) \tag{21}\]
By using the generalized expressions of Eqs. (14) and (15), for the parameters $m$ and $\beta_0$, the vapor-liquid equilibria and saturated densities of both vapor and liquid phases for several binary mixtures common in LNG process design could be correlated by the SFSRK EOS with the mixing rules of Eqs. (16)-(18). The values of the exponent parameters $\beta_{11}, \beta_{21}$ and $\beta_{22}$ were fixed at unity for simplicity and the remaining three parameters
$k_{12}, l_{12}$ and $\beta_{12}$ were determined by minimizing the sum of the absolute relative average errors for the experimental vapor and liquid phase compositions, which are more sensitive than the densities to the binary parameters. The vapor-liquid equilibria were calculated using the thermodynamic conditions under which the fugacities of the $i$-th component in both vapor and liquid phases are equal at the given temperature and pressure.

Vapor-liquid equilibria and saturated densities for several binary mixtures are available\textsuperscript{8)–11). The critical properties and other related properties of pure substances are shown in Table 1. The correlation of the results obtained from the SFSRK EOS is presented in Table 2. As typical examples, the correlations for CH\textsubscript{4} + C\textsubscript{3}H\textsubscript{8} and CH\textsubscript{4} + CO\textsubscript{2} systems are shown in Figs. 3–6. The calculations using the SRK EOS are also represented as the dotted lines in these figures. As shown in Table 2 and Figs. 3–6, the SFSRK EOS achieves better correlations than the SRK EOS, especially for the calculation of liquid phase densities. As shown in Table 2, the effect of the $l_{12}$ or the exponent $\beta_{12}$ seems to be small although the correlation for liquid phase composition $x$ is improved. These interaction parameters $l_{12}$ and $\beta_{12}$ may become more important when the SFSRK EOS is applied to an asymmetric mixture with components of different molecular sizes and polarities.

### Nomenclatures

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>$A$</td>
<td>value defined by Eq. (21)</td>
</tr>
<tr>
<td>$a$</td>
<td>parameter of SFSRK, Eq. (1)</td>
</tr>
<tr>
<td>$B$</td>
<td>value defined by Eq. (22)</td>
</tr>
<tr>
<td>$b$</td>
<td>parameter of SFSRK, Eq. (1)</td>
</tr>
<tr>
<td>$C$</td>
<td>value defined by Eq. (23)</td>
</tr>
<tr>
<td>$c$</td>
<td>parameter of SFSRK, Eq. (1)</td>
</tr>
<tr>
<td>$f_i$</td>
<td>fugacity of component $i$</td>
</tr>
<tr>
<td>$k_{ij}$</td>
<td>interaction parameter between components $i$ and $j$</td>
</tr>
<tr>
<td>$l_{ij}$</td>
<td>interaction parameter between components $i$ and $j$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
</tr>
<tr>
<td>$\omega$</td>
<td>acentric factor</td>
</tr>
<tr>
<td>$\phi_{ij}$</td>
<td>exponent in Eq. (16)</td>
</tr>
<tr>
<td>$\rho_0$</td>
<td>parachor</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>$v$</td>
<td>molar volume</td>
</tr>
<tr>
<td>$x$</td>
<td>mole fraction of liquid phase</td>
</tr>
<tr>
<td>$y$</td>
<td>mole fraction of vapor phase</td>
</tr>
<tr>
<td>$Z$</td>
<td>compressibility factor</td>
</tr>
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### References

要　旨

一般化 Scott-Fuller-Soave-Redlich-Kwong 状態方程式による 2 成分系気液平衡ならびに飽和密度の相関

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前者で、気液平衡ならびに気液両相の飽和密度計算に適用できる新しい状態方程式として、Scott-Fuller-Soave-Redlich-Kwong（SFSRK）式を提案した。しかしながら、提案された SFSRK 式のパラメーターは純物質ごとに与えられていた。そこで本研究では、LNG のプロセス設計に重要となる流体を対象に、臨界定数と偏心因子を用いてパラメーターの一様化を試みた。さらに、一般化されたパラメーターに指数型の混合則を適用し、メタン+プロパン、メタン+ブタン、メタン+二酸化炭素など 2 成分混合物の気液平衡ならびに飽和密度の計算を行い、良好な相関結果を得た。特に液相飽和密度の計算精度は良好であった。

Keywords

Equation of state, Phase equilibria, Density, Thermodynamics, Gas, Separation

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