Mixing rules for van-der-Waals type equation of state based on thermodynamic perturbation theory

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Abstract

A concept based on the thermodynamic perturbation theory for a ‘simple fluid’ has been applied to the attractive term of a van-der-Waals type equation of state (EOS) to derive a simple mixing rule for the $a$ parameter. The new mixing rule is a small correction to the original one-fluid approximation to account for the influence of particles of $j$-type on the correlation function of $ii$-type in a mixture consisting of particles of $i$ and $j$ types. The importance of the correction has been shown by comparison of the calculated results for binary mixtures of Lennard–Jones fluids with the data obtained by numerical method (Monte-Carlo simulation). The new mixing rules can be considered as a flexible generalization of the conventional mixing rules and can be reduced to the original v-d-W mixing rules by defaulting the extra binary parameters to zero. In this way the binary parameters already available in the literature for many systems can be used without any additional regression work. Extension of the new mixing rules to a multicomponent system do not suffer from ‘Michelsen–Kistenmacher syndrome’ and provide the correct limit for the composition dependence of second virial coefficients. Their applicability has been illustrated by various examples of vapor–liquid and liquid–liquid equilibria using a modified Patel–Teja EOS. The new mixing rules can be applied to any EOS of van-der-Waals type, i.e., EOS containing two terms which reflect the contributions of repulsive and attractive intermolecular forces. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cubic equations of state (EOS) have become very popular in process design due to their simplicity and ability to describe wide ranges of components and conditions. Most of these EOS are based on the original van-der-Waals type EOS with two terms which accounts for contributions of repulsive and attractive intermolecular forces. Recently, there has been considerable effort to extend the use of
cubic EOS to handle complex phase equilibrium problems containing polar and non-polar components. In most cases, improvement in the representation of pure component properties is achieved by using a flexible temperature dependence for the attractive parameter $a$, while the improvement in representing the binary and multicomponent vapor–liquid equilibrium (VLE) and liquid–liquid equilibrium (LLE) data is achieved by modifying the mixing rule for this parameter. A brief review of various attempts to enhance conventional mixing rules for cubic EOS is presented by Mathias et al. [1]. Many empirically designed ‘flexible’ mixing rules [2–5] suffer from ‘Michelsen–Kistenmacher syndrome’ [6] or ‘the problem of invariance’ [1]. The main difficulty lies in the extension of binary results to calculate multicomponent systems. Mathias et al. [1] provided an empirical modification which overcomes the problem of invariance but retains another problem which is due to the wrong composition dependence of the second virial coefficient. This second problem is less significant in practice. Wong and Sandler [7] proposed a mixing rule which addresses the problem of composition dependence of the second virial coefficient but it is based on the Huron and Vidal [8] type approach which duplicates the excess properties from the activity coefficient models and suffers from some thermodynamic inconsistency as shown by Michelsen and Heidemann [9].

The main purpose of the present work is to extend the popular van-der-Waals one fluid model in such a way as to avoid some of the deficiencies outlined above and to demonstrate its application to systems which are difficult to correlate using currently available mixing rules, e.g., hydrocarbon–alcohol and hydrocarbon–water. The present approach provides a theoretically-based generalization of conventional mixing rules. The generalization is based on the first-order perturbation theory which can be identified with the van-der-Waals EOS under certain conditions [10,11]. The correction of conventional mixing rules arises in a natural way of enhancing the ‘one-fluid approximation’ [12] for the first-order term of perturbation theory. The result was briefly mentioned by Abovsky [13,14] in regards to the application of perturbation theory to strongly nonideal fluid mixtures. This result is now extended to cubic EOS. It is shown that the way to improve conventional mixing rules is to consider a correction to terms contributed by the interaction of similar particles. Work by Kabadi and Danner [15] and Michel et al. [16] provides examples of empirical efforts using such a correction for fitting liquid–liquid equilibrium data.

2. Perturbation theory and ‘one-fluid approximation’ for mixture

Consideration [10] of a system of particles interacting with hard-core-with-attraction potential leads to the following expression for Helmholtz free energy;

$$A = A_r + A_a$$

where $A_r$ is the contribution of a reference system represented by particles with repulsive interaction only and $A_a$ is the first-order perturbation term. For simplicity we shall consider the $A_a$ term for spherically symmetric intermolecular interaction, although results could be extended, without restrictions, to system with angular-dependent interaction [14]:

$$A_a = -2\pi N\sigma^3 e/\nu \int_0^\infty g_0(r,v,d)\phi_a(r)r^2 dr$$

$$= -2\pi N\sigma^3 e/\nu \int_0^\infty \left[1 + h_0(r,v,d)\right]\phi_a(r)r^2 dr$$

(2)
where $N$—number of particles in the system; $\sigma$—geometric parameter of the attractive part of the pair potential function; $\varepsilon$—energy parameter of the pair potential function; $\phi(r)$—nondimensional part of the pair potential function; $v$—specific volume per particle; $g_0(r,v,d)$—radial distribution function of a reference system; its dependence on temperature arises from the reduced diameter of ‘effective’ hard sphere $d = D(T)/\sigma$; the system of ‘effective’ hard spheres is used to replace a reference system with ‘soft’ repulsive interaction; $r$—reduced intermolecular distance; and $h_0(r,v,d)$—correlation function of a reference system.

Introducing the following relations,

$$S_0(T) = \int_{d(T)}^{\infty} \phi_0(r)r^2\,dr$$

(3)

and

$$S_h(v,T) = \int_{d(T)}^{\infty} h_0(r,v,d)\phi(r)r^2\,dr$$

(4)

results in

$$A_x = -a_0(T)[1 + s(v,T)]/v$$

(5)

where $a_0(T) = 2\pi Ne\sigma^3S_0(T)$ and $s(v,T) = S_h/S_0$. Eq. (5) is obtained for a pure substance; the first term on the right hand side is the contribution of the first order perturbation theory to the second virial coefficient; the second term is the contribution of interactions of more than two particles.

Generalization of Eq. (5) for mixtures leads to

$$A_{am} = -(1/v)\sum_i x_i \sum_j x_j a_{0ij}(T) - (1/v)\sum_i x_i \sum_j x_j a_{0ij}(T) s_{ij}(x,v,T)$$

(6)

where the first term is the contribution of the mixture second virial coefficient. $s_{ij}(x,v,T)$ is the ratio of values defined by Eqs. (3) and (4) for mixtures and is generally a function of composition because of the composition dependence of the correlation function $h_{0ij}(r_{ij},x,v,d_{ij})$. However, if we assume $s_{ij}(x,v,T)$ to be independent of composition, then it follows that:

$$s_{ij}(v,T) = s(v,T)$$

(7)

Eq. (7) represents the ‘one-fluid approximation’ [12] for the first-order term of a perturbation expansion for mixtures. The structure of $A_{am}$ within this approximation becomes identical to the structure of $A_x$ for a pure component:

$$A_{am} = -a_{0m}(T)[1 + s(v,T)]/v$$

(8)

where

$$a_{0m} = \sum_i x_i \sum_j x_j a_{0ij}(T)$$

(9)

which is the well known conventional one-fluid mixing rule for parameter $a_{0m}$. $s$ is different for each EOS as will be shown later.
In general, \( s_{ij} \) is composition-dependent and can be expressed as [14]

\[
s_{ij}(x,v,T) = s(v,T)[1 + c_{ij}(x,v,T)]
\]  

(10)

where \( c_{ij} \) is a correction to the one-fluid approximation and is related to \( h_{0ij} \) through Eq. (4). Calculations by Lee and Levesque [17] have shown that \( h_{0ij}(r_{ij},x,v,d_{ij}) \) can be substantially different from \( h_{0}(r,v,d) \) if diameters of hard spheres are significantly different which results in \( c_{ij} \) being nonzero.

3. Correction to ‘one-fluid approximation’

Figs. 1 and 2 illustrate applicability of perturbation theory described by Abovsky [14] for model binary systems with a Lennard–Jones potential function. Results of computational experiment by Monte-Carlo simulation [18] were used for comparison. While the ‘one-fluid approximation’ (Eq. (7)) was sufficient for mixture of particles with equal size parameters (Fig. 1), one correction parameter was required to fit adequately the simulation results for system with particles of substantially different sizes (Fig. 2). Correction \( c_{21} \) for this system is equal to 0.2 \( x_1 \) which confirms the assumption \( c_{ij} \ll 1 \). These results were based on the assumption that \( c_{ij} \) is independent of volume. Neglecting the

Fig. 1. Reduced pressure \( \rho \sigma^3 / \epsilon_1 \) vs. mole fraction \( x_1 \) and vs. reduced density \( \rho / \sigma^3 \) for binary system with Lennard–Jones interaction at reduced temperature \( k_B T / \epsilon_1 = 1.15 \). The ratios of parameters are: \( \sigma_2 / \sigma_1 = 1.0 \). \( x_1 / \epsilon_2 = 0.5 \). The circles are results of Monte–Carlo simulations [18]. The line represents ‘one-fluid approximation’ of perturbation theory [14].
volume dependence of $c_{ij}$ and expanding it in power series of compositions while keeping only the linear terms we obtain:

$$c_{ij}(x,T) = \sum_{x_i} x_i \left( \frac{\partial c_{ij}}{\partial x_i} \right)_{x_i=0} = \sum_{x_i} x_i k_{e_{ij}}(T)$$  \hspace{1cm} (11)

$c_{ij}$ should go to zero at the limit of a pure component according to Eq. (10). To satisfy this condition,

$$k_{e_{iii}} = \left( \frac{\partial c_{ii}}{\partial x_i} \right)_{x_i=0} = 0$$  \hspace{1cm} (12)

Combining Eqs. (6), (9) and (10) yields:

$$A_{am} = -a_{0m}(x,T)/v - a_{0m}(x,T)[1 + c_{ij}] s(v,T)/v$$  \hspace{1cm} (13)

Letting $a_m(x,T) = a_{0m}(x,T)[1 + c_{ij}]$, then

$$A_{am} = -a_{0m}(x,T)/v - a_m(x,T) s(v,T)/v$$  \hspace{1cm} (14)

where $a_m$ is the mixture a parameter. Note that $a_m$ can be considered as the sum of the one-fluid $a_{0m}$, and a correction term $\Delta a$, i.e.,

$$a_m = a_{0m} + \Delta a$$  \hspace{1cm} (15)
with $\Delta a$ defined subsequently in Eq. (28). For a binary mixture:

$$a_{0m} = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2$$  \hspace{1cm} (16)

$$a_m = a_{11}x_1^2(1 + x_2k_{c12}) + 2a_{12}x_1x_2(1 + x_1k_{c121} + x_2k_{c122}) + a_{22}x_2^2(1 + x_1k_{c221})$$

$$a_{12} = (a_1a_2)^{1/2}(1 - k_{12})$$  \hspace{1cm} (17)

By collecting terms and defining,

$$k_{c12} = k_{c112} + 2k_{c121}a_{12}/a_{11}$$  \hspace{1cm} (18)

$$k_{c21} = k_{c221} + 2k_{c122}a_{12}/a_{22}$$  \hspace{1cm} (19)

$$a_m = a_{11}x_1^2(1 + x_2k_{c12}) + 2a_{12}x_1x_2 + a_{22}x_2^2(1 + x_1k_{c21})$$  \hspace{1cm} (20)

Eq. (20) contains two new adjustable parameters $k_{c12}$ and $k_{c21}$ in addition to conventional parameter $k_{12}$ in Eq. (17). The parameter $k_{cij}$ reflects the influence of component $j$ on contribution of $ii$-interaction to mixture free energy, and, similarly $k_{cji}$ reflects the influence of component $i$ on contribution of $jj$-interaction to mixture free energy. Eq. (20) can be generalized for a multicomponent mixture as shown below:

$$a_m = \sum_i x_i^2a_{ii} \left[1 + \sum_{j \neq i} k_{cij}x_j \right] + \sum_i x_i\sum_{j \neq i} x_ja_{ij} \left[1 + \sum_{l \neq ij} k_{cijl}x_l \right],$$  \hspace{1cm} (21)

where parameter $k_{cijl}$ reflects the influence of component $l$ on contribution of interaction $ij$. Although $k_{cijl}$ is strictly a ternary parameter, it is more useful to evaluate this parameter from binary data. For this, a careful choice has to be made regarding the calculation of the cross term to avoid the ‘Michelsen–Kistenmacher syndrome’. The geometric mean with retention of proper sign is necessary. Thus, $k_{cijl}$ can be calculated as follows:

$$k_{cijl} = (k_{cil}k_{cjl})^{1/2}$$  \hspace{1cm} (22)

where $k_{cii}$ and $k_{cii}$ are binary parameters which can be positive or negative. If both are positive, then the positive sign is used for the square root; if both are negative, then the negative sign must be used; if $k_{cii}$ and $k_{cii}$ have alternate signs, then it is appropriate to assume zero for $k_{cijl}$ since comparable values of opposite sign will result in zero interaction, and if one of the values is much less than the other, the square root of the product will tend to be close to zero because binary parameters are generally less than unity.

4. Equation of state of van-der-Waals type

The v-d-W EOS can be derived from perturbation theory as shown by Smith and Alder [10] and Kac et al. [11] following the pioneering work by Zwanzig [19] on perturbation expansions based on a hard sphere reference system. From Eq. (14), we obtain the attractive term of any v-d-W type EOS:

$$p_{am} = -a_{0m}/\nu^2 - \left[ s - \nu(\partial s/\partial \nu) \right] a_m/\nu^2$$  \hspace{1cm} (23)
where \( a_{0m} \) and \( a_m \) can be calculated using Eqs. (16), (17) and (21) and the \([s - v(\partial s/\partial v)]\) term is different for each EOS. If we neglect the volume dependence of \( s \), then Eq. (23) reduces to the v-d-W attractive term. For other EOS \([s - v(\partial s/\partial v)]\) can be obtained by matching the attractive term of the EOS with Eq. (23) and by noting that \( a_m = a_{0m} = a \) for pure components. For the Redlich–Kwong (R–K) EOS [20] we obtain:

\[
s - v(\partial s/\partial v) = -(b/v)/(1 + b/v)
\]  

(24)

Similarly, for the three-parameter Patel–Teja (P–T) EOS [21] for which the pure component pressure equation is

\[
p = RT/(v - b) - a/[v(v + b) + c(v - b)]
\]  

(25)

we obtain

\[
s - v(\partial s/\partial v) = -[b/v + c/v(1 - b/v)]/[1 + b/v + c/v(1 - b/v)]
\]  

(26)

For a mixture, \( a_{0m} \) is different from \( a_m \), therefore, if we substitute Eqs. (15) and (26) into Eq. (23) we obtain the mixture form of the P–T EOS:

\[
p = RT/(v - b) - a_m/[v(v + b) + c(v - b)] + \Delta a/v^2
\]  

(27)

where the mixing rule for \( a_m \) is given by Eq. (21) and

\[
\Delta a = \sum_i x_i^2 a_i + \sum_{j \neq i} k_{ij} x_j + \sum_i x_i \sum_{j \neq i} x_j a_{ij} \sum_{k \neq i} k_{ij} x_k
\]  

(28)

If all parameters \( k_{ij} \) are equal to zero, then \( \Delta a = 0 \) and \( a_m = a_{0m} \), which results in the conventional one-fluid mixing rule. When \( \Delta a = 0 \), the mixture form of the EOS, Eq. (27) will also reduce to the pure component form, Eq. (25). The second virial coefficient from Eq. (27) is made up of contributions from \( a_m \) and \( \Delta a \) terms. The effect of the last term in Eq. (27) is to cancel out the contribution of the \( \Delta a \) term embedded in \( a_m \), leaving only the contribution of \( a_{0m} \) which is quadratic in composition. Therefore, Eq. (27) provides the correct composition dependence for the second virial coefficient of the mixture. This term can be used with any EOS to satisfy this constraint on the mixture second virial coefficient. The use of this term makes Peng–Robinson and Patel–Teja EOS quartic instead of cubic in volume which is less desirable if an analytical solution is required for the density root, however, this is not a problem when a numerical solution is used to calculate the density. In this study, we use a general three parameter Patel–Teja EOS. This EOS when combined with a flexible attractive term, allows accurate representations of vapor pressure, liquid density, and liquid heat capacity data [22], the three most important pure component properties needed for a successful process design. The EOS is given by Eq. (27), with pure component parameters defined as follows,

\[
a = \Omega_a \frac{R^2 \tau^2}{P_c} \alpha [\tau], \quad b = \Omega_b \frac{RT_c}{P_c}, \quad c = \Omega_c \frac{RT_c}{P_c}
\]  

(29)

where, \( \Omega_a, \Omega_b, \) and \( \Omega_c \) are functions of the predicted critical compressibility factor denoted by \( \zeta_c \).
The following constraints at the critical points are applied to the EOS:
\[
\left( \frac{\partial P}{\partial v} \right)_{T_c} = 0, \quad \left( \frac{\partial^2 P}{\partial v^2} \right)_{T_c} = 0, \quad \frac{P V_c}{RT_c} = \xi_c
\]  
(30)

With the critical constraints, the following relationships are established between the three dimensionless parameters \( \Omega_a, \Omega_b, \) and \( \Omega_c \) with \( \xi_c \):
\[
\Omega_c = 1 - 3\xi_c
\]  
(31)
\[
\Omega_b^3 + (2 - 3\xi_c)\Omega_b^2 + 3\xi_c^2\Omega_b - \xi_c^3 = 0
\]  
(32)
\[
\Omega_a = 3\xi_c^2 + 3(1 - 2\xi_c)\Omega_b + \Omega_b^2 + 1 - 3\xi_c
\]  
(33)

\( \Omega_b \) is obtained by solving for the smallest positive root of Eq. (32). For the attractive term, the following function of reduced temperature is used.
\[
\alpha[T] = 1 + c_1(T_e - 1) + c_2\left(\frac{T_r}{T_e} - 1\right) + c_3(T_r^N - 1)
\]  
(34)

Constants \( c_1, c_2, c_3, N \) and \( \xi_c \) were obtained by simultaneous regression of pure component experimental data for vapor pressure, liquid density, and liquid heat capacity. Table 1 shows the values of pure component parameters used in this work. Experimental data were taken from the DIPPR data compilation [23].

For mixtures, the following mixing rules were used.
\[
a_{m} = a_0 + \Delta a
\]  
(35)
where \( \Delta a \) is given by Eq. (28); however, it is more convenient to write Eq. (28) as follows:
\[
\Delta a = -\sum_i \sum_j x_i x_j \sum_{i \neq j} x_i k_{ij} (a_i a_j)^{1/2}, \quad k_{ij} = (k_{i1} k_{j1})^{1/2}
\]  
(36)
\[
a_0 = \sum_i x_i \sum_j x_j (a_i a_j)^{1/2}(1 - k_{ij}), \quad k_{ij} = k_{ji}
\]  
(37)
\[
b = \sum_i x_i \sum_j x_j \left(\frac{b_i^{1/3} + b_j^{1/3}}{2}\right)^3 (1 - 1_{ij}), \quad 1_{ij} = 1_{ji}
\]  
(38)
\[
c = b \sum_i x_i \sum_j x_j \left(\frac{c_i/b_i + c_j/b_j}{2}\right)(1 - m_{ij}), \quad m_{ij} = m_{ji}
\]  
(39)

For a given binary system, we can have as many as five binary parameters \( k_{12}, k_{c12}, k_{c21}, l_{12}, m_{12} \). In most cases, however, we do not need all five parameters. Only one or two parameters are required for most VLE calculations, and three parameters are required for complex VLE and LLE calculations. To cover a wide range of temperatures, the parameters need to be temperature dependent. We have used the following temperature dependence:
\[
k_{ij} = k1_{ij} + k2_{ij}/T + k3_{ij} \ln(T)
\]  
(40)
Table 1
Pure component parameters

<table>
<thead>
<tr>
<th>Component</th>
<th>$T_c$ (K)</th>
<th>$P_c$ (MPa)</th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$c_3$</th>
<th>$N$</th>
<th>$\xi_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>369.83</td>
<td>4.248</td>
<td>2.28968</td>
<td>-4.97686</td>
<td>-0.30851</td>
<td>2</td>
<td>0.3076</td>
</tr>
<tr>
<td>Butane</td>
<td>425.12</td>
<td>3.796</td>
<td>1.16274</td>
<td>-3.21657</td>
<td>-0.13352</td>
<td>2</td>
<td>0.3158</td>
</tr>
<tr>
<td>Pentane</td>
<td>469.70</td>
<td>3.370</td>
<td>1.65121</td>
<td>-3.99114</td>
<td>-0.21328</td>
<td>2</td>
<td>0.3121</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>553.58</td>
<td>4.073</td>
<td>2.43049</td>
<td>-4.79121</td>
<td>-0.38096</td>
<td>2</td>
<td>0.3142</td>
</tr>
<tr>
<td>Benzene</td>
<td>562.16</td>
<td>4.898</td>
<td>3.69025</td>
<td>-6.21024</td>
<td>-0.66095</td>
<td>2</td>
<td>0.3119</td>
</tr>
<tr>
<td>Methanol</td>
<td>512.64</td>
<td>8.097</td>
<td>-0.56959</td>
<td>-1.39897</td>
<td>0.05333</td>
<td>6</td>
<td>0.2753</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>536.05</td>
<td>4.179</td>
<td>-5.34670</td>
<td>1.02041</td>
<td>2.02301</td>
<td>2</td>
<td>0.2988</td>
</tr>
<tr>
<td>Water</td>
<td>647.13</td>
<td>22.055</td>
<td>0.34350</td>
<td>-2.28139</td>
<td>0.05145</td>
<td>2</td>
<td>0.2724</td>
</tr>
</tbody>
</table>

$c_3 = 1.08604$ was used to match the pure component vapor pressure reported with the binary VLE data for the butane–methanol system [30]. $T_c$ and $P_c$ were taken from DIPPR data compilation [23].

A temperature dependence similar to Eq. (40) is used for all parameters. In most cases, only the first two terms of Eq. (40) are needed. For some parameters ($l_{12}$, $m_{12}$), the temperature dependence is rarely required.

5. Results and discussions

Pure component parameters are listed in Table 1. These parameters give accurate representation of pure component vapor pressure data which is important for VLE calculations. The binary parameters are listed in Table 2.

In Fig. 3, results for $n$-butane–methanol system are shown for 373.15 K. This system is very difficult to correlate due to a flat region in the temperature vs. liquid composition curve. Many EOS mixing rules will give false liquid–liquid phase splitting that is often indicated by the maxima and minima in the bubble point curve. As can be seen, the worst results are obtained when the size

Table 2
Binary interaction parameters

<table>
<thead>
<tr>
<th>System</th>
<th>Binary parameters (see Eq. (38) for description of parameters)</th>
<th>$k_{ij}$</th>
<th>$k^2_{ij}$</th>
<th>$k_{3ij}$</th>
<th>$k^2_{12ij}$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$m_{ij}$</th>
<th>$l_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane–Methanol(2)</td>
<td></td>
<td>0.2553</td>
<td>0.4496</td>
<td>-1.4873</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentane–Methanol(2)</td>
<td></td>
<td>-0.1711</td>
<td>156.4</td>
<td>-0.1326</td>
<td>191.4</td>
<td>-1.3857</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane–Water(2)</td>
<td></td>
<td>0.2532</td>
<td>154.8</td>
<td>0.8445</td>
<td>-0.4188</td>
<td>828.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene–Water(2)</td>
<td></td>
<td>0.3038</td>
<td>-4.458</td>
<td>0.3044</td>
<td>321.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane–Water(2)</td>
<td></td>
<td>0.2621</td>
<td>60.3</td>
<td>-0.6324</td>
<td>840.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane–Benzene(2)</td>
<td></td>
<td>0.0247</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Butanol–Water(2)</td>
<td></td>
<td>8.9838</td>
<td>-118.2</td>
<td>-1.5057</td>
<td>-1.0909</td>
<td>-0.7422</td>
<td>325.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Given in kelvin.

Data references: Butane–Methanol [30], Pentane–Methanol [31], Propane–Water [25], Benzene–Water [27,28], Cyclohexane–Water [27,28], Cyclohexane–Benzene [32], 2-Butanol–Water [26].
parameters are not adjusted \((l_{12} \text{ and } m_{12} \text{ equal to zero})\), and the best results are obtained by using the new corrections \(k_{c12}, k_{c21}\), and the size parameter \(m_{12}\). It is interesting to note that there is no liquid phase instability shown by the solid line and the results are identical to the gamma–phi method using the best available activity coefficient model for this type of system, e.g., the Wilson model [24]. The results for the Wilson-RK gamma–phi method are not shown in Fig. 3 because they fall on the same solid line shown for the EOS results.

In Fig. 4, results for the \(n\)-pentane–methanol system for two isotherms at 372.69 K and 422.59 K are shown. In this case temperature-dependent parameters were used to improve the overall representation of the data. This system was recently analyzed by Michelsen and Heidemann [9]. They also
found that the Wilson model used to represent activity coefficients for this binary system could be improved with the temperature-dependent parameters. Our results are slightly better than the MHV-2 model used by Michelsen and Heidemann; however, this is to be expected since we correlated the data directly with the use of binary parameters while their results are based on calculations associated with the implementation of an activity coefficient model into an EOS.

In Fig. 5, results of VLE and LLE data correlations are shown for the propane–water system. This is a typical hydrocarbon–water system which exhibits VLE and LLE behavior. To evaluate binary parameters, we used experimental data for VLE, LLE and GLE (gas solubility) covering the temperature range from 313.15 to 413.15 K and the pressure range of 0.5 to 20.2 MPa. The binary parameters are listed in Table 2. Two temperature-dependent parameters ($k_{ij}$ and $k_{e,ij}$) were used with one additional constant parameter ($k_c$). The results are also compared with the Schwartzentruber et al. [5] mixing rule for the modified SRK equation of state. This is labeled SR-POLAR on the plots. The SR-POLAR EOS needed a total of six binary parameters which includes the adjustable parameter for the constant $b$ in the EOS. As can be seen, the new mixing rules give better representation of the solubility of propane in the water-rich phase for both VLE and LLE data. In Fig. 6, results for the amount of water in the organic phase are shown; again the new mixing rules give a correct behavior for the $P$–$x$ curve. Results for the amount of water in the vapor phase are in Fig. 7; the results are within 5% for the data at 373.15 K. However, the vapor phase data reported by Kobayashi and Katz [25] for 413.15 K gave deviations in the range of 15–20% and the data appear to be inconsistent with those at 373.15 K.

In Fig. 8, LLE data for 2-butanol–water system are shown as a function of temperature and pressure. This system shows the closed-loop LLE behavior. Only data from 0.1 to 70.0 MPa reported by Moriyoshi et al. [26] were used. At higher pressures, we had some problems in convergence and the data close to the hyper-critical solution point were not used in the regression. The new mixing rules clearly show improved performance over the Schwartzentruber et al. mixing rules used in the

![Fig. 5. Comparison of new mixing rules with the Schwartzentruber et al. [5] mixing rules. VLE and LLE data for propane–water system [25].](image-url)
Fig. 6. Comparison of new mixing rules with the Schwartzentruber et al. [5] mixing rules, showing water content in organic phase.

SR-POLAR EOS. The closed solubility loops in the isobaric $T-x$ diagram are very well represented by the new mixing rules. The pressure effect on the LLE data is normally small and is often neglected in most modeling efforts. Fig. 8 shows that it is possible to model the effect of pressure on LLE data using a simple cubic EOS. Most activity coefficient models give adequate representation for low pressure data but fail at higher pressure due to the fact that activity coefficients are independent of pressure.

Finally, Fig. 9 shows that our new mixing rules for the $a$ parameter are free from the ‘Michelsen–Kistenmacher’ syndrome [29]. There is no unusual maximum in the predicted water

Fig. 7. Comparison of new mixing rules with the Schwartzentruber et al. [5] mixing rules, showing water content in vapor phase.
solubility in the benzene–cyclohexane mixture. As shown, the SR-POLAR model based on the Schwartzentruber et al. mixing rules does suffer from this syndrome. We have also checked the case in which one of the binary components is split to give a ternary mixture. In this case, the same numerical value was obtained for the parameter $a$ and the composition derivative of $a$ with respect to mole number before and after the split indicating that the new mixing rules are free from this well known deficiency. The equilibrium calculations were also identical before and after the split.
6. Conclusion

(1) A new mixing rule has been derived for the parameter $a$ of the van-der-Waals type EOS using
the first-order perturbation theory which leads to a small correction to the nonlinear by density term in
the expression for free energy departure.

(2) The new mixing rule gives extra flexibility by considering the contribution of intermolecular
interactions at infinite dilution. In particular, the influence of particles of $j$-type on the correlation
function of $ii$-type in a mixture consisting of $i$ and $j$ types has been accounted for by the new mixing
rule.

(3) The new mixing rule is free from the ‘Michelsen–Kistenmacher’ syndrome and provides the
correct composition dependence of the second virial coefficient.

(4) The new mixing rule is able to describe difficult phase equilibrium data such as those found in
hydrocarbon–alcohol and hydrocarbon–water systems, and it is also capable of describing closed-loop
LLE data such as those found in alcohol–water systems.

7. List of symbols

$A$ Helmholtz free energy
$a$ Temperature-dependent parameter of a cubic EOS
$b$ ‘Covolume’ parameter of a cubic EOS
$c$ Parameter of Patel–Teja EOS
$c_{ij}$ Correction to ‘one-fluid approximation’
$d$ Reduced diameter of ‘effective’ hard sphere
$g_0$ Radial distribution function of a reference system
$h_0$ Correlation function of a reference system
$k_B$ Boltzmann constant
$k_{\text{subscript}}$ Any parameter of mixing rules
$N$ Avogadro’s number
$p$ Pressure
$r$ Reduced intermolecular distance
$R$ Gas constant
$S_0$ Integral defined by Eq. (3)
$S_b$ Integral defined by Eq. (4)
$s$ Ratio of $S_b$ to $S_0$
$T$ Temperature
$\nu$ Specific volume per particle
$x$ Composition

Greek letters
$\alpha$ Temperature dependent function for the attractive term in EOS
$\varepsilon$ Energy parameter of the attractive part of pair potential function
$\phi_s$ Nondimensional part of the pair potential function
$\sigma$ Geometric parameter of the pair potential function
\[ \sum \] \text{Summation}
\[ \zeta_c \] \text{Predicted critical compressibility from EOS}
\[ \Omega \] \text{Dimensionless coefficient in EOS}

\textbf{Subscripts}

- \text{a} \quad \text{Contribution of attractive forces}
- \text{c} \quad \text{Correction}
- \text{i,j,l} \quad \text{Components}
- \text{m} \quad \text{Mixture}
- \text{r} \quad \text{Contribution of repulsive forces}

\textbf{References}