MIXING RULE CONTAINING REGULAR-SOLUTION AND RESIDUAL EXCESS FREE ENERGY

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A mixing rule is indispensable to the prediction of high-pressure vapor-liquid equilibria by means of the cubic equation of state. This paper proposes a new mixing rule of the energy parameter consisting of terms for geometrical mean of pure energy parameters and the residual part of the excess free energy at infinite pressure.

Also, by using the new mixing rule and the SRK equation, high-pressure vapor-liquid equilibria are correlated with good accuracy for 14 binary systems consisting of non-polar, polar, and associating substances.

Introduction

A mixing rule of the energy parameter in an equation of state is important for prediction of high-pressure vapor-liquid equilibria (VLE). Conventionally, the mixing rule that has been widely applied for mixtures consisting of non-polar substances makes use of the geometrical mean of pure energy parameters and the binary interaction parameter. On the other hand, Huron and Vidal's mixing rule⁷⁾ using the excess free energy at infinite pressure is useful for mixtures containing polar substances.

This paper proposes a new mixing rule for general cubic equations of state, considering that a mixing rule combining the characteristics of both the above would be useful for industrial purposes.

1. Theory

To derive the mixing rule for the energy parameter in the cubic equation of state, attention is fixed first on the following equation, in which the molar excess free energy g^E is expressed in terms of the sum of the excess free energy obtained for a regular solution $g^{E(R.Sol)}$ and the residual part of the excess free energy $g^{E(Res)}$.^{1,3,14,15)}

$$g^E = g^{E(R.Sol)} + g^{E(Res)} \quad (1)$$

Developing Abbott's cubic equation of state and dividing it into a hard sphere term and an attraction term, Eq. (2) is given for general cubic equations of state.^{1,2,6)}

$$P = \frac{RT(v + \mu)}{(v - b)(v - \tau)} - \frac{\lambda}{(v - \tau)(v - \phi)} \quad (2)$$

where λ is the target mixture energy parameter for this study, and b , μ , τ and ϕ are mixture parameters which depend on the temperature and the composition of the mixture considered.

The excess free energy G^E for n [mol] of a mixture is defined by Eq. (3),

$$G^E = H^E - TS^E = U^E + PV^E - TS^E \quad (3)$$

where U^E , the excess internal energy, V^E , the excess volume, and S^E , the excess entropy for n [mol] of a mixture are given by:

$$U^E = U - \sum_i^N n_i u_i \quad (4)$$

$$V^E = V - \sum_i^N n_i v_i \quad (5)$$

$$S^E = \left(S - \sum_i^N n_i s_i \right) - R \sum_i^N n_i \ln x_i \quad (6)$$

U , the internal energy, and S , the entropy for n [mol] of a mixture in Eqs. (4) and (6) are obtained from Eqs. (7) and (8) using the known pressure-volume-temperature behavior of a mixture.

$$U = \int_V^\infty \left\{ P - T \left(\frac{\partial P}{\partial T} \right)_{V, n_i} \right\} dV + \sum_i^N n_i u_i^{id} \quad (7)$$

$$S = \int_V^\infty \left\{ \frac{nR}{V} - \left(\frac{\partial P}{\partial T} \right)_{V, n_i} \right\} dV + R \sum_i^N n_i \ln \frac{V}{n_i RT} + \sum_i^N n_i s_i^{id} \quad (8)$$

Substituting Eq. (2) in Eqs. (7) and (8) and applying Eqs. (3) to (6), the molar excess free energy g^E is given as follows:

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$$\begin{aligned}
g^E = \frac{G^E}{n} = & \frac{\lambda}{\tau - \phi} \ln \left(\frac{v - \tau}{v - \phi} \right) - \sum_i^N x_i \left\{ \frac{\lambda_{ii}}{\tau_i - \phi_i} \ln \left(\frac{v_i - \tau_i}{v_i - \phi_i} \right) \right\} \\
& - RT \left[\frac{\mu + b}{b - \tau} \ln(v - b) - \sum_i^N x_i \left\{ \frac{\mu_i + b_i}{b_i - \tau_i} \ln(v_i - b_i) \right\} \right] \\
& + RT \left[\frac{\tau + \mu}{b - \tau} \ln(v - \tau) - \sum_i^N x_i \left\{ \frac{\tau_i + \mu_i}{b_i - \tau_i} \ln(v_i - \tau_i) \right\} \right] \\
& + Pv - P \sum_i^N x_i v_i
\end{aligned} \quad (9)$$

In the next step, the excess free energy is derived for a regular solution, defined as a mixture satisfying the following relations:²⁰⁾

$$S^E = 0 \quad \text{and} \quad V^E = 0 \quad (10)$$

For a regular solution, it is assumed that Eq. (11) holds for the mixture energy parameter so that the mixture energy parameter is given by Eq. (12).

$$\lambda_{ij} = (\lambda_{ii} \lambda_{jj})^{0.5} \quad (11)$$

$$\lambda = \sum_i^N \sum_j^N x_i x_j \lambda_{ij} \quad (12)$$

Substituting Eqs. (10) to (12) in Eq. (9), the molar excess free energy for a regular-solution $g^{E(R.Sol)}$ is obtained as follows:

$$\begin{aligned}
g^{E(R.Sol)} = & \frac{\sum_i^N \sum_j^N x_i x_j (\lambda_{ii} \lambda_{jj})^{0.5}}{\tau - \phi} \ln \left(\frac{\sum_i^N x_i v_i - \tau}{\sum_i^N x_i v_i - \phi} \right) \\
& - \sum_i^N x_i \left\{ \frac{\lambda_{ii}}{\tau_i - \phi_i} \ln \left(\frac{v_i - \tau_i}{v_i - \phi_i} \right) \right\} \\
& - RT \left[\frac{\mu + b}{b - \tau} \ln \left(\sum_i^N x_i v_i - b \right) \right. \\
& \left. - \sum_i^N x_i \left\{ \frac{\mu_i + b_i}{b_i - \tau_i} \ln(v_i - b_i) \right\} \right] \\
& + RT \left[\frac{\tau + \mu}{b - \tau} \ln \left(\sum_i^N x_i v_i - \tau \right) \right. \\
& \left. - \sum_i^N x_i \left\{ \frac{\tau_i + \mu_i}{b_i - \tau_i} \ln(v_i - \tau_i) \right\} \right]
\end{aligned} \quad (13)$$

Equations (9) and (13) give the molar excess free energy for a mixture and a regular solution, respectively. Substituting Eqs. (9) and (13) into Eq. (1), Eq. (14) is given.

$$\frac{\lambda}{\tau - \phi} \ln \left(\frac{v - \tau}{v - \phi} \right) = \frac{\sum_i^N \sum_j^N x_i x_j (\lambda_{ii} \lambda_{jj})^{0.5}}{\tau - \phi} \ln \left(\frac{\sum_i^N x_i v_i - \tau}{\sum_i^N x_i v_i - \phi} \right)$$

$$\begin{aligned}
& + RT \left\{ \frac{\mu + b}{b - \tau} \ln \left(\frac{v - b}{\sum_i^N x_i v_i - b} \right) \right. \\
& \left. + \frac{\tau + \mu}{b - \tau} \ln \left(\frac{\sum_i^N x_i v_i - \tau}{v - \tau} \right) \right\} + Pv - P \sum_i^N x_i v_i + g^{E(Res)}
\end{aligned} \quad (14)$$

Applying the condition of infinite pressure ($P \rightarrow \infty$, $v \rightarrow b$, $g^{E(Res)} \rightarrow g_{\infty}^{E(Res)}$) and rearranging Eq. (14), the following relation consisting of a term based on a regular solution and a term for the residual part of the excess free energy at infinite pressure is given as the mixing rule for the energy parameter of mixtures.

$$\lambda = \sum_i^N \sum_j^N x_i x_j (\lambda_{ii} \lambda_{jj})^{0.5} - \frac{(\tau - \phi)}{\ln \{ (b - \phi) / (b - \tau) \}} \cdot g_{\infty}^{E(Res)} \quad (\tau \neq \phi) \quad (15)$$

If $\tau = \phi$, however, Eq. (16) instead of Eq. (15) is given:

$$\lambda = \sum_i^N \sum_j^N x_i x_j (\lambda_{ii} \lambda_{jj})^{0.5} - (b - \phi) \cdot g_{\infty}^{E(Res)} \quad (\tau = \phi) \quad (16)$$

To derive Eqs. (15) or (16), mixture size parameter b has been expressed by Eq. (17).

$$b = \sum_i^N x_i b_i \quad (17)$$

2. Correlation of High-Pressure Vapor-Liquid Equilibria

To confirm the applicability of the new mixing rule, high-pressure VLE are correlated by the Soave-Redlich-Kwong (SRK) equation²⁴⁾ for 14 binary systems consisting of carbon dioxide, hydrogen, nitrogen and *n*-paraffins as non-polar substances, and acetone, water, ammonia, methanol and ethanol as polar and associating substances.

The new mixing rule of the energy parameter is expressed by substituting the mixture parameters shown in **Table 1** into Eqs. (15) or (16). For the SRK equation, the following mixing rule is given.

$$a = \sum_i^N \sum_j^N x_i x_j (a_{ii} a_{jj})^{0.5} - \frac{\sum_i^N x_i b_i}{\ln 2} \cdot g_{\infty}^{E(Res)} \quad (18)$$

where $g_{\infty}^{E(Res)}$ is the residual part of the excess free energy at infinite pressure. To express $g_{\infty}^{E(Res)}$, the following Redlich-Kister equation²²⁾ is applied:

$$\begin{aligned}
g_{\infty}^{E(Res)} = & RT x_1 x_2 \{ A + B(x_1 - x_2) \\
& + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + E(x_1 - x_2)^4 \\
& + F(x_1 - x_2)^5 + \dots \}
\end{aligned} \quad (19)$$

Table 1. Parameters in Eqs. (2) to (17)

Equation of state	b	λ	μ	τ	ϕ
Soave-Redlich-Kwong ²⁴⁾	b	a	0	0	$-b$
Peng-Robinson ¹⁹⁾	b	a	$(1 + \sqrt{2})b$	$-(1 + \sqrt{2})b$	$-(1 + \sqrt{2})b$
Martin ¹²⁾	b	a	c	$-c$	$-c$
Ishikawa-Chung-Lu ⁸⁾	b	$a/T^{0.5}$	b	0	$-2b$
Pater-Teja ¹⁸⁾	b	a	c	$-c$	$-b$

Fig. 1. Correlated results of vapor-liquid equilibria for the carbon dioxide-methanol system.

Fig. 3. Correlated results of vapor-liquid equilibria for the hydrogen-nitrogen system.

Fig. 2. Correlated results of vapor-liquid equilibria for the propane-ethanol system.

Fig. 4. Correlated results of vapor-liquid equilibria for the methane-*n*-hexadecane system.

The number of parameters in Eq. (19) is adjusted to obtain exact results for each system. Table 2 shows the correlated results given by using the new mixing rule. Table 2 also shows the results given by the conventional mixing rule containing the binary interaction parameter k_{ij} and by Huron and Vidal's mixing rule. As an example, the correlated results for the systems carbon dioxide-methanol (298.15 K),^{10,16)} propane-ethanol (425.00 K),⁵⁾ hydrogen-nitrogen (83.67 K)²⁵⁾ and methane-*n*-hexadecane (542.65 K)¹¹⁾ and shown in Figs. 1 to 4.

When high-pressure VLE are correlated by Huron

and Vidal's mixing rule, the excess free energy at infinite pressure is evaluated by the Redlich-Kister equation which is expressed by Eq. (19). The pure component parameters of the SRK equation are obtained from the generalized equation²⁴⁾ using critical temperature, critical pressure, and the acentric factor.²²⁾

From Table 2, it is evident that the new mixing rule gave better results than the conventional mixing rule using the binary interaction parameter, and slightly better results than Huron and Vidal's mixing rule.

Table 2. Correlated results of high-pressure vapor-liquid equilibria for binary systems by applying the new mixing rule, Huron and Vidal's mixing rule (HV) and the conventional mixing rule (k_{ij})

System	T [K]	Pressure range [MPa]	n	New mixing rule		HV		k_{ij}		Lit.
				A B C	$ \Delta P/P $ av.(%)	A B C	$ \Delta P/P $ av.(%)	k_{12}	$ \Delta P/P $ av.(%)	
Ethane -acetone	298.15	0.48–3.97	8	1.448 0.4216 0.0	1.71	1.612 0.4615 0.0	1.81	0.1341	3.22	17
Ethane -methanol	298.15	1.09–4.12	5	0.2336 –0.003965 0.1864	1.33	1.853 –0.05520 0.1184	1.79	0.0163	5.55	17
Propane -acetone	400.00	1.39–4.20	4	0.4602 0.4394 0.0	0.72	0.5912 0.4522 0.0	0.72	0.0638	4.88	5
Propane -ethanol	425.00	1.03–5.68	13	0.09908 0.2400 0.0	1.15	0.6325 0.1868 0.0	1.29	0.0109	3.09	4
Carbon dioxide -methanol	298.15	0.22–5.95	21	0.4466 0.2955 0.05795 $D = -0.01373$ $E = 0.5246$ $F = 0.4534$	0.94	1.010 0.4120 0.05795 $D = -0.03233$ $E = 0.5132$ $F = 0.4445$	0.98	0.0336	4.56	10, 16
Ammonia -water	353.15	0.05–0.17	8	–4.186 –0.5671 0.0	1.65	–2.453 –0.8058 0.0	1.71	–0.2700	6.85	2
	363.15	0.08–0.14	7	–5.366 –2.174 0.0	1.87	–3.180 –1.828 0.0	1.77	–0.2443	4.86	2
Methanol -water	373.15	0.10–0.34	16	–1.321 0.3318 –0.4034	1.45	0.7916 –0.4984 –0.1093	1.38	–0.0805	3.37	8
Carbon dioxide - <i>n</i> -decane	510.93	1.38–15.33	10	0.5290 0.2752 0.0	1.30	0.6225 0.3430 0.0	1.62	0.1833	2.80	21
Hydrogen -propane	173.15	0.23–20.68	8	0.05114 –0.1866 0.0	1.69	1.754 0.2715 0.0	1.70	0.0811	2.59	27
Hydrogen -nitrogen	83.67	11.27–15.68	6	0.1488 –0.2093 0.0	0.43	1.299 –0.009000 0.0	0.51	0.0167	3.38	25
Nitrogen - <i>n</i> -pentane	310.71	0.25–20.75	14	0.2745 –0.001939 0.0	1.81	0.7240 0.1604 0.0	1.83	0.1037	3.48	9
Methane - <i>n</i> -octane	293.15	7.09–28.37	9	–0.8842 1.224 –0.6359	1.09	–0.8461 1.222 –0.6037	1.09	0.0095	10.95	28
Methane - <i>n</i> -hexadecane	542.65	2.08–22.55	7	0.08648 0.1324 0.0	1.19	0.08459 0.1341 0.0	1.19	0.0351	2.89	11
Ethane - <i>n</i> -heptane	449.82	2.76–8.27	14	0.1334 0.2473 0.0	0.80	0.1351 0.2423 0.0	0.84	0.0486	2.04	3

n = No. of data points

A, B, C, D, E, F = Redlich-Kister parameter in Eq. (19)

Huron and Vidal's mixing rule

$$a = \sum_{i=1}^N x_i b_i \left(\sum_{i=1}^N x_i a_{ii} / b_i - g_{\infty}^E / \ln 2 \right)$$

Conclusions

For the energy parameter in the cubic equations of

state, a mixing rule containing the geometrical mean of pure energy parameters and the residual part of the excess free energy at infinite pressure was derived.

This mixing rule was applied to the SRK equation and high-pressure VLE were correlated with good accuracy for 14 binary systems consisting of non-polar, polar, and associating substances.

Nomenclature

A	= parameter in Redlich-Kister equation	[—]
a	= energy parameter in SRK equation of state	[MPa(m ³ /mol) ²]
B	= parameter in Redlich-Kister equation	[—]
b	= parameter in SRK equation of state or general equation of state	[m ³ /mol]
C, D, E, F	= parameter in Redlich-Kister equation	[—]
G	= free energy per n [mol] of a mixture	[J]
g	= molar free energy of a mixture	[J/mol]
g^E	= molar excess free energy	[J/mol]
$g^{E(Res)}$	= molar residual excess free energy	[J/mol]
$g^{E(R.Sol)}$	= molar excess free energy obtained for a regular solution	[J/mol]
H	= enthalpy per n [mol] of a mixture	[J]
k_{ij}	= binary interaction parameter	[—]
N	= number of components	[—]
n	= number of moles	[—]
P	= pressure	[MPa]
R	= gas constant	[J/(mol·K)]
S	= entropy per n [mol] of a mixture	[J/K]
s	= molar entropy of a mixture	[J/(mol·K)]
T	= temperature	[K]
U	= internal energy per n [mol] of a mixture	[J]
u	= molar internal energy of a mixture	[J/mol]
V	= volume per n [mol] of a mixture	[m ³]
v	= molar volume of a mixture	[m ³ /mol]
x	= mole fraction	[—]
λ	= energy parameter in general cubic equation of state	[MPa(m ³ /mol) ²]
μ, τ, ϕ	= parameter in general cubic equation of state	[m ³ /mol]
<Subscripts>		
1, 2, i, j	= molecule 1, 2, i , and j	
∞	= infinite pressure	
<Superscripts>		
E	= excess property	
id	= ideal gas condition	

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