PREDICTION OF VLE USING ASOG AND ZERO PRESSURE G^E MIXING RULE CONSISTENT THE SECOND VIRIAL COEFFICIENT CONDITION

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Introduction

ASOG has been used for predicting low-pressure VLE (Danner and Daubert, 1983) and recently for predicting high-pressure VLE from a zero pressure g^E mixing rule with low-pressure parameters (Tochigi et al., 1993, Tochigi et al., 1994, Tochigi 1995).

This paper proposes a zero pressure g^E mixing rule consistent with the second virial coefficient condition for Soave-Redlich-Kwong equation. High-pressure VLE have then been predicted for binary systems using low-pressure ASOG parameters (Tochigi et al., 1990b). The predicted results are compared with those by UNIFAC (Hansen et al., 1991).

1. Zero Pressure g^E Mixing Rule Consistent with Second Virial Coefficient Condition

The equation of state used in this study is the Soave-Redlich-Kwong EOS (Soave, 1972),

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)} \tag{1}$$

where a and b are mixture energy and size parameters, respectively.

The g^E mixing rule proposed in this study can be derived as follows. The excess Gibbs energy g^E is obtained by a P-v-T relation using the following equation (Prausnitz et al., 1986).

$$g^E = \int_v^\infty \left[P - \frac{RT}{V} \right] dV - \sum_i \int_{V_i}^\infty \left[P - \frac{RT}{V_i} \right] dV_i$$
$$- RT \sum_i x_i \ln \frac{V}{V_i} + P(V - \sum_i X_i V_i) \tag{2}$$

By substituting Eq.(1) into Eq.(2), g^E is given by Eq.(3).

$$\frac{g^E}{RT} = \frac{a}{RTb} \ln(\frac{v}{v + b}) - \sum_i x_i \frac{a_{ii}}{RTb_i} \ln(\frac{v_i}{v_i + b_i})$$
$$+ \sum_i x_i \ln(\frac{v_i - b_i}{v - b}) + \frac{P}{RT}(v - \sum_i x_i v_i) \tag{3}$$

From the condition of zero pressure, Eq.(4) is derived thermodynamically as follows;

$$\frac{a}{b} = \frac{RT}{\ln(\frac{v_0 / b}{v_0 / b + 1})} [\sum_i x_i \frac{a_{ii}}{RTb_i} \ln(\frac{v_{io} / b_i}{v_{io} / b_i + 1})$$
$$+ \sum_i x_i \ln(\frac{v_0 / b - 1}{v_{io} / b_i - 1}) + \sum_i x_i \ln(\frac{b}{b_i}) + \frac{g_0^E}{RT}] \tag{4}$$

where g_0^E is g^E at zero pressure, v_0/b and v_{io}/b_i are reduced volume of mixture and pure component i, respectively, at zero pressure.

Equation (4) reduces to the modified Huron-Vidal First Order mixing rule (MHV1) by Michelsen (1990) from the assumption that v_{io}/b_i is 1.235 (constant).

$$\frac{a}{b} = \sum_i x_i \frac{a_{ii}}{b_i} - \frac{RT}{0.593}[\frac{g_0^E}{RT} + \sum_i x_i \ln(\frac{b}{b_i})] \tag{5}$$

As the second equation, the conventional linear mixing rule for size parameter b has been used in MHV1.

$$b = \sum_i^n x_i b_i \tag{6}$$

But MHV1 violates the second virial coefficient condition (Wong and Sandler, 1992). So the following second virial coefficient condition by Wong and Sandler (1992) has been utilized as the second equation;

$$B = b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \frac{B_{ii} + B_{jj}}{2}(1 - k_{ij}) \tag{7}$$

where k_{ij} is the composition independent binary interaction parameter. Recently, Eq.(7) with zero k_{ij} for PRSV EOS (Stryjek and Vera, 1986) has been discussed to predict high-pressure VLE using low-pressure activity coefficient correlation (Tochigi et al., 1994, Tochigi, 1995), though its composition dependence becomes linear. In the case that k_{ij} is assumed by Eq.(8),

$$k_{ij} = \frac{(\sqrt{a_{ii}} - \sqrt{a_{jj}})^2}{(a_{ii} + a_{jj}) - (b_i + b_j)RT} \tag{8}$$

Eq.(7) becomes Eq.(9).

Table 1 Predicted results of high-pressure VLE for binary sytems* Using SRK EOS with four mixing rules

System		T [K]	$|\Delta P / P|$ av. [%]			
			ASOG			UNIFAC
(1)	(2)		$g_0{}^{E+}$EQ. (9)	$g_0{}^{E+}$Eq. (6)	$g_\infty{}^{E+}$Eq. (6)	$g_0{}^{E+}$Eq. (9)
Methanol	Water	373.15	4.20	4.00	2.30	3.06
		423.15	2.77	—	1.40	2.46
		473.15	2.90	1.80	1.60	1.51
		523.15	2.18	2.60	4.90	3.17
Acetone	Water	373.15	2.92	3.70	6.10	6.35
		423.15	1.76	5.00	6.60	5.04
		473.15	1.61	1.10	7.40	6.93
		523.15	1.87	1.40	—	6.38
Acetone	Methanol	373.15	2.08	1.00	3.50	3.39
		423.15	1.42	3.70	0.60	1.88
		473.15	4.89	6.80	2.30	4.23
Overall average			2.60	2.83	3.67	4.04

*The VLE data are reported by Griswold and Wong (1952)

$$b - \frac{a}{RT} = \sum_i \sum_i x_i x_j \left\{ \frac{b_{ii} + b_{jj}}{2} - \frac{\sqrt{a_{ii}a_{jj}}}{RT} \right\} \qquad (9)$$

Equation (9) keeps the quadratic composition dependence of the second virial coefficient. Equations (5) and (9) are mixing rule proposed in this study.

2. Prediction of High-Pressure VLE Using ASOG

High-pressure VLE for binary systems can be predicted by calculating $g_0{}^E$ in Eq.(5) using low-pressure ASOG parameters (Tochigi *et al.*, 1990b).

The predicted results of total pressure using Eqs.(5) and (9) are shown for three binary systems in Table 1. Table 1 shows the predicted results using Eq.(6) with Eq.(5), and the following infinite pressure g^E mixing rule (Tochigi et al., 1990a).

$$a = \sum_i \sum_j x_i x_j \sqrt{a_{ii}a_{jj}} - \frac{b}{\ln 2} g_\infty^{E(R)} \qquad (10)$$

In **Table 1**, the predicted results using UNIFAC (Hansen et al., 1991) with Eqs.(5) and (9) are also shown. From the predicted results in Table 1, it can be pointed out that each accuracy depends on the mixing rules and group contribution models used, however Eqs. (5) and (9) with ASOG proposed in this study give the best results for average deviation of total pressure.

Acknowledgment

Nomenclature

a	=	equation of state energy parameter	[m^{6}Pa·mol^{-2}]
b	=	equation of state size parameter	[m^{3}mol^{-1}]

g^E	=	excess Gibbs energy	[J·mol^{-1}]
P	=	pressure	[Pa]
R	=	universal gas constant	[m^{3}Pa·ol^{-1}K^{-1}]
T	=	temperature	[K]
v	=	molar volume	[m^3·mol^{-1}]
x	=	mole fraction	[-]

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