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Direct prediction of the binary parameters of a cubic equation of state from those of a low-pressure g^E model

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ABSTRACT

This paper discusses a method for directly converting a set of binary interaction parameters of a thermodynamic model to that of another thermodynamic model without calculating phase equilibria. The proposed method assumes that the excess Gibbs energy calculated by the original model at a liquid condition is equivalent to that by the other model. To remove iterative procedures in these calculations, an empirical correlation for liquid molar volume is proposed to analytically derive activity coefficients from the equation of state. Performance of the method is examined in obtaining binary interaction parameters of an empirical mixing rule for the SRK equation of state from those of NRTL or molecular sub-group contribution parameters of UNIFAC.

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1. Introduction

Although numerous mixing rules for equations of state have been published for handling highly non-ideal mixtures, industrial usage of the advanced models in engineering works is often restricted by time and cost in obtaining values for binary interaction parameters. It is often the case that parameter values for some binary pairs of interest are available for a conventional thermodynamic model, but are not available for a new thermodynamic model which is presumed to be more suitable for the system.

It is beneficial to establish a swift and reliable method for obtaining parameter values of a new model from those of a conventional one. Although the most straightforward and sure approach is to fit the parameters of a model to the phase equilibrium calculated by a conventional models – assuming the experimental data that were originally used to fit the model parameters are not available, such an approach requires effort to know existing phases accurately when the system shows complex phase behavior, and is eventually difficult to fully automate.

Jaubert and Privat [8] proposed a method to directly convert binary parameter of SRK EOS to that of Peng-Robinson EOS utilizing the rigorous equivalence between the classical mixing rules with temperature dependent k_{ij} and the combination at constant packing fraction of a Van Laar-type excess Gibbs energy model with a cubic EOS. This work tries to establish a method to directly convert binary parameters of activity coefficient models (g^E models) to those of a cubic EOS.

The authors has been working on a direct conversion method for the parameter values by equating excess Gibbs energy or, alternatively, infinite dilution activity coefficient at liquid conditions. These approaches are indicated by the following equations:

$$g^E_{MODEL-1,T,P,x1} = g^E_{MODEL-2,T,P,x1} \tag{1}$$

or

$$\left(\frac{\partial G^E_{MODEL-1,T,P}}{\partial n_i}\right)_{nj\neq i, ni\to 0} = \left\{\frac{\partial G^E_{MODEL-2,T,P}}{\partial n_i}\right\}_{nj\neq i, ni\to 0} \tag{2}$$

Schuwarzrentruber et al. [7] developed a method to predict binary parameters from UNIFAC based on Eq. (2). However it is obvious that the parameters predicted by infinite dilute activity coefficient produces fairly large deviation at the middle part of mole fractions especially when the non-ideality of the mixture is large. This work tries to incorporate Eq. (1) while taking advantage of the simplification of Eq. (2) at the same time.

Abbreviations: SRK, Soave–Redlich–Kwong; NRTL, non-random two liquid; UNIFAC, UNIversal functional activity coefficient; EOS, equation of state.

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When using equations of state, liquid molar volume is required to calculate the excess Gibbs energy. However rigorously calculating liquid molar volume requires multi-loop iterative calculations. Although a zero pressure model [1] is applied Schuwarzrentruber et al. [7], and is widely applied in the development of mixing rules, Schuwarzrentruber et al. showed that the zero pressure model has a solution for SRK EOS only when the following condition is satisfied.

$$\frac{1}{3+2\sqrt{2}} \leq \frac{bRT}{a} \tag{3}$$

This means that the zero pressure model cannot be applied above a certain temperature (around 0.8 Tc). Also, the zero pressure models cannot consider the effect of pressure on liquid molar volume. This paper discusses an empirical correlation to approximately calculate liquid molar volume for the purpose of calculating excess Gibbs energy from cubic equations of state. The correlation should be applicable to a wide range of temperatures and pressures without extensive iterative calculations.

2. Theory

2.1. Liquid molar volume correlation for SRK EOS

As an example case for the proposed approach, this work applies the following SRK equation of state [2] combined with an empirical mixing rule which was proposed by Cunningham et al. [3] by modifying the mixing rule of Panagiotopoulos and Reid [4]. However, the same approach can be applied to other cubic equations of state with two parameters:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{4}$$

$$a = \sum\sum x_i x_j \sqrt{a_i a_i} \left\{ (1-k_{ij}) + (k_{ij}-k_{ji}) \frac{x_i}{x_i+x_j} \right\} \tag{5}$$

$$b = \sum x_i b_i \tag{6}$$

Rearranging the above Eq. (4) in terms of dimensionless numbers (a/bRT), (Pb/RT) and (v/b), the following dimensionless EOS is obtained:

$$\left(\frac{a}{bRT}\right) = \beta(\beta+1)\left\{\frac{1}{\beta-1} - \left(\frac{Pb}{RT}\right)\right\} \tag{7}$$

where,

$$\beta \equiv \frac{v}{b} \tag{8}$$

The above equation indicates that (v/b) depends only on (a/bRT) and (Pb/RT) regardless to the form of temperature dependency of a or b. Instead of iteratively solving the above question for beta, this work proposes the following empirical correlation equation with respect to the dimensionless numbers:

$$\beta = 1 + A\left\{\exp\left(B \times \frac{RTb}{a}\right) - 1\right\} \tag{9}$$

where,

$$A = C_1\left(\frac{Pb}{RT}\right) + C_2 \tag{10}$$

$$B = F_1\left(\frac{Pb}{RT}\right)^4 + F_2\left(\frac{Pb}{RT}\right)^3 + F_3\left(\frac{Pb}{RT}\right)^2 + F_4\left(\frac{Pb}{RT}\right) + F_5 \tag{11}$$

The parameter values indicated in Table 1 were determined to minimize the sum of the absolute values of relative errors between beta by Eq. (7) and that by Eq. (9) in the range of 0–0.8 in beta and 0–0.6 in (Pb/RT). When (Pb/RT) is small, the accuracy of the proposed equation is much better than that of the zero-pressure model as seen in Fig. 1. When (Pb/RT) is large, both models give almost the same accuracy as seen in Fig. 2. However, the correlation Eq. (9) can be applied below the low limit of the zero pressure model in terms of (RTb/a).

Table 1
Parameter values of correlating liquid volume by SRK EOS.

Parameter	Value
C_1	−12.9180
C_2	9.7253
F_1	12.1040
F_2	−9.0196
F_3	3.0468
F_4	0.0693
F_5	0.1969

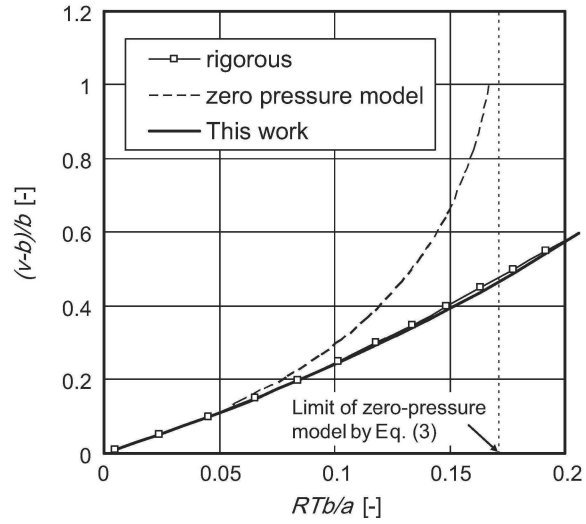

Fig. 1. Effect of parameters of SRK EOS on liquid molar volume $(Pb/RT = 0.5)$.

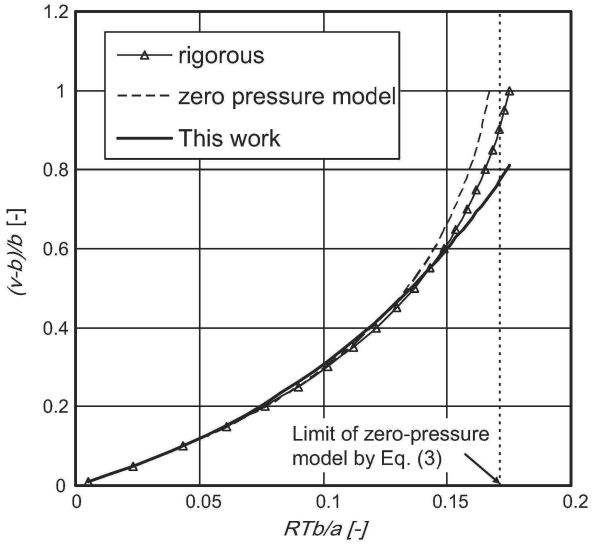

Fig. 2. Effect of parameters of SRK EOS on liquid molar volume $(Pb/RT = 0.5)$.

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2.2. Excess free energy and infinite dilution activity coefficient

The following equation for excess Gibbs energy is derived from the equations above:

$$\frac{g^E_{SRK,T,P,x_1}}{RT} = -\sum x_i \ln\left\{\frac{\beta-1}{\beta_i^o-1}\cdot\left(\frac{b}{b_i}\right)\right\} + \frac{1}{RT}\left\{\frac{a}{b}\ln\frac{\beta}{\beta+1} - \sum\frac{a_i}{b_i}x_i\ln\frac{\beta_i^o}{\beta_i^o+1}\right\} + \frac{Pb}{RT}\left\{\beta - \sum x_i\beta_i^o\left(\frac{b_i}{b}\right)\right\} \tag{12}$$

Activity coefficients at the liquid condition are as follows:

$$\ln(\gamma_i) = -\ln\left(\frac{\beta-1}{\beta_i^o-1}\times\frac{b}{b_i}\right) - \frac{n}{\beta-1}\left(\frac{\partial\beta}{\partial n_i}\right)_{nj\neq i,T,P} + 1 - \frac{b_i}{b} + \frac{a}{RTb}\left[\left\{2-\frac{b_i}{b}+\frac{n}{a}\left(\frac{\partial a}{\partial n_i}\right)_{nj\neq i,T,P}\right\}\ln\left(\frac{\beta}{\beta+1}\right) - \left(\frac{1}{\beta}-\frac{1}{\beta+1}\right)n\left(\frac{\partial\beta}{\partial n_i}\right)_{nj\neq i,T,P}\right] - \frac{a_i}{RTb_i}\ln\left(\frac{\beta_i^o}{\beta_i^o+1}\right) + \frac{Pb}{RT}\left\{\frac{b_i}{b}\left(\beta-\beta_i^o\right) + n\left(\frac{\partial\beta}{\partial n_i}\right)_{nj\neq i,T,P}\right\} \tag{13}$$

where,

$$n\left(\frac{\partial\beta}{\partial n_i}\right)_{nj\neq i,T,P} = \frac{(b_1-b_2)P}{RT}\times\left\{\frac{dA}{d\left(Pb/RT\right)}\right\}_{b=b2}\left\{\exp\left(B\frac{RTb_2}{a_2}\right)-1\right\} + A\ \exp\left(B\frac{RTb_2}{a_2}\right)\frac{RTb_2}{a_2}\left[\left\{\frac{dB}{d\left(Pb/RT\right)}\right\}_{b=b_2}\frac{P(b_1-b_2)}{RT} + B\left(\frac{b_1}{b_2}-1\right) - B\frac{n}{a}\left(\frac{\partial a}{\partial n_i}\right)_{ni\neq j,T,P}\right] \tag{14}$$

$$\frac{n}{a}\left(\frac{\partial a}{\partial n_i}\right)_{ni\neq j,T,P} = 2\frac{a_i}{a}x_i - 2 + \sum_{j\neq i}x_j\left(\frac{a_{ij}}{a}+\frac{a_{ji}}{a}\right) + 2x_i\sum_{j\neq i}\frac{x_j^2}{\left(x_i+x_j\right)^2}\frac{\sqrt{a_ia_j}}{a}\left(k_{ij}-k_{ji}\right) \tag{15}$$

Infinite dilution activity coefficients for a binary system can be readily derived from Eq. (13) as follows:

$$\ln(\gamma_1^\infty) = Y_{12}\left\{2\sqrt{\frac{a_1}{a_2}}(1-k_{12})-2\right\} + X_{12} \tag{16}$$

where,

$$X_{12} = D_2\times E_{12} - \ln\left(\frac{\beta_2^o-1}{\beta_1^o-1}\times\frac{b_2}{b_1}\right) + 1 - \frac{b_1}{b_2} + \frac{a_2}{RTb_2}\left(2-\frac{b_1}{b_2}\right)\ln\left(\frac{\beta_2^o}{\beta_2^o+1}\right) - \frac{a_1}{RTb_1}\ln\left(\frac{\beta_1^o}{\beta_1^o+1}\right) + \frac{Pb_1}{RT}\left(\beta_2^o-\beta_1^o\right) \tag{17}$$

$$Y_{12} = D_2\times J_2 + \frac{a_2}{RTb_2}\ln\left(\frac{\beta_2^o}{\beta_2^o+1}\right) \tag{18}$$

$$D_2 = -\frac{1}{\beta_2^o-1} + \frac{a_2}{RTb_2}\left(\frac{1}{\beta_2^o}-\frac{1}{\beta_2^o+1}\right) + \frac{Pb_2}{RT} \tag{19}$$

$$E_{12} = \frac{(b_1-b_2)P}{RT}\times\left\{\frac{dA}{d\left(Pb/RT\right)}\right\}_{b=b_2}\left\{\exp\left(B\frac{RTb_2}{a_2}\right)-1\right\} + A\ \exp\left(B\frac{RTb_2}{a_2}\right)\frac{RTb_2}{a_2}\left[\left\{\frac{dB}{d\left(Pb/RT\right)}\right\}_{b=b_2}\frac{P(b_1-b_2)}{RT} + B\left(\frac{b_1}{b_2}-1\right)\right] \tag{20}$$

$$J_2 = -A\ \exp\left(B\frac{RTb_2}{a_2}\right)B\frac{RTb_2}{a_2} \tag{21}$$

Solving the above equitation for the binary interaction parameter k_{ij} yields:

$$k_{12} = 1 - \frac{\ln(\gamma_1^\infty) - X_{12} + 2Y_{12}}{2Y_{12}\sqrt{a_1/a_2}} \tag{22}$$

Exchanging the subscripts gives:

$$k_{21} = 1 - \frac{\ln(\gamma_2^\infty) - X_{21} + 2Y_{21}}{2Y_{21}\sqrt{a_2/a_1}} \tag{23}$$

β_1^o and β_2^o are calculated by Eq. (9). Pressure is assumed to be 1 atm because many of the binary parameters of NRTL is determined at ambient pressures.

3. Results

3.1. Binary interaction parameters from infinite dilution activity coefficients

Once the infinite dilution activity coefficients are obtained from other thermodynamic models or experimental data, the binary interaction parameters of the above EOS can be readily obtained using Eqs. (22) and (23).

Performance of the approach is tested on converting binary parameters between NRTL [5] and the above EOS for the ethanol–water system. The infinite dilution activity coefficients for the ethanol–water system were calculated by NRTL, and then simply substituted into these equations. The vapor–liquid equilibrium calculated by the obtained set of the parameter values fairly well matches with that by NRTL as seen in Fig. 3. However the procedure failed to reproduce the occurrence of the azeotrope. The binary interaction parameters obtained from infinite dilution activity coefficients do not give an exact match at the middle composition range as seen in Fig. 4.

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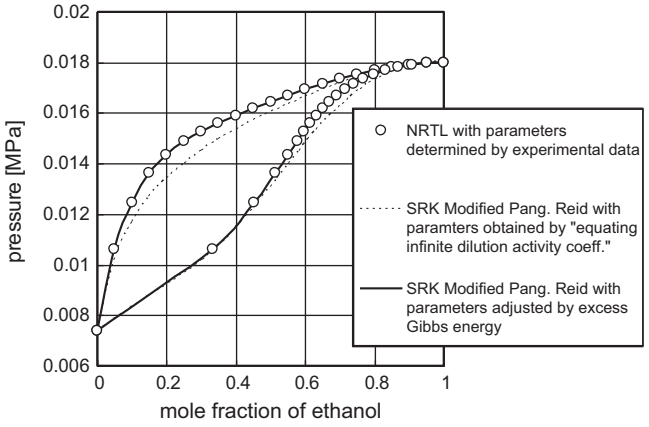

Fig. 3. Vapor–liquid equilibrium for ethanol–water system (313.2 K).

3.2. Correction to make g^E match

The cause of the error in duplicating the curve of excess Gibbs energy is attributed to the difference in the nature of the thermodynamic models. Each model predicts a different curve, even when infinite dilution coefficients are the same. To improve the accuracy of duplicating the curve of excess Gibbs energy, the following simple correction procedure is applied.

Instead of using the infinite dilution activity coefficients obtained from NRTL, we use "practical" infinite dilution activity coefficients which are obtained by multiplying by the correction factor theta.

$$\ln(\gamma_i^{\infty}) = \theta \bullet \ln(\gamma_i^{\infty})\big|_{NRTL} \tag{24}$$

The value of the theta is determined, so that the excess Gibbs energy at the middle of the curve ($x_1 = 0.5$) by one model matches that by the other model:

$$g^E_{EOS,T,P,x1=0.5} = g^E_{NRTL,T,x1=0.5} \tag{25}$$

where,

$$\frac{g^E_{NRTL,T,x1=0.5}}{RT} = 0.5\ \ln(\gamma_{1,x1=0.5}) + 0.5\ \ln(\gamma_{2,x1=0.5}) \tag{26}$$

The excess Gibbs energy by the above equation of state was close to that obtained from NRTL as shown in Fig. 4. The obtained parameter set successfully reproduced the vapor–liquid equilibrium as shown in Fig. 3. For ethanol–water system the obtained value of theta was around 1.11.

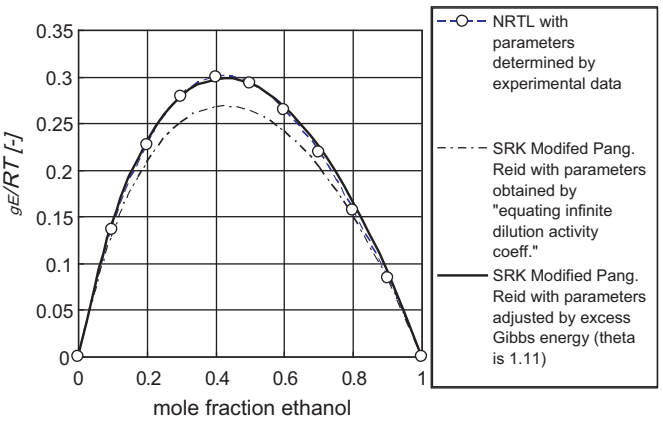

Fig. 4. Excess Gibbs energy for ethanol–water system (313.2 K).

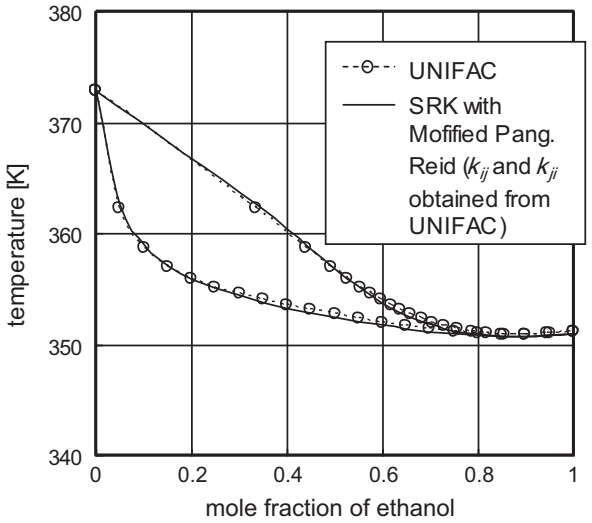

Fig. 5. Vapor–liquid equilibrium for ethanol–water system (100 kPa).

3.3. Combination with UNIFAC

The above approach can be applied to any activity coefficient models including UNIFAC [6]. The combination with UNIFAC enables the prediction of binary interaction parameters from molecular structures. One of the important merits of this approach is that binary interaction parameters obtained from experimental data for (a) certain pair(s) can be used together with those predicted from molecular structures for (an) other pair(s).

As an example, the values of k_{ij} and k_{ji} for the ethanol–water system were calculated at multiple levels of temperature by applying the above procedure to UNIFAC. Then the temperature dependence of k_{ij} and k_{ji} was expressed by the following simple equations.

$$k_{ij} = \alpha_{ij} + \frac{\tau_{ij}}{T} \tag{27}$$

$$k_{ji} = \alpha_{ji} + \frac{\tau_{ji}}{T} \tag{28}$$

Isobaric vapor–liquid equilibria for ethanol–water system predicted by the above equation of state agreed well with those predicted by UNIFAC as shown in Fig. 5. The mole fraction of ethanol at the azeotropic point predicted by the above equation of state at 100 kPa was 0.88 and was close to 0.89 that was predicted by UNIFAC.

4. Conclusions

This work discussed a method for directly converting a set of binary interaction parameters of a thermodynamic model to that of another thermodynamic model without calculating phase equilibria. The proposed method assumed that the excess Gibbs energy at a certain composition and ratio between the values of infinite dilution activity coefficient of the components calculated by the original model at a liquid condition were equivalent to those by the other model.

An empirical correlation for liquid density was proposed to analytically derive the excess free energy and/or activity coefficient from cubic equations of state. The correlation successfully reproduced the liquid molar volume in the model of the SRK equation of state over a wide range of conditions without any iterative calculations.

Performance of the method was examined in obtaining binary interaction parameters of an empirical mixing rule which had been proposed by Cunningham et al. by modifying the mixing rule of

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Panagiotopoulos and Reid. The proposed procedure gave excellent performance in converting the parameters with very limited loss in predictive accuracy for phase equilibrium of the tested pairs. It was also demonstrated that the approach can be applied to obtain binary interaction parameters of equations of state from the UNIFAC activity coefficient model.

List of symbols

a	energy parameter of cubic equation of state (kJm^3/mol^2)
A	parameter for empirical correlation for liquid molar volume
B	parameter for empirical correlation for liquid molar volume
b	volumetric parameter of cubic equation of state (m^3/mol)
C_k	parameter for empirical correlation for liquid molar volume
D	auxiliary parameter
E	auxiliary parameter
F_k	parameter for empirical correlation for liquid molar volume
g	molar Gibbs energy (kJ/mol)
G	Gibbs energy (kJ)
J	auxiliary parameter
k_{ij}	binary interaction parameter of modified Pang–Reid mixing rule
n	molar number (mol)
P	pressure (kPa)
R	Gas constant (kJ/(mol K))
T	absolute temperature (K)
v	molar volume (m^3/mol)
x	molar fraction in liquid
X	auxiliary parameter
Y	auxiliary parameter

Greek letters

α_{ij}	parameter to express the temperature dependency of k_{ij}
β	dimensionless liquid volume
γ	activity coefficient
θ	correction factor for infinite dilution activity coefficient
τ_{ij}	parameter to express the temperature dependency of k_{ij} (K)

Superscripts

E	excess properties
∞	infinite dilution state
o	pure component
k	identification number for parameters of liquid volume correlation

Subscripts

i	component identification number
j	component identification number

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