Methodology for Applying EoS to Phase Equilibrium Calculation for Mixtures

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ABSTRACT

Two methodologies of applying an equation of state (EoS) to mixtures were discussed in terms of calculation stability in VLE of asymmetric mixtures. One is conventional EoS parameters mixing rules such as van der Waals ones and the other is corresponding state principle. The conventional mixing rules were studied with focusing how PVT behaviors at lower reduced temperatures come out for asymmetric mixtures by using cubic EoSs or virial type EoSs such as BWRS EoS having multi-constants. At lower temperatures, BWRS EoS shows PVT curve having three stable regions of which one is hypothetically produced due to polynomial functional form in volume, and it is indicated that this anomalous curves may induce some influence of PVT for highly asymmetric mixtures. While cubic EoSs have no chance of having such anomalous curves. On the second methodology, it was proposed that an approach based on corresponding principle can be used as a new mixing rule combining an EoS for each component of mixtures regardless of its functional form. This allows us to select accurate/suitable EoS for each component for mixtures.

Keywords

Equation of state, Mixing Rules, Corresponding State Principle,

1. INTRODUCTION

Equations of state (EoS) are basically developed to represent the pressure-volume-temperature (PVT) behavior as well as the saturated properties of pure component. In applying such EoS to mixture property calculations, the effect of composition should be considered and several approaches have been proposed. Most popular approach is the mixing rules which defined the EoS constants/parameters of mixtures by defining functional relations of the parameters in terms of composition. The mixing rules can provide very good performance for most cases. However the performance tends to decrease with

highly asymmetric mixtures that consist of different size/polarity components. It would be noted that one possible reason is the difference in reduced temperature of each component even at same temperature. This indicates that, for a large asymmetric system, it is difficult to represent the PVT behaviors for both components by the same functional form of an EoS. It has been sometimes observed singular PVT curves having multiple thermodynamic unstable regions in the case of virial type EoSs. The van der Waals mixing models, which combine the equation constants as a function of composition, can be regarded as a mixing of the PVT curves of each pure component at the temperature. In other words, the model combines the stable and unstable PVT regions depending on the condition.

The corresponding state principle is a good methodology to calculate the mixture properties from pure component information with pseudocritical values. We can adopt this method to combine the thermodynamic properties of each component with confirming the values in stable state. By extending the Lee-Kesler method, a kind of mixing rule can be derived to combine the functionally different type EoSs for each component of the mixtures.

In the presentation, I will discuss the features of two methodologies and indicate a possible extension for phase equilibrium calculation of mixtures.

2. EQUATIONS of STATE

There have been proposed various types of equations of state for mainly hydrocarbons. Cubic equations of state, which are modified van der Waals equation [Eq.1], are widely used to calculate thermodynamic properties in process simulators. However, it has been pointed that cubic EoSs are inferior to virial type EoSs in representing density/enthalpy while cubic EoSs are very suitable in calculating the saturated properties of pure component and phase equilibria of mixtures from viewpoint of simple functional form and calculation stability.

$$P = \frac{RT}{v-b} - \frac{a\alpha(T_r)}{v^2 + \delta v + \varepsilon} \qquad (1)$$

A BWR equation[1], which is the first virial type equation applicable to gas and liquid phases, was proposed by Benedict, Webb and Rubin by combining polynomials in temperature with power series and exponentials of density into 8-constant form. Then many modifications of BWR EoS have been proposed by adding constants optimized with measured data, some of which can be recognized to be able to provide high accuracy for volumetric and thermodynamic properties. It would be noted that some modified equation was adopted as a reference expression of corresponding state form, such as Starling-BWR (BWRS) Eq.[2] and BWR-Saito-Nishiumi (GBWRSN) Eq.[3], with generalized parameters.

$$Z = \frac{Pv}{RT} = 1 + \frac{f_1(T)}{v} + \frac{f_2(T)}{v^2} + \frac{f_3(T)}{v^n} + f_4(T)\frac{\left(\alpha + \gamma/v^2\right)}{v^m}\exp\left[-\frac{\gamma}{v^2}\right] \qquad (2)$$

Comparing these two types of EoS, the differences are the order of polynomial in volume, the number of parameters and their parameter determination procedure, which results in the features of each type of EoS.   Table 1 summarizes the typical ones for both type EoSs.

Table 1   General features of cubic and virial type EoSs

EoS Type	Parameters	Fitting Data	Critical Points	Vapor Press.	Liq. Dens	Enthalpy	VLE LLE	Versatility
cubic vdW	Few	Saturated Prop.	○	○	△	△	○	○
virial mBWR	Many	PVT Sat.Prop.	△	○	○	○	△	△

Since cubic EoS constants are determined by fitting to saturated properties together with critical constrain, their performance for saturated properties is good[4,5] while it would descend for heavier hydrocarbons whose measured critical values are rarely reported. This trend can be seen in Fig.1, the plots of the average absolute deviation (%AAD) of three EoSs[3,4,5] for saturated liquid density and vapor pressure for pure hydrocarbons as a function of acentric factor, ω.
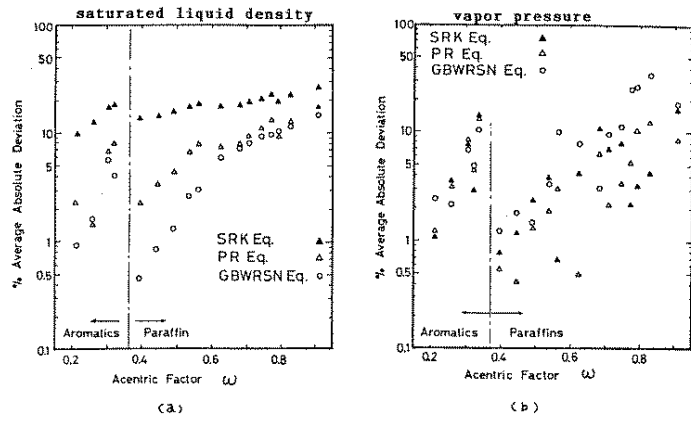

Fig.1   Calculation deviation (%AAD) for saturated properties of hydrocarbons for three EoSs

3. MIXING RULES

To extend an EoS to mixtures, the EoS constants must be given to reflect the mixtures in terms of some algebraic function of composition and pure component parameters. A typical one is van der Waals (vdW) mixing rules in which a mixture constant Q_m is expressed in terms of composition and pure component constants as follows;

$$Q_m = \sum_i \sum_j x_i x_j Q_{ij} \qquad (3)$$

$$Q_{ij} = (1-k_{ij})\sqrt{Q_{ii} \cdot Q_{jj}} \quad or \quad Q_{ij} = (1-k_{ij})\frac{Q_{ii}+Q_{jj}}{2} \qquad (4)$$

In eq.(3), the mole fraction x_i and x_j may apply to a liquid or vapor phase. Q_{ii} and Q_{jj} represent the constants of pure components i and j. Q_{ij}, the cross term of components i and j is given

as the arithmetic average or geometric mean with an interaction parameter, k_{ij}, representing non-ideality of i-j pair potential energy. Quadratic function comes from the widely used assumption that the total energy is the sum of every pair potential.

Cubic type Eos can provide fairly good performance for mixture VLE with vdW mixing rules for few EoS constants. However, it has been pointed that cubic EoSs are not suitable for calculating enthalpy due to their poor density representation. Whereas the virial type EoSs are well known to be capable of providing accurate densities. In applying virial type EoS to mixtures, many EoS constants are represented as a function of composition. For largely asymmetric mixtures, the values of EoS constants become a difference of several orders between components. In such case, it should be noticed that the mixing rule combines fairly different PVT curves of components. When we convert the temperature to the reduced one(T_r), T_r of heavier component may be low as 0.4~0.5 while that of lighter component is above 1.0. Fig.2 shows the examples of Pressure-Density-Temperature (PρT) curves by GBWRSN[3] and SRK[4] EoSs. The curves at lower temperatures by GBWRSN exhibit two minima and two unstable regions in the medium density range while those by SRK show no such behavior. Fig.3 shows PρT curves of GBWRSN EoS for CO_2+n-decane binary at 300 K with varying composition. At lower CO_2 composition, it can be seen two mechanistic unstable regions even in PρT curves of the binary, which may have some influence in evaluating
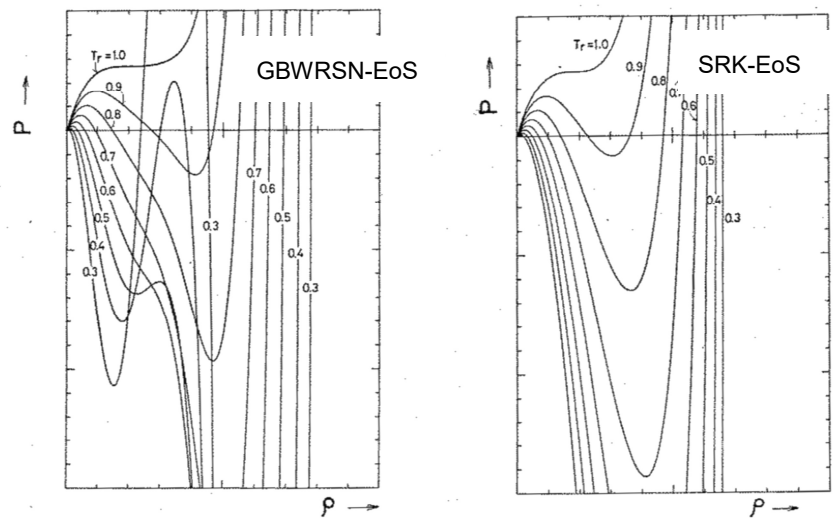

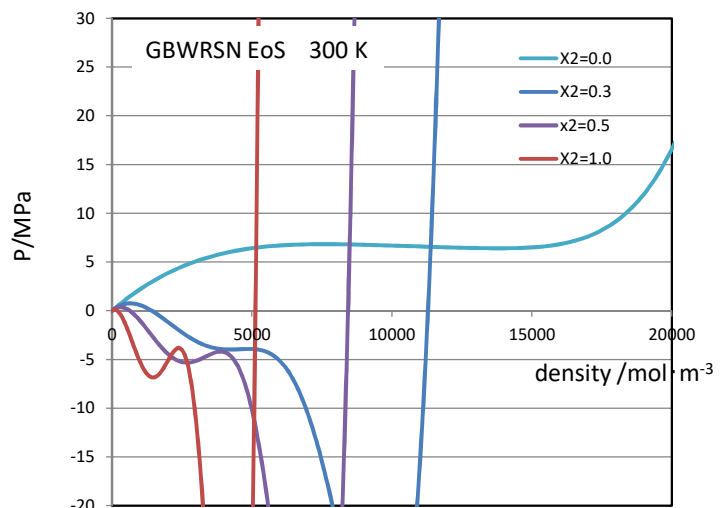Fig. 2   Schematic PρT curves of 2 types of equations of state at T_r=0.3 ~ 1.0

Fig. 3   PρT curves of CO_2-decane binary with difference compositions (x_2=0.0, 0.3, 0.5, 1.0)

chemical potential of both components and phase equilibrium calculation. Such behaviors are strongly dependent on EoS constants, indicating the importance of considering PVT curves in the unstable region in determining EoS constants.

4. CORRESPONDING STATE PRINCEPLE

The corresponding state principle is a good methodology to calculate the mixture properties from pure component information with pseudocritical values. We can adopt this method to mix the thermodynamic properties of each component with confirming the values in stable state. By extending the Lee-Kesler method[6] based on 3-parameter corresponding state principle, a kind of mixing rule can be derived to combine the different type EoSs for each component of the mixtures.

Teja et al.[8,9] modified the Lee-Kesler method by taking a general reference instead of a simple fluid and proposed the following equation for a thermodynamic properties, F, in terms of two reference fluid contributions, F(r1) and F(r2).

$$F(T_r, P_r, \omega) = F^{(r1)}(T_r, P_r, \omega_{r1}) + \frac{\omega - \omega_{r1}}{\omega_{r2} - \omega_{r1}} \left\{ F^{(r2)}(T_r, P_r, \omega_{r2}) - F^{(r1)}(T_r, P_r, \omega_{r1}) \right\} \quad (4)$$

Here we can regard the components 1 and 2 as references 1 and 2 for binary mixtures. Accordingly, the compressibility factor of a binary Z_m can be rewritten from Eq.(4).

$$Z_m(T_r, P_r, \omega_m) = Z^{(1)}(T_r, P_r, \omega_1) + \frac{\omega_m - \omega_1}{\omega_2 - \omega_1} \left\{ Z^{(2)}(T_r, P_r, \omega_2) - Z^{(1)}(T_r, P_r, \omega_1) \right\} \quad (5)$$

$$Z^{(i)} = \frac{P_r \cdot v_r^{(i)}}{T_r}, \quad T_r = \frac{T}{T_{cm}}, \quad P_r = \frac{P}{P_{cm}}, \quad v_r^{(i)} = \frac{1}{\rho_r^{(i)}} = \frac{v^{(i)} \cdot P_{cm}}{R \cdot T_{cm}} \quad (6)$$

Here the reduced properties in Eq.(5) are evaluated for pseudocritical values of the mixture. Considering that Z is given by an equation of state similar to Plocker et al.[7], Eq.(5) is considered as a combing rule of equations of state, where there is no restriction for the functional forms of $Z^{(1)}$ and $Z^{(2)}$, indicating the possibility of combining cubic EoS and virial type EoS with considering their applicability to each component. When the acentric factor of the mixture ω_m in Eq.(5) is given as the following mole fraction average;

$$\omega_m = x_1 \omega_1 + x_2 \omega_2 \quad (7)$$

Eq.(5) reduces to the following equation, and EoS for each component can be recognized as a reduced EoS to evaluate the partial molar compressibility for the component[10].

$$Z_m(T_r, P_r, \omega_m) = x_1 Z^{(1)}(T_r, P_r, \omega_1) + x_2 Z^{(2)}(T_r, P_r, \omega_2) \quad (8)$$

Compressibility factor of a mixture can be evaluated by specifying the pseudocritical values for reduced properties. Attempt was made by using the following equations for pseudocritical values similarly to Plocker et al.[7].

$$T_{cm} = \frac{1}{v_{cm}} \sum_i \sum_j x_i x_j v_{cij} (1 - k_{ij}) \sqrt{T_{c,i} T_{c,j}}, \quad v_{cm} = \sum_i \sum_j x_i x_j v_{cij}$$

$$P_{cm} = (0.2905 - 0.085 \omega_m) \frac{R T_{cm}}{v_{vm}}, \qquad v_{cij} = \frac{1}{8} \left(v_{ci}^{1/3} + v_{cj}^{1/3} \right)^3 \tag{9}$$

Fig.4(a) shows the calculation result of VLE for Nitrogen-Ethane system by conventional constant combining mixing rules and CPS mixing rule (Eq.(8)) with using GBWRSN EoS. It can be seen that the difference of mixing rule becomes larger at high pressures, especially near mixture critical point. Since there has been proposed a very accurate EoS for nitrogen by Bender, we determined the EoS parameters for Ethane using PVT data and these EoSs were used to correlate VLE for the mixture. The correlation results shown in Fig.4(b) indicate that the binary interaction parameter seems to be similar for CPS mixing rule even with different EoSs and the correlation performance could be improved by adopting more accurate EoS for each component.

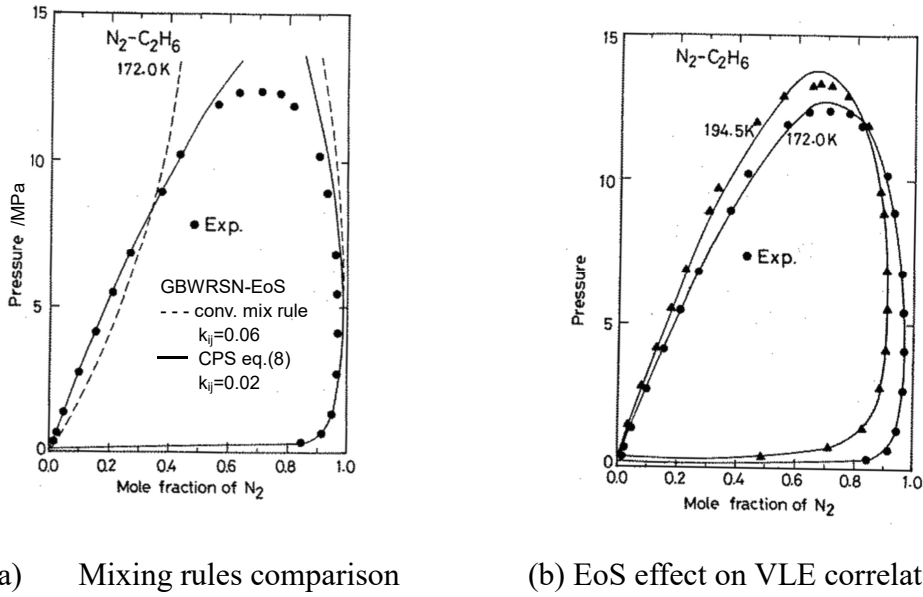(a)   Mixing rules comparison   (b) EoS effect on VLE correlation

Fig. 4   Correlation results of VLE for Nitrogen-Ethane binary; (a) GBWRSN EoS with conventional mixing rules and with CPS eq.(8),   (b) Bender EoS for both comp. with CPS eq.(8)

Fig.5 shows another example for nitrogen-n-heptane binary with taking EoSs of different type for each component; both cases used modified BWR for n-heptane whereas Bender EoS[11,12] or SRK EoS for nitrogen.   It was clearly shown that the combination of accurate EoS can provide better correlation. This suggests us to select a suitable/accurate EoS for each component in calculating phase equilibria for the mixture and also to optimize EoS constants by using available enough PVT data.
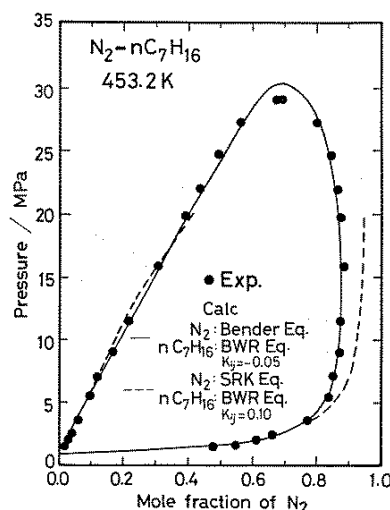
Fig. 5   Correlation of VLE for Nitrogen-n-Heptane binary;   —: Bender EoS+ BWR EoS, and ---: SRK+BWR EoS combination with CPS eq.(8)

5. CONCLUSION

Two methodologies of applying EoS to mixtures were studied with focusing on PVT behaviors of components. On conventional mixing rule method, it was pointed out that the PVT curve by BWR type, multi-constants virial EoSs of heavier component of the mixture at lower temperatures may have some influence on phase equilibrium calculation and such behaviors should be considered in determining EoS constants. On corresponding state principle, a new equation was proposed for reduced EoS which can combine functionally different EoSs, which allows us to select suitable/accurate EoS for each component for phase equilibrium calculation of mixtures.

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