CEOS/ A^E Mixing Rules Constrained by vdW Mixing Rule and Second Virial Coefficient

Chorng H. Twu and John E. Coon
Simulation Sciences Inc., Brea, CA 92621

A new class of mixing rules, with van der Waals one-fluid mixing rule and second virial coefficient constraints, was developed for cubic equations of state (EOS) for application to various asymmetric, highly nonideal chemical systems. This approach evolved from previous research in the EOS field. The resulting mixing rule is practical in application, yet more flexible than Huron-Vidal or Wong-Sandler mixing rules and depends only on composition and temperature. It also avoids the problems associated with the Wong-Sandler mixing rules. A cubic EOS with the new mixing rules was applied successfully to complex mixtures. The new rules reduce to van der Waals mixing rules when the parameters in the nonrandom excess Helmholtz free energy are set to zero. Since many times the classic mixing rules worked very well for nonpolar systems, it is extremely desirable that the composition-dependent mixing rules reduce to the classic mixing rules. Preserving this capability also ensures that the binary interaction parameters for the classic quadratic mixing rules in the DECHEMA Chemistry Data Series for mixtures of low boiling substances and other existing databases for systems involving hydrocarbons and gases can be used directly in the new EOS mixing rules, in addition to liquid-activity coefficient model parameters currently reported in the Series.

Introduction

Cubic equations of state have probably been the most widely used methods in the petroleum-refining-process industries for the calculation of vapor–liquid equilibrium (VLE) since Soave (1972) successfully developed a generalized alpha function for cubic equations of state. To apply cubic equations of state to model the complex phase behavior of highly nonideal chemical systems, a more flexible composition-dependent mixing rule than the van der Waals (vdW) one-fluid mixing rule is required. Many efforts in recent years have been made to develop alternate mixing rules. Huron and Vidal (1979) successfully formulated the equation of state a parameter as a suitable composition-dependent function by forcing the excess Gibbs free energy at infinite pressure derived from a cubic equation of state (CEOS) to be equal to that from a liquid-activity coefficient model. Wong and Sandler (1992) equated the excess Helmholtz free energy at infinite pressure from a cubic equation of state to that from an activity coefficient model and also constrained the equation-of-state parameters a and b to satisfy the second virial coefficient condition. The Huron–Vidal approach required the excess volume to be zero. The Wong–Sandler approach released the equation-of-state b parameter from its traditional linear mixing rule. However, neither the Huron–Vidal (1979) nor the Wong–Sandler (1992) mixing rules reduce to the vdW mixing rules when zero values of the binary interaction parameters are applied in the excess free-energy models.

While these excess free-energy mixing rules have been successfully applied to strongly polar systems, the results from either the Huron–Vidal or the Wong–Sandler mixing rules are no better than the vdW one-fluid mixing rules for nonpolar systems, even though they use more binary parameters (Voros and Tassios, 1993). Additionally, the Wong–Sandler mixing rules encounter a singularity problem for mixtures of nonpolars with light gases (Orbey and Sandler, 1995b). The systems of nonpolars with light gases usually are well represented by CEOS, with the vdW one-fluid mixing rules using only one or two parameters per binary.

In an effort to reduce the Wong–Sandler mixing rules to the conventional vdW mixing rules, Orbey and Sandler (1995b) modified the G^E model of NRTL to a different form.

Correspondence concerning this article should be addressed to C. H. Twu.

The modified NRTL interaction parameters g_{ii} and g_{ij} (per binary pair) are then evaluated from the equation of state a and b parameters and the original vdW binary interaction parameter k_{ij}. These calculated values are finally used as the input binary interaction parameters to their mixing rule for nonpolar binaries in a system. Since the excess Gibbs-free-energy model used is a modification of the original NRTL equation, the parameters for the NRTL model reported in the DECHEMA Chemistry Data Series for other binaries in the same system can no longer be used in the mixing rules. As a result of this, the reformulated Wong–Sandler mixing rule becomes similar to the Huron–Vidal mixing rules and offers no additional major advantages over the Huron–Vidal mixing rule, except that it obeys the second virial coefficient constraint.

This article presents an evolution of the approaches proposed by Wong and Sandler (1992) and Mollerup (1983) for constructing a new class of composition-dependent mixing rules that will retain the excellent features of the Wong–Sandler mixing rules, but avoid the problems associated with it, and will reduce to the vdW one-fluid mixing rules by simply setting the binary interaction parameters to zero in the nonrandom excess Helmholtz free energy model.

Theoretical Derivation of Equation-of-State Mixing Rules

Any two-parameter cubic equation of state (CEOS) can be expressed by the following equation:

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

where P is the pressure, T is the absolute temperature, and v is the molar volume. The constants u and w are numbers (for the Soave–Redlich–Kwong equation, 1972: $u = 0$, $w = 1$). The parameters a and b at the critical temperature, a_c and b_c, are found by setting the first and second derivatives of pressure with respect to volume to zero at the critical point. The parameter a in Eq. 1 is a function of temperature and the parameter b is a constant for pure components. The value of $a(T)$ at temperatures other than the critical temperature can be calculated from

$$a(T) = \alpha(T) a_c, \tag{2}$$

where the alpha function, $\alpha(T)$, is a function only of reduced temperature, $T_r = T/T_c$. Since it is important that the prediction of pure-component vapor pressure be of high accuracy for accurate vapor–liquid calculations, we use the alpha correlation of Twu et al. (1991):

$$\alpha = T_r^{N(M-1)} e^{L(1-T_r^{NM})}. \tag{3}$$

Equation 3 has three parameters, L, M, and N. These parameters are unique to each component and are determined from the regression of pure-component vapor pressure. Using the alpha given in Eq. 3 in a CEOS results in a very accurate prediction of vapor pressure for all chemical pure components.

A CEOS can be used to obtain the Helmholtz-free-energy (A) departure function, ΔA, which is the difference between the molar Helmholtz free energy of a mixture and that of the same mixture as an ideal gas at the same temperature, pressure, and composition. The Helmholtz-free-energy departure function derived from Eq. 1 is given below:

$$\frac{\Delta A}{RT} = -\ln(Z - b^*) - \frac{1}{(w-u)} \frac{a^*}{b^*} \ln\left(\frac{Z + wb^*}{Z + ub^*}\right). \tag{4}$$

The parameters a^* and b^* in Eq. 4 are defined as:

$$a^* = Pa/R^2T^2 \tag{5}$$

$$b^* = Pb/RT. \tag{6}$$

Z in Eq. 4 is the compressibility factor, which is the solution of the following equation of state for the phase of interest:

$$Z^3 + [(u+w-1)b^* - 1]Z^2 + [(uw - u - w)b^{*2} - (u+w)b^* + a^*]Z - (uwb^{*3} + uwb^{*2} + a^*b^*) = 0. \tag{7}$$

The Helmholtz departure function, ΔA, is related to the excess Helmholtz free energy, A^E, and the Helmholtz-free-energy departure functions of pure components i, ΔA_i, at the same temperature, pressure, and composition, by

$$A^E = \Delta A - \sum_i^n x_i \Delta A_i, \tag{8}$$

where x_i is the liquid mole fraction of component i.

Wong and Sandler (1992) used an ideal solution as a reference fluid to develop equation-of-state mixing rules. This division of the Helmholtz free energy is shown in Eq. 9. For an ideal solution, the excess Helmholtz energy is zero and the Helmholtz energy departure function of the ideal solution is the summation of the Helmholtz-free-energy departure functions of pure components i, ΔA_i.

$$A_{ws}^E = A^E - A_{\text{ideal solution}}^E \tag{9}$$

or

$$A_{ws}^E = \Delta A - \Delta A_{\text{ideal solution}}. \tag{10}$$

The subscript ws defines the excess Helmholtz free energy used by Wong and Sandler (1992). In Eq. 10 ΔA is calculated from a CEOS. The general expression for ΔA is given by Eq. 4. Nevertheless, the ideal solution reference used by Wong and Sandler (1992) is only one of many choices for the reference. There are other references that can be chosen and that we feel are preferable. For example, if a vdW fluid is chosen as the reference, then the following equation is derived by applying Eq. 8 to a vdW mixture and subtracting it from Eq. 8:

$$A^E_{nr} = A^E - A^E_{vdw} \tag{11}$$

or

$$A^E_{nr} = \Delta A - \Delta A_{vdw}. \tag{12}$$

The expression of Eq. 11 was proposed by Mollerup (1983). However, from our derivation, A^E_{nr} is clearly defined by Eq. 12. The subscript *nr* is an abbreviation for *nonrandom*, which is what we have chosen to call this portion of the excess Helmholtz energy. A^E_{vdw} is the excess Helmholtz energy evaluated from a CEOS using the vdW mixing rules for its a and b parameters, and A^E_{nr} accounts for the noncentral force contribution that can be included using a nonrandom-liquid theory based on the local composition concept. As mentioned previously, ΔA in Eq. 12 is evaluated from Eq. 4.

Equation 10 was used by Wong and Sandler (1992) in the development of their mixing rules. With an ideal solution as the reference, however, the mixing rules cannot reduce to the classic mixing rules. Because of this, the Wong–Sandler mixing rules encounter problems on application to problems that are handled very well by the traditional mixing rules. We propose to use Eq. 12 to develop a new class of CEOS mixing rules. One of the advantages of using the vdW mixture as the reference is that it is easy to recover the classic mixing rules. Substituting Eq. 4 into Eq. 12 results in

$$\frac{A^E_{nr}}{RT} = -\ln(Z - b^*) - \frac{1}{(w-u)}\frac{a^*}{b^*}\ln\left(\frac{Z + wb^*}{Z + ub^*}\right) + \ln(Z - b^*)_{vdw} + \frac{1}{(w-u)}\frac{a^*_{vdw}}{b^*_{vdw}}\ln\left(\frac{Z + wb^*}{Z + ub^*}\right)_{vdw}, \tag{13}$$

where a_{vdw} and b_{vdw} are equation-of-state a and b parameters that are evaluated from the vdW mixing rules:

$$a_{vdw} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - k_{ij}) \tag{14}$$

$$b_{vdw} = \sum_i \sum_j x_i x_j \left[\frac{1}{2}(b_i + b_j)\right](1 - l_{ij}), \tag{15}$$

with the binary interaction parameters k_{ij} and l_{ij}. It is traditional to assume a linear combining rule for b_{vdw}. This is not completely correct, however, even for spherical molecules (Rowlinson, 1969). Therefore, a binary interaction parameter l_{ij} is introduced in b_{vdw}.

In the limit of infinite pressure, $P \to \infty$, v approaches b and v_{vdw} approaches b_{vdw}. Equation 13 becomes

$$\frac{A^E_{nr}}{RT} = c\left(\frac{a^*}{b^*} - \frac{a^*_{vdw}}{b^*_{vdw}}\right) \tag{16}$$

with the constant c being:

$$c = -\frac{1}{(w-u)}\ln\left(\frac{1+w}{1+u}\right). \tag{17}$$

The constant c is specific to the CEOS chosen; for the Soave–Redlich–Kwong (1972) equation of state $c = -\ln(2)$ and for the Peng–Robinson (1976) equation $c = \ln(\sqrt{2} - 1)/\sqrt{2}$.

Equation 16 can be rewritten as

$$\frac{a^*}{b^*} = \frac{a^*_{vdw}}{b^*_{vdw}} + \frac{l}{c}\frac{A^E_{nr}}{RT}. \tag{18}$$

Eq. 18 is analogous to the relation found by Huron and Vidal (1979) and Wong and Sandler (1992). A two-parameter CEOS allows two degrees of freedom to choose the two mixture parameters a and b. The application of infinite pressure to derive the interrelationship between the equation of state a and b parameters given by Eq. 18 uses one degree of freedom. The Huron–Vidal approach required the excess volume to be zero at infinite pressure. Consequently, a linear mixing rule for the b parameter had to be utilized that used the remaining degree of freedom. Since we do not require that the excess volume at infinite pressure be zero, one degree of freedom is still left. The remaining degree of freedom is used to satisfy the second virial coefficient, as suggested by Wong and Sandler (1992). From statistical mechanics, the composition dependence of the second virial coefficient is

$$B(x,T) = \sum_i \sum_j x_i x_j B_{ij}(T), \tag{19}$$

where B_{ij} is the composition-independent cross second virial coefficient. When a two-parameter CEOS, such as Eq. 1, is expanded in a power of molar volume to obtain the virial form, one obtains

$$B(x,T) = b - \frac{a}{RT} = \sum_i^n \sum_j^n x_i x_j \left(b_{ij} - \frac{a_{ij}}{RT}\right). \tag{20}$$

Following the Wong–Sandler approach, our mixing rules use Eq. 20 as the constraint on the equation of state a and b parameters. Equation 20 does not determine a or b individually but uses their summation. Equation 20 insures that no matter what specific choices are made for a and b, the quadratic composition dependence of the second virial coefficient boundary condition will be satisfied. In this work, we propose the following equation for the cross parameters a_{ij} and b_{ij} as

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{21}$$

$$b_{ij} = \frac{1}{2}(b_i + b_j)(1 - l_{ij}). \tag{22}$$

The reason for proposing the relationships between cross parameters and pure component parameters given by Eqs. 21 and 22 is to ensure that the vdW mixing rules can be recovered from our new mixing rules. Substituting Eqs. 21 and 22 into Eq. 20, we have

$$b = b_{vdw} + \frac{l}{RT}(a - a_{vdw}). \tag{23}$$

Equations 18 and 23 can then be solved for two parameters a and b. Inserting Eq. 18 into Eq. 23, we have the new mixing rule for the equation-of-state mixture b parameter.

$$b^* = \frac{b^*_{vdw} - a^*_{vdw}}{1 - \left(\frac{a^*_{vdw}}{b^*_{vdw}} + \frac{1}{c} \frac{A^E_{nr}}{RT} \right)}. \tag{24}$$

The mixing rule for the equation-of-state mixture a parameter is obtained from Eqs. 18 and 24:

$$a^* = b^* \left(\frac{a^*_{vdw}}{b^*_{vdw}} + \frac{1}{c} \frac{A^E_{nr}}{RT} \right). \tag{25}$$

Equations 24 and 25 completely define the two mixture parameters a and b in terms of A^E_{nr} at infinite pressure. These two mixing rules reduce to the vdW one-fluid mixing rules when A^E_{nr} is zero. As mentioned previously, the classic vdW mixing rules work very well for nonpolar systems; therefore, it is very desirable that the new composition-dependent mixing rules retain this capability so that the same binary interaction parameters available in existing databases for those systems can be used directly in equation-of-state mixing rules, and the same quality of predicted vapor–liquid equilibrium behavior for nonpolar and light-gas systems from the vdW mixing rule can be preserved.

It is interesting to point out that Wong and Sandler (1992) had presented the following mixing rules for the equation-of-state a and b parameters that will satisfy the second virial coefficient:

$$b = \frac{\sum_i^n \sum_j^n x_i x_j \left(b_{ij} - \frac{a_{ij}}{RT} \right)}{1 - \frac{F(x)}{RT}} \tag{26}$$

and

$$a = bF(x), \tag{27}$$

where $F(x)$ is an arbitrary function of composition vector x. Their approach results in the following $F(x)$:

$$\frac{F(x)}{RT} = \sum_i x_i \frac{a^*_i}{b^*_i} + \frac{1}{c} \frac{A^E_{ws}}{RT}. \tag{28}$$

Compare this with ours, which is given by:

$$\frac{F(x)}{RT} = \frac{a^*_{vdw}}{b^*_{vdw}} + \frac{1}{c} \frac{A^E_{nr}}{RT}. \tag{29}$$

The major difference between Wong–Sandler and our mixing rules is that Wong–Sandler mixing rules do not reduce to the vdW mixing rules when A^E_{ws} is zero, and our mixing rules do when A^E_{nr} is zero.

Expression for the Mixture Fugacity Coefficients of Components

The solution of phase-equilibrium problems is determined by equality of the fugacities in existing phases. Using the equation-of-state model in phase-equilibrium calculations, the fugacities can be replaced with fugacity coefficients. An expression for the fugacity coefficient can be derived from Eq. 1:

$$\ln\left(\frac{f_i}{x_i P} \right) = (Z-1)\left[\frac{1}{b} \left(\frac{\partial nb}{\partial n_i} \right) \right] - \ln(z - b^*) + \frac{1}{(w-u)} \frac{a^*}{b^*} \left\{ \left[\frac{1}{b} \left(\frac{\partial nb}{\partial n_i} \right) \right] - \left[\frac{1}{na} \left(\frac{\partial n^2 a}{\partial n_i} \right) \right] \right\} \ln\left(\frac{Z + wb^*}{Z + ub^*} \right) \tag{30}$$

The partial derivatives of a and b are:

$$\frac{1}{na} \left(\frac{\partial n^2 a}{\partial n_i} \right) = \frac{1}{b} \left(\frac{\partial nb}{\partial n_i} \right) + \frac{1}{D} \left(\frac{\partial nD}{\partial n_i} \right) \tag{31}$$

$$\frac{1}{b} \left(\frac{\partial nb}{\partial n_i} \right) = \frac{1}{Q} \left[\frac{1}{n} \left(\frac{\partial n^2 Q}{\partial n_i} \right) \right] - \frac{1}{(1-D)} \left[1 - \left(\frac{\partial nD}{\partial n_i} \right) \right], \tag{32}$$

with D and Q defined as:

$$D = \frac{a^*_{vdw}}{b^*_{vdw}} + \frac{1}{c} \frac{A^E_{nr}}{RT} \tag{33}$$

$$Q = b_{vdw} - \frac{a_{vdw}}{RT}, \tag{34}$$

with the partial derivatives of D and Q given by:

$$\left(\frac{\partial nD}{\partial n_i} \right) = \frac{a^*_{vdw}}{b^*_{vdw}} \left\{ \left[\frac{1}{na_{vdw}} \left(\frac{\partial n^2 a_{vdw}}{\partial n_i} \right) \right] - \left[\frac{1}{b_{vdw}} \left(\frac{\partial nb_{vdw}}{\partial n_i} \right) \right] \right\} + \frac{1}{c} \ln \gamma_{i,nr} \tag{35}$$

$$\frac{1}{Q} \left[\frac{1}{n} \left(\frac{\partial n^2 Q}{\partial n_i} \right) \right] = \frac{2 \sum_j x_j (b^*_{ij} - a^*_{ij})}{\sum_i \sum_j x_i x_j (b^*_{ij} - a^*_{ij})}, \tag{36}$$

and with the partial derivatives of a_{vdw} and b_{vdw} given by:

$$\frac{1}{na_{vdw}} \left(\frac{\partial n^2 a_{vdw}}{\partial n_i} \right) = \frac{2}{a_{vdw}} \sum_j x_j a_{ij} \tag{37}$$

$$\frac{1}{b_{vdw}} \left(\frac{\partial nb_{vdw}}{\partial n_i} \right) = \frac{2}{b_{vdw}} \sum_j x_j b_{ij} - 1. \tag{38}$$

Cross parameters a_{ij} and b_{ij} in Eqs. 36 to 38 are given by Eqs. 21 and 22. The constant c in Eq. 35 is given by Eq. 17.

Though any Helmholtz-free-energy model could have been used, we have chosen the NRTL model for A^E_{nr}.

$$\frac{A^E_{nr}}{RT} = \sum_j^n x_j \frac{\sum_k^n x_i \tau_{kj} G_{kj}}{\sum_k^n x_k G_{kj}}, \tag{39}$$

with τ_{ij} and G_{ij} defined as

$$\tau_{ji} = \frac{A_{ji}}{T} \tag{40}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}). \tag{41}$$

The term $\ln \gamma_{i,nr}$ in Eq. 35 is defined by the following equation:

$$\ln \gamma_{i,nr} = \frac{1}{RT}\left(\frac{\partial n A^E_{nr}}{\partial n_i}\right). \tag{42}$$

The partial derivatives of A^E_{nr} with respect to the mole number of each species, which is the logarithm of the species-activity coefficient, is given by substituting Eq. 39 into Eq. 42:

$$\ln \gamma_{i,nr} = \frac{\sum_j^n x_j \tau_{ji} G_{ji}}{\sum_k^n x_k G_{ki}} + \sum_j^n \frac{x_j G_{ij}}{\sum_k^n x_k G_{kj}} \left[\tau_{ij} - \frac{\sum_k^n x_k \tau_{kj} G_{kj}}{\sum_k^n x_k G_{kj}}\right]. \tag{43}$$

Discussion of CEOS/G^E Mixing Rules

The success of a proposed new CEOS/G^E mixing rule model depends on its ability to reproduce the incorporated excess free energy behavior of the liquid-activity coefficient model. The Wong–Sandler mixing rule was derived from basic thermodynamics of how liquid and vapor mixtures should behave and is very effective in the correlation and the prediction of phase equilibrium data for highly nonideal systems. Wong et al. (1992) used a binary interaction parameter, k_{ij}, in the Wong–Sandler mixing rules to ensure that low-pressure excess Gibbs free energy from their equation of state matched as closely as possible that from the liquid-activity coefficient model. For a relatively symmetric system (similar values of the infinite dilution activity coefficients), the Wong–Sandler mixing rules will reproduce satisfactorily activity coefficients over the entire composition range. However, it has been shown that the Wong–Sandler mixing rules do not produce acceptable activity coefficients over the entire composition range for an asymmetric system having infinite dilution activity coefficients that are quite different from each other (Coutsikos et al., 1995).

It should be noted that our new mixing rule contains one more parameter than the Wong–Sandler mixing rule. While adding parameters is not generally a desirable thing, the flexibility this gives us is very important. Because there are two infinite dilution activity coefficients per binary, two parameters are required to match exactly the two infinite dilution activity coefficients for each binary and our model possesses two added parameters, k_{ij} and l_{ij}. The Wong–Sandler model has only one parameter, k_{ij}, so it can represent only one infinite dilution activity coefficient exactly. For a symmetric system, one k_{ij} parameter may be enough for reproducing satisfactorily the G^E model over the entire composition range, but it will not be sufficient for asymmetric systems. With increasing system asymmetry, the deviation of reproducing activity coefficients using the Wong–Sandler model increases. Currently there are no other mixing-rule models having this capability, because none of them possess the two added parameters, k_{ij} and l_{ij}, of our new mixing rules. Although the Wong–Sandler mixing rules can be reformulated to include two parameters, k_{ij} and l_{ij}, as given by Eqs. 21 and 22, this does not help to improve the accuracy of reproducing the G^E model, due to the highly correlated nature of these two parameters in the Wong–Sandler mixing rules.

As we stated earlier, our new mixing rule contains two more parameters than the incorporated excess free-energy model. This, however, is not the problem it might seem. As pointed out by Wong et al. (1992), if these two parameters could be derived from the reported parameters of the activity coefficient model, not from any additional data or correlation, then k_{ij} and l_{ij} in the new mixing rules require no additional data or regression. The new mixing rule essentially has the same number of adjustable parameters as the incorporated liquid-activity coefficient model. This capability of our new mixing rules will be demonstrated in this article by utilizing the interaction parameters k_{ij} and l_{ij} to reproduce the activity coefficients for both symmetric and asymmetric systems from the incorporated excess free-energy function.

In cases where the parameters of the liquid-activity coefficient model cannot be obtained from the literature for the system of interest (such as nonpolar systems with light gas components), the Wong–Sandler mixing rules do have one more parameter than the free-energy model. The Wong–Sandler mixing rules require four parameters, if the NRTL model is applied, for any binary in the correlation of data regardless of whether the system is simple or complex. However, our mixing rules will reduce to the vdW one-fluid mixing rules and require only the same number of parameters as the vdW mixing rules for simple systems. This is a unique feature of our new mixing rules. Voros and Tassios (1993) have compared six mixing rules, including the Wong–Sandler mixing rules. They concluded that the two-parameter vdW mixing rules, Eqs. 14 and 15, give the best results for nonpolar with inorganic gases systems.

The difficulty of applying the Wong–Sandler mixing rules to simple systems was illustrated by the work of Huang et al. (1994). Huang et al. have applied the Wong–Sandler mixing rules to correlate vapor–liquid equilibria of some hydrogen and hydrocarbon systems. They use the NRTL model, and therefore, four parameters are required for each simple binary system. There is a strong dependence on the parameter, k_{ij}, of those mixing rules for those systems. The k_{ij} becomes unrealistically large, resulting in values close to or larger than one. Their generalized k_{ij} correlation predicts k_{ij} exactly equal to unity at 357.54 K. When k_{ij} equals unity, the equation-of-state cross parameters a and b and cross second virial coefficient become zero.

The denominator of the Wong–Sandler mixing rules (1992) and our mixing rules both contain an excess free-energy term. The value of the excess free energy can be either positive or negative. If the excess free-energy term becomes zero, our mixing rules reduce to the vdW mixing rules. The denominator of the Wong–Sandler mixing rules, however, becomes zero at some composition and temperature of the mixture, resulting in a singularity (Orbey and Sandler, 1995b). Nevertheless, Orbey and Sandler (1995b) explained that this singularity is due to the peculiar behavior of the α function in the equation of state, rather than the mixing rule itself.

Because of the inherent temperature and pressure dependence of the equation of state, the binary interaction parameters in the mixing rules are much less temperature dependent than when the parameters are used in the same excess free-energy model directly in the phase-equilibrium calculations. We believe that the use of the appropriate composition-dependent mixing rule and the constraints on the vdW mixing rules and the second virial coefficient should result in even smaller and less temperature-dependent binary interaction parameters for complex systems, thereby allowing extrapolation over larger ranges of temperature and pressure. In this article, we show how to predict vapor–liquid equilibria at high pressures from the parameters for the NRTL model reported at the low pressure in the DECHEMA Chemistry Data Series.

Results

The systems considered are highly nonideal mixtures that are traditionally described by liquid activity models. In this work, we have rigorous tests of the ability of correlating and predicting data using an equation of state combined with our new mixing rules. The tests are designed for four cases. Case 1 is to test the ability of correlating vapor–liquid equilibrium data at one temperature for each system, and compares the results with those obtained from the vdW mixing rules. Case 2 is to test the ability of correlating vapor–liquid equilibrium data over wide ranges of temperature and pressure, and compares the results with those obtained from the Wong–Sandler mixing rules. Case 3 is to test the ability of using currently available activity coefficient model parameters in equations of state with our new mixing rules. We use only the activity coefficient parameters at the lowest isothermal temperature to predict high-pressure phase behavior for nonideal systems. This leaves only two binary interaction parameters, k_{ij} and l_{ij}, unspecified. In Case 3, these two parameters, which are not functions of temperature, are obtained from the regression of VLE data. In Case 4, they are derived from the information in the NRTL model itself. The parameters k_{ij} and l_{ij} are used to compensate the difference between the Helmholtz free energy with respect to the vdW fluid and the Helmholtz free energy with respect to an ideal solution. For both Cases 3 and 4, the results will also be compared with those obtained from the Wong–Sandler mixing rules. We use the modification of the Soave–Redlich–Kwong CEOS by Twu et al. (1991) for all systems. The L, M, and N parameters for all pure components used to get the correct pure-component vapor pressure are listed in Table 1.

Case 1. The ability of correlating vapor–liquid equilibrium data at one temperature for each system is tested. The results are compared with those obtained from the vdW mixing rules. It is well known that the binary interaction parameters k_{ij} and l_{ij}, appearing in the vdW mixing rules, are generally functions of temperature. Therefore, to be fair to the vdW mixing rules in comparison, only VLE data at one temperature are used. We are aware that this comparison might still be unfair to the vdW mixing rules, because our mixing rules contain more parameters than the vdW mixing rules. However, it is worth pointing out that even increasing the number of parameters in the vdW mixing rules may not be able to improve the accuracy of correlating VLE data for nonideal systems.

We use "vdWMR1" to refer to the one-parameter vdW mixing rules; that is, Eqs. 14 and 15 with nonzero k_{ij} and zero l_{ij}, and "vdWMR2" to refer to the two-parameter vdW mixing rules with both nonzero k_{ij} and l_{ij}. "TCMR1" is used to represent the mixing rules developed by us in this work, that is, Eqs. 24 and 25 with nonzero k_{ij} and zero l_{ij}, and "TCMR2" to represent the mixing rules with both nonzero k_{ij} and l_{ij}. The NRTL model is used in this work. Because we do not use reported NRTL parameters in the mixing rules in this case, we do have two more independent parameters than the NRTL free-energy model. However, this will be considered as an advantage of our mixing rules, because it provides additional flexibility to achieve higher accuracy in correlating data. The five parameters of the mixing rules in the case of TCMR2 are A_{ij}, A_{ji}, α_{ij}, k_{ij}, and l_{ij}.

Table 1. L, M, and N Parameters of Temperature-Dependent α Function Given by Eq. 3 for Pure Components Used with the SRK Cubic Equation of State

Component	T_c (K)	P_c (bar)	L	M	N
n-pentane	469.70	33.70	0.379229	0.841706	1.82331
n-hexane	507.85	30.31	0.158080	0.872819	3.84418
n-heptane	540.16	27.36	0.340339	0.844963	2.38332
Cyclohexane	553.58	40.73	0.245880	0.845046	2.25895
Benzene	562.16	48.98	0.163664	0.860016	2.98498
Acetone	508.20	47.01	0.479844	0.870627	1.79010
Methanol	512.64	80.97	0.690551	0.911298	1.96941
Ethanol	513.92	61.48	1.07646	0.964661	1.35369
Water	647.13	220.55	0.413297	0.874988	2.19435

The nonideal systems selected for testing the new mixing rules are listed in Table 2. Binary interaction parameters are obtained from the regression of data for these systems at the temperatures of interest. Table 2 gives the values of binary interaction parameters for each system. The accuracy of the correlation, which is in terms of average absolute deviation percentage (AAD%) in bubble-point pressure and k-values of components 1 and 2, is also given in Table 2.

The one-parameter vdW mixing rules, not surprisingly, give poor results for polar/polar and polar/nonpolar systems. The two-parameter vdW mixing rules provide satisfactory correlation of the bubble-point pressure and k-values for many polar/polar systems, but not for polar/nonpolar systems. Since our mixing rules always reduce to the vdW mixing rules, the results from our mixing rules can never be worse than those from the vdW one-fluid model. Comparing the results shown in Table 2, the new mixing rules, not surprisingly, also are significantly better than vdW mixing rules. The AAD% is normally less than 1%.

Case 2. The ability of correlating vapor–liquid equilibrium data over wide ranges of temperature and pressure is tested. Since the Wong–Sandler mixing rules have been widely considered for the application of a CEOS to strongly nonideal systems at low and high pressures, the results from our mixing rules will be compared with those obtained from the Wong–Sandler mixing rules. "WSMR1" is used to refer to the original Wong–Sandler mixing rules, and "WSMR2" refers to the reformulated Wong–Sandler mixing rules with the cross second virial coefficient term given by

$$b_{ij} - \frac{a_{ij}}{RT} = \frac{1}{2}(b_i + b_j)(1 - l_{ij}) + \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij}). \quad (44)$$

Thermodynamically consistent data at several isotherms appearing in the DECHEMA Chemistry Data Series were chosen for each binary. Binary interaction parameters were obtained by the regression of these data for the systems selected. The parameters of the mixing rules in the case of WSMR2 and TCMR2 are A_{ij}, A_{ji}, α_{ij}, k_{ij}, and l_{ij}. Table 3 gives the range of temperature, the results for the binary interaction parameters, and the accuracy of the correlation for each binary.

Table 2. Interaction Parameters and Results of Correlation in Terms of Average Absolute Deviation Percentage (AAD%) in Bubble-Point Pressure and k-Values

Mix Rule	A_{12} (K)	A_{21} (K)	α_{12}	k_{12}	l_{12}	P (%)	k_1 (%)	k_2 (%)
**n-Pentane(1)/acetone(2) at − 35°C; I/3 + 4/188*								
vdWMR1				0.0896		4.18	2.19	8.59
vdWMR2				0.3250	0.2758	2.93	1.64	6.39
TCMR1	503.586	288.694	0.5311	0.0161		0.97	0.11	0.37
TCMR2	434.604	325.568	0.8128	0.1525	0.1298	0.92	0.08	0.27
**Ethanol(1)/water(2) at 24.99°C; I/1b/108*								
vdWMR1				−0.1132		4.47	4.46	8.18
vdWMR2				0.1031	0.2079	0.89	0.50	1.10
TCMR1	−26.6764	2,140.32	0.1052	−0.3041		0.75	0.42	0.98
TCMR2	17.8501	1,089.93	0.0761	−0.5182	−0.2585	0.74	0.37	0.87
**Methanol(1)/cyclohexane(2) at 25°C; I/2c/208*								
vdWMR1				0.0762		16.31	17.22	24.15
vdWMR2				1.1745	1.1770	11.36	11.26	15.51
TCMR1	806.873	1,074.34	0.3125	−0.0722		1.69	0.60	0.87
TCMR2	624.150	1,051.31	0.3230	−0.1849	−0.1357	1.70	0.59	0.86
**Ethanol(1)/benzene(2) at 25°C; I/2a/415*								
vdWMR1				0.0782		5.94	13.30	7.48
vdWMR2				0.5513	0.5429	3.28	8.47	4.71
TCMR1	99.2312	777.847	0.4520	0.0158		0.56	1.64	0.92
TCMR2	159.625	743.153	0.6545	0.1812	0.1735	0.54	1.18	0.68
**Ethanol(1)/n-heptane(2) at 30.12°C; I/2e/377*								
vdWMR1				0.0193		14.56	18.27	23.03
vdWMR2				0.7511	0.7580	9.20	14.32	17.51
TCMR1	372.023	927.938	0.3826	−0.0595		0.64	0.94	1.13
TCMR2	255.790	920.339	0.4324	0.0499	0.0950	0.67	0.74	0.90
**Methanol(1)/water(2) at 24.99°C; I/1b/29*								
vdWMR1				−0.0926		2.00	1.71	3.69
vdWMR2				−0.0292	0.0638	0.70	0.62	1.72
TCMR1	−71.6198	1,328.20	0.1254	−0.2189		0.27	0.25	0.71
TCMR2	−113.233	1,204.39	0.1123	−0.2438	−0.0353	0.17	0.16	0.48
**Methanol(1)/n-hexane(2) at 25°C; I/2c/219*								
vdWMR1				0.0208		20.88	23.83	18.96
vdWMR2				0.6531	0.6542	14.47	19.72	15.99
TCMR1	980.790	1,166.73	0.3147	−0.1333		0.66	1.05	0.84
TCMR2	999.523	1,055.45	0.4863	0.3650	0.4460	0.43	0.60	0.48

*Data taken from DECHEMA Chemistry Data Series by Gmehling, Onken, and Arlt; numbers corresponding to volume/part/page.

Table 3. Interaction Parameters and Results of Correlation in Terms of Average Absolute Deviation Percentage (AAD%) in Bubble-Point Pressure and k-Values

Mix Rule	A_{12} (K)	A_{21} (K)	α_{12}	k_{12}	l_{12}	P (%)	k_1 (%)	k_2 (%)
**n-Pentane(1)/acetone(2) from − 35 to 25°C; I/3 + 4/188, 189, 190*								
WSMR1	636.533	491.490	0.3017	−0.1404		1.17	0.37	0.86
WSMR2	601.981	454.239	0.3332	0.0175	0.8886	1.14	0.34	0.80
TCMR1	485.547	249.504	0.5815	0.0242		1.19	0.32	0.67
TCMR2	503.650	263.979	0.5245	0.0081	−0.0115	1.18	0.33	0.70
**Ethanol(1)/water(2) from 24.99 to 120°C; I/1b/93, 106, 107, 108*								
WSMR1	155.150	410.282	1.0663	0.3491		1.14	2.32	2.58
WSMR2	45.7156	489.796	0.4944	0.1235	−0.8958	0.93	2.71	2.74
TCMR1	151.393	1,004.78	0.2578	−0.2130		1.06	1.60	1.62
TCMR2	45.1888	1,135.11	0.1975	−0.2258	−0.0071	0.97	1.76	1.78
**Methanol(1)/cyclohexane(2) from 25 to 55°C; I/2c/208, 209; I/2a/242*								
WSMR1	594.479	1,175.49	0.3930	0.3532		1.52	1.89	2.93
WSMR2	627.528	1,165.72	0.3826	0.1645	−1.0463	1.41	1.76	2.70
TCMR1	2,665.28	1,399.87	0.1146	−0.3048		2.02	2.39	3.50
TCMR2	716.652	1,125.36	0.4464	0.4735	0.5315	1.53	1.57	2.37
**Ethanol(1)/benzene(2) from 25 to 55°C; I/2a/398, 407, 415, 417, 418, 421, 422*								
WSMR1	173.521	735.208	0.5666	0.3107		0.92	2.16	1.95
WSMR2	178.199	736.691	0.5638	0.3176	0.5309	0.92	2.15	1.94
TCMR1	733.517	999.603	0.2408	−0.0830		1.08	2.56	2.14
TCMR2	311.516	638.374	0.8072	0.3776	0.3937	0.92	2.03	1.87
**Ethanol(1)/n-heptane(2) from 30.12 to 70.02°C; I/2e/377, 379; I/2c/457, 458*								
WSMR1	449.967	994.230	0.4298	0.3682		1.10	1.12	2.39
WSMR2	521.967	988.600	0.4024	0.1188	−1.1793	0.77	0.97	1.78
TCMR1	2,680.62	1,271.63	0.1188	−0.3210		1.33	1.86	3.39
TCMR2	628.953	916.647	0.4745	0.4133	0.4873	0.98	0.99	1.71
**Methanol(1)/water(2) from 24.99 to 100°C; I/1b/29; I/1/41, 49, 72, 73*								
WSMR1	−129.099	91.5010	0.6921	0.3552		1.27	1.98	2.43
WSMR2	−95.5585	123.414	0.9008	0.1978	−0.6376	1.30	1.99	2.52
TCMR1	1.1406	856.410	0.2091	−0.1765		1.15	1.85	2.29
TCMR2	71.5708	888.802	0.1970	−0.2252	−0.0349	1.09	1.81	2.16
**Methanol(1)/n-hexane(2) from 25 to 45°C; I/2c/219; I/2a/252*								
WSMR1	841.419	1,159.89	0.3567	0.2772		1.20	1.81	1.67
WSMR2	869.590	1,156.01	0.3478	0.0847	−0.8706	1.06	1.57	1.45
TCMR1	2,314.88	1,313.58	0.1596	−0.2804		1.77	2.99	2.68
TCMR2	1,037.83	1,045.11	0.4845	0.3842	0.4644	1.31	1.19	1.11

*Data taken from DECHEMA Chemistry Data Series by Gmehling, Onken, and Arlt; numbers corresponding to volume/part/page.

Comparing the results shown in Table 3 indicates that all four mixing rules represent similarly high accuracy in correlating data covering wide ranges of temperature and pressure with a typical error of 1% to 2% deviation in bubble-point pressure and k-values of components for highly nonideal systems. The reformulated five-parameter Wong–Sandler mixing rule generally does not provide substantially better results than the four-parameter model due to the highly correlated nature of these two parameters in the Wong–Sandler mixing rules. The model in this work with five parameters, however, results in a significant improvement in VLE correlation over the four-parameter model. This indicates that the new mixing rule has more flexibility in correlating data than the Wong–Sandler mixing rules. Table 3 shows that the new mixing rule (TCMR2) in general gives slightly better correlation results than the other mixing rules.

Case 3. The capability of using currently available activity coefficient parameters in equations of state with our new mixing rules is tested. The NRTL parameters, A_{ij}, A_{ji}, and α_{ij}, at the lowest temperature of each binary reported in the DECHEMA Chemistry Data Series are used directly in the mixing rule models. The remaining two binary interaction parameters, k_{ij} and l_{ij}, are obtained from the regression of VLE data. The results from our mixing rules will be compared with those obtained from the Wong–Sandler mixing rules.

Table 4 gives the results of binary interaction parameters for each binary and the accuracy of the correlation. Comparing the results shown in Table 4 indicates that all four mixing rules using the reported NRTL parameters and the k_{ij} and l_{ij} parameters obtained from the regression of VLE data similarly produce high accuracy in correlating data covering wide ranges of temperature and pressure with a typical error of 1% to 3% deviation in bubble-point pressure and k-values of components for highly nonideal systems. The reformulated five-parameter Wong–Sandler mixing rules (WSMR2) again generally do not provide substantially better results than the four-parameter model because of the reason mentioned in Case 2: the highly correlated nature of these two parameters in the Wong–Sandler mixing rules. The model developed in this work with five parameters, however, once again results in a significant improvement in VLE correlation over the four-parameter model for most of the systems. This proves once

Table 4. Interaction Parameters and Results of Correlation in Terms of Average Absolute Deviation Percentage (AAD%) in Bubble-Point Pressure and k-Values

Mix Rule	A_{12} (K)	A_{21} (K)	α_{12}	k_{12}	l_{12}	P (%)	k_1 (%)	k_2 (%)
**n-Pentane(1)/acetone(2) from − 35 to 25°C; I/3 + 4/188, 189, 190*								
WSMR1	485.086	483.326	0.4683	−0.1900		3.87	3.44	4.42
WSMR2	485.086	483.326	0.4683	0.2351	1.6812	2.79	2.01	3.61
TCMR1	485.086	483.326	0.4683	−0.0029		2.93	2.29	4.07
TCMR2	485.086	483.326	0.4683	0.1156	0.1315	2.61	1.35	2.07
**Ethanol(1)/water(2) from 24.99 to 120°C; I/1b/93, 106, 107, 108*								
WSMR1	13.3878	437.683	0.2945	−0.3104		1.94	3.38	2.73
WSMR2	13.3878	437.683	0.2945	0.0711	−1.6253	1.34	3.18	2.76
TCMR1	13.3878	437.683	0.2945	−0.1510		2.42	2.32	2.43
TCMR2	13.3878	437.683	0.2945	−0.1089	0.0403	2.16	1.96	1.63
**Ethanol(1)/cyclohexane(2) from 25 to 55°C; I/2c/208, 209; I/2a/242*								
WSMR1	644.886	784.966	0.4231	0.3741		3.68	4.48	6.56
WSMR2	644.886	784.966	0.4231	0.2765	−0.3118	3.62	4.51	6.62
TCMR1	644.886	784.966	0.4231	−0.02696		5.45	4.36	6.75
TCMR2	644.886	784.966	0.4231	0.5531	0.6168	2.06	2.48	3.68
**Ethanol(1)/benzene(2) from 25 to 55°C; I/2a/398, 407, 415, 417, 418, 421, 422*								
WSMR1	115.954	584.473	0.2904	0.2326		1.98	5.11	3.16
WSMR2	115.954	584.473	0.2904	0.0692	−1.8099	1.86	5.01	3.10
TCMR1	115.954	584.473	0.2904	0.0133		2.46	5.54	3.47
TCMR2	115.954	584.473	0.2904	0.2496	0.2671	1.70	4.19	2.89
**Ethanol(1)/n-heptane(2) from 30.12 to 70.02°C; I/2e/377, 379; I/2c/457, 458*								
WSMR1	521.746	727.003	0.4598	0.3517		2.83	3.79	5.33
WSMR2	521.746	727.003	0.4598	0.1756	−1.0839	2.74	3.75	5.26
TCMR1	521.746	727.003	0.4598	−0.0551		4.76	4.90	9.10
TCMR2	521.746	727.003	0.4598	0.4235	0.4832	1.89	2.34	3.59
**Methanol(1)/water(2) from 24.99 to 100°C; I/1b/29; I/1/41, 49, 72, 73*								
WSMR1	−23.1150	188.147	0.3022	0.1372		1.91	2.29	2.90
WSMR2	−23.1150	188.147	0.3022	−0.0368	−1.6943	1.66	2.02	2.77
TCMR1	−23.1150	188.147	0.3022	−0.1070		1.50	2.22	2.96
TCMR2	−23.1150	188.147	0.3022	−0.0943	0.0126	1.55	2.08	2.69
**Methanol(1)/n-hexane(2) from 25 to 45°C; I/2c/219; I/2a/252*								
WSMR1	823.172	848.519	0.4388	0.3999		5.39	6.05	5.17
WSMR2	823.172	848.519	0.4388	0.3208	0.1109	5.39	6.06	5.18
TCMR1	823.172	848.519	0.4388	−0.0854		6.61	7.71	6.75
TCMR2	823.172	848.519	0.4388	0.2646	0.3543	2.48	3.64	3.16

*Data taken from DECHEMA Chemistry Data Series by Gmehling, Onken, and Arlt; numbers corresponding to volume/part/page.

more that the new model has more flexibility in correlating the vapor–liquid equilibrium data than the Wong–Sandler mixing rules. The results in Table 4 verify that TCMR2 in general gives better correlation results than other mixing rules.

Case 4. Same as in Case 3 except that the remaining two binary interaction parameters, k_{ij} and l_{ij}, are derived from the information in the NRTL model itself. When these two parameters are derived from the excess free-energy model, the new mixing rules can be considered containing the same number of parameters as the incorporated liquid-activity coefficient model. We demonstrate this ability of our new mixing rules in this case by utilizing the interaction parameters k_{ij} and l_{ij} to reproduce the activity coefficients from the incorporated excess free-energy function. The procedures used to do this have already been described by Twu et al. (1992). A brief description of the procedure is given here.

The activity coefficient of component i in a mixture can be derived from the fugacity coefficients of the equation of state:

$$\gamma_i = \frac{\phi_i}{\phi_i^o}, \tag{45}$$

where γ_i is the activity coefficient of component i at the equilibrium temperature and pressure, ϕ_i is the fugacity coefficient of component i in the mixture, and ϕ_i^o is the fugacity coefficient of pure component i at the same temperature and pressure. Both ϕ_i and ϕ_i^o are available from Eq. 30. The available activity coefficient model parameters are used to calculate the liquid-activity coefficients over the entire range of composition. The k_{ij} and l_{ij} parameters in the equation-of-state mixing rules are then obtained from the regression of the liquid-activity coefficients calculated from the activity coefficient model at a low temperature. The results are shown in Table 5.

The absolute deviations in pressure and k-values exhibited by TCMR2 and the Wang–Sandler models at higher temperatures and pressures is slightly better than TCMR1, and have the capability of representing VLE data with acceptable accuracy. The best results are obtained using the TCMR2 model in the prediction of the high-pressure phase behavior for most strongly nonideal systems using available activity coefficient parameters at low temperature.

The results in Table 5 confirm that the TCMR2 model always reproduces the activity coefficients more closely than

Table 5. Interaction Parameters and Results of Correlation in Terms of Average Absolute Deviation Percentage in Liquid Activity Coefficients, Bubble-Point Pressure, and k-Values

Mix Rule	A_{12} (K)	A_{21} (K)	α_{12}	k_{12}	l_{12}	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
**n-Pentane(1)/acetone(2): from − 35 to 25°C; I/3 + 4/188, 189, 190*										
WSMR1	485.086	483.326	0.4683	0.2288		1.73	3.30	5.28	4.47	5.99
WSMR2	485.086	483.326	0.4683	0.2120	−0.0235	1.73	3.30	5.47	4.61	6.16
TCMR1	485.086	483.326	0.4683	0.0047		2.43	3.89	3.27	3.22	4.41
TCMR2	485.086	483.326	0.4683	0.0655	0.0658	1.71	2.06	3.75	3.05	4.23
**Ethanol(1)/water(2) from 24.99 to 120°C; I/1b/93, 106, 107, 108*										
WSMR1	13.3878	437.683	0.2945	0.2308		2.34	3.10	3.51	5.45	4.09
WSMR2	13.3878	437.683	0.2945	0.1375	−0.0810	2.34	3.10	3.63	5.59	4.19
TCMR1	13.3878	437.683	0.2945	−0.1641		4.59	5.67	4.61	5.61	5.28
TCMR2	13.3878	437.683	0.2945	−0.0697	0.0857	0.06	0.06	2.32	4.11	3.12
**Methanol(1)/cyclohexane(2) from 25 to 55°C; I/2c/208, 209; I/2a/242*										
WSMR1	644.886	784.966	0.4231	0.3593		10.01	5.25	4.05	4.31	6.07
WSMR2	644.886	784.966	0.4231	0.2860	−0.0712	10.01	5.25	3.87	4.37	6.24
TCMR1	644.886	784.966	0.4231	−0.0373		10.33	6.49	7.27	5.30	7.71
TCMR2	644.886	784.966	0.4231	0.5217	0.5810	5.13	4.09	2.15	2.95	4.29
**Ethanol(1)/benzene(2) from 25 to 55°C; I/2a/398, 407, 415, 417, 418, 421, 422*										
WSMR1	115.954	584.473	0.2904	0.1941		4.90	3.64	2.26	5.22	3.06
WSMR2	115.954	584.473	0.2904	0.1766	0.0020	4.90	3.64	1.18	5.18	3.03
TCMR1	115.954	584.473	0.2904	0.0030		5.48	4.24	3.95	6.57	4.33
TCMR2	115.954	584.473	0.2904	0.1979	0.2139	1.23	1.02	1.87	4.12	2.97
**Ethanol(1)/n-heptane(2) from 30.12 to 70.02°C; I/2e/377, 379; I/2c/457, 458*										
WSMR1	521.746	727.003	0.4598	0.3368		10.13	5.69	3.21	3.90	5.56
WSMR2	521.746	727.003	0.4598	0.2587	0.0129	10.13	5.69	3.03	3.81	5.23
TCMR1	521.746	727.003	0.4598	−0.0629		10.80	6.92	6.43	5.68	10.22
TCMR2	521.746	727.003	0.4598	0.4875	0.5577	4.71	3.53	2.23	2.59	3.94
**Methanol(1)/water(2) from 24.99 to 100°C; I/1b/29; I/1/41, 49, 72, 73*										
WSMR1	−23.1150	188.147	0.3022	0.0745		0.37	0.42	2.58	4.03	4.29
WSMR2	−23.1150	188.147	0.3022	0.0381	0.0156	0.37	0.42	2.64	4.15	4.41
TCMR1	−23.1150	188.147	0.3022	−0.1136		1.64	1.97	2.60	3.25	4.68
TCMR2	−23.1150	188.147	0.3022	−0.0876	0.0251	0.04	0.04	2.21	3.11	3.67
**Methanol(1)/n-hexane(2) from 25 to 45°C; I/2c/219; I/2a/252*										
WSMR1	823.172	848.519	0.4388	0.3954		11.95	5.61	5.20	5.98	5.08
WSMR2	823.172	848.519	0.4388	0.3112	0.0238	11.95	5.61	5.32	6.02	5.14
TCMR1	823.172	848.519	0.4388	−0.0980		13.19	7.85	8.55	11.36	10.22
TCMR2	823.172	848.519	0.4388	0.2169	0.3058	7.38	4.61	2.36	3.48	2.96

*Data taken from DECHEMA Chemistry Data Series by Gmehling, Onken, and Arlt; numbers corresponding to volume/part/page.

the Wong–Sandler mixing rules. Once again, WSMR2 does not offer any improvement over WSMR1 in the reproduction of the activity coefficients because of the highly correlated nature of the k_{ij} and l_{ij} parameters in the Wong–Sandler mixing rules. However, this is not the case for TCMR2. The activity coefficients reproduced from TCMR2 are significantly better than TCMR1. The new model once more demonstrates that it has more flexibility in fitting the activity coefficients than the Wong–Sandler mixing rules.

A system can be considered as relatively symmetric if it has similar values of the NRTL infinite dilution activity coefficients. For symmetric systems, our mixing rules and Wong–Sandler mixing rules reproduce satisfactory activity coefficients over the entire composition range. The activity coefficient reproducibility for the symmetric systems by Wong–Sandler mixing rules and ours has been demonstrated in Table 5 for n-pentane(1)/acetone(2) ($\gamma_1^\infty = 16.88$, $\gamma_2^\infty = 16.80$ at −35°C) and methanol(1)/water(2) ($\gamma_1^\infty = 1.74$, $\gamma_2^\infty = 1.54$ at 24.99°C).

A system is considered to be asymmetric if the NRTL infinite dilution activity coefficients are quite different from each other. The following systems in Table 5 are characterized by very different NRTL infinite dilution activity coefficients: methanol(1)/cyclohexane(2) ($\gamma_1^\infty = 150.20$, $\gamma_2^\infty = 39.24$ at 25°C); ethanol(1)/benzene(2) ($\gamma_1^\infty = 16.50$, $\gamma_2^\infty = 5.07$ at 25°C); ethanol(1)/n-heptane(2) ($\gamma_1^\infty = 35.0$, $\gamma_2^\infty = 12.5$ at 30.12°C); methanol(1)/n-hexane(2) ($\gamma_1^\infty = 79.36$, $\gamma_2^\infty = 52.91$, at 25°C). The results in Table 5 illustrate that for these asymmetric mixtures a CEOS with our new mixing rules can reproduce better activity coefficients over the entire composition range than the Wong–Sandler mixing rules. The errors in the reproduction of activity coefficients for these asymmetric systems with the new mixing rules when used with the Soave–Redlich–Kwong equation of state are, on average, about half of the errors associated with the Wong–Sandler mixing rules.

Conclusions

It is desirable to have a mixing rule that can handle highly nonideal binaries as well as simple binaries in the same system, because the same mixing rule has to be applied to all binaries, whether they are polars, nonpolars, inorganic gases, or any combination of these, in phase-equilibrium calculations. We propose a vdW fluid as the reference to develop a new class of CEOS mixing rules for industrial applications to systems usually containing chemicals as well as hydrocarbons and industrial gases. One of the major advantages of using the vdW mixture as the reference is that the mixing rules in the vdW mixture limit reduce to the classic mixing rules suggested by van der Waals.

The capability of the new mixing rules has been demonstrated by correlating data of highly nonideal systems with a high degree of accuracy. We also demonstrate that our new mixing rules can be applied with high accuracy to the prediction of phase equilibria using available parameters for the liquid activity coefficient model. Because our new mixing rules reduce to the vdW one-fluid mixing rules, the results prove that our mixing rules not only achieve the purpose of preserving the excellent features of the Wong–Sandler mixing rules for dealing with highly nonideal systems, but also avoid the problems encountered from the application of the Wong–Sandler mixing rules to simple systems.

Notation

a^*, b^* = reduced parameters of a and b

B = second virial coefficient

f_i = fugacity of component i in the mixture

k_i = k-value of component i defined as y_i/x_i

n = total number of moles

R = gas constant

y_i = vapor mole fraction of component i

Superscript

$*$ = reduced property

Literature Cited

Coutsikos, P., N. S. Kalospiros, and D. P. Tassios, "Capabilities and Limitations of the Wong-Sandler Mixing Rules," *Fluid Phase Equilib.*, **108**, 59 (1995).

Huang, H., S. I. Sandler, and H. Orbey, "Vapor-Liquid Equilibria of Some Hydrogen + Hydrocarbon Systems with the Wong-Sandler Mixing Rule," *Fluid Phase Equilib.*, **96**, 143 (1994).

Huron, M. J., and J. Vidal, "New Mixing Rules in Simple Equations of State for Representing Vapor-Liquid Equilibria of Strongly Nonideal Mixtures," *Fluid Phase Equilib.*, **3**, 255 (1979).

Mollerup, J., "Correlation of Thermodynamic Properties of Mixtures using a Random-mixture Reference State," *Fluid Phase Equilib.*, **15**, 189 (1983).

Orbey, H., and S. I. Sandler, "Reformulation of Wong-Sandler Mixing Rule for Cubic Equations of State," *AIChE J.*, **41**(3), 683 (1995a).

Orbey, H., and S. I. Sandler, "On the Combination of Equation of State and Excess Free Energy Models," *Fluid Phase Equilib.*, **111**, 53 (1995b).

Peng, D.-Y., and D. B. Robinson, "A New Two-constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).

Rowlinson, J. S., *Liquid and Liquid Mixtures*, 2nd ed., Butterworth, London (1969).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Twu, C. H., D. Bluck, J. R. Cunningham, and J. E. Coon, "A Cubic Equation of State with a New Alpha Function and a New Mixing Rule," *Fluid Phase Equilib.*, **69**, 33 (1991).

Voros, N. G., and D. P. Tassios, "Vapor-liquid Equilibria in Nonpolar/Weakly Polar Systems with Different Types of Mixing Rules," *Fluid Phase Equilib.*, **91**, 1 (1993).

Wong, S. H., and S. I. Sandler, "A Theoretically Correct Mixing Rule for Cubic Equations of State," *AIChE J.*, **38**(5), 671 (1992).

Wong, S. H., H. Orbey, and S. I. Sandler, "Equation of State Mixing Rule for Nonideal Mixtures Using Available Activity Coefficient Model Parameters and that Allows Extrapolation over Large Ranges of Temperature and Pressure," *Ind. Eng. Chem. Res.*, **31**(8), 2033 (1992).

Manuscript received Sept. 5, 1995, and revision received May 6, 1996.