

Equations of state using an extended Twu–Coon mixing rule incorporating UNIFAC for high temperature and high pressure phase equilibrium predictions

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Abstract

A mixing rule recently developed by Twu and Coon [C.H. Twu, J.E. Coon, CEOS/ A^E mixing rules constrained by the vdW mixing rule and the second virial coefficient, *AIChE J.* 42 (1996) 3212–3222] is extended to incorporate the UNIFAC group contribution method into an equation of state for the prediction of phase behavior of highly non-ideal systems over wide ranges of temperature and pressure. The mixing rule developed by Twu and Coon reduces to the van der Waals mixing rule. The Helmholtz excess free energy function with respect to a van der Waals fluid at infinite pressure has been related rigorously to the Helmholtz excess free energy at zero pressure. This extension of the Twu–Coon Mixing Rule goes gracefully from the classical van der Waals one-fluid mixing rule for non-polar fluids needed in the refining and gas processing industries to a mixing rule combining excess free energy models at low pressure with equations of state for the strongly polar systems found in the chemical industries. When the UNIFAC group contribution method is incorporated, the mixing rule becomes totally predictive. The completely predictive equation of state is shown to give accurate results for systems for which the UNIFAC model is in agreement with the experimental activity coefficients at low pressure. The UNIFAC-incorporated mixing rule provides a simple way to extend the UNIFAC group contribution method to high temperatures and pressures. © 1997 Elsevier Science B.V.

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1. Introduction

Recently, cubic equations of state have become very powerful in correlating and predicting phase equilibrium behavior for either non-polar or/and polar systems. This capability comes both from the

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ability to predict pure component vapor pressure accurately for polar and non-polar components (Soave [1]; Mathias [2]; Stryjek and Vera [3]; Twu et al. [4–6]) and the latest development of new mixing rules for cubic equations of state (Huron and Vidal [7]; Michelsen [8]; Dahl and Michelsen [9]; Twu et al. [4]; Wong and Sandler [10]; Twu and Coon [11]).

There are two successful approaches in developing equation of state mixing rules for highly non-ideal systems. One is to combine equations of state and excess free energy models at infinite pressure. The other is to combine them at zero pressure. The mixing rules derived from the zero pressure approach can theoretically make use of the reported activity coefficient model parameters in the equation of state mixing rule model without the need for further adjustment. The mixing rules derived from the infinite pressure approach, however, require additional binary interaction parameters to match as closely as possible the incorporated excess Gibbs free energy model. Recently, Coutisikis et al. [12] have analyzed the capabilities and limitations of the infinite pressure type such as the Wong–Sandler mixing rule. They concluded that the Wong–Sandler mixing rule is unable to reproduce the G^E model with which it is combined. Kalospiros et al. [13] also analyzed the zero-pressure mixing rules and they demonstrated that, in general, zero-pressure models do not reproduce the G^E models either.

This paper extends the Twu–Coon mixing rule from infinite pressure to zero pressure. A new methodology has been developed so that the incorporated G^E model can be reproduced accurately from this new mixing rule. The ability of this new model to reproduce low-pressure information (such as the liquid activity coefficients) stored in the excess Gibbs energy model will be demonstrated. Due to this capability, the UNIFAC group contribution method can be incorporated with the new mixing rule into an equation of state to yield a completely predictive thermodynamic model for the prediction of high pressure vapor–liquid phase equilibrium.

2. Extension of Twu–Coon mixing rule

Twu and Coon [11] used a van der Waals solution, instead of an ideal solution as utilized by Wong and Sandler [10], as a reference fluid to develop equation of state mixing rules. Twu and Coon found that, in this way, the mixing rule developed satisfies not only the quadratic composition dependence of the second virial coefficient, but also includes the van der Waals one-fluid mixing rule. Since it has been shown many times that the classical mixing rule works very well for non-polar systems, it is extremely desirable that a new mixing rule reduces to the classical mixing rule. The Twu–Coon mixing rule has been shown previously to give excellent results for highly non-ideal systems. The following mixing rules for the cubic equation of state mixture a and b parameters developed by Twu and Coon [11] are:

$$b^* = \frac{b_{\text{vdw}}^* - a_{\text{vdw}}^*}{1 - \left(\frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} + \frac{1}{C_1} \frac{A_{\infty\text{nr}}^E}{RT} \right)} \quad (1)$$

$$a^* = b^* \left(\frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} + \frac{1}{C_1} \frac{A_{\infty\text{nr}}^E}{RT} \right) \quad (2)$$

The constant C_1 is specific to the cubic equation of state used ($C_1 = -\ln(2)$ for the Soave–Redlich–Kwong [1] equation of state used here). a_{vdw} and b_{vdw} are the equation of state a and b parameters which are evaluated from the van der Waals mixing rules:

$$a_{\text{vdw}} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (3)$$

$$b_{\text{vdw}} = \sum_i \sum_j x_i x_j \left[\frac{1}{2} (b_i + b_j) \right] (1 - l_{ij}) \quad (4)$$

with two binary interaction parameters, k_{ij} and l_{ij} .

Eqs. (1) and (2) completely define the two mixture parameters a and b in terms of $A_{\infty\text{nr}}^E$ at infinite pressure. These two mixing rules reduce to the van der Waals one-fluid mixing rules when $A_{\infty\text{nr}}^E$ is zero. The subscript nr is the abbreviation of non-random. The definition of the excess function $A_{\infty\text{nr}}^E$ is with respect to a van der Waals fluid, instead of an ideal solution:

$$\frac{A_{\infty\text{nr}}^E}{RT} = \frac{A_{\infty}^E}{RT} - \frac{A_{\infty\text{vdw}}^E}{RT} \quad (5)$$

The infinite pressure mixing rule requires additional binary interaction parameters k_{ij} and l_{ij} to reproduce adequately the incorporated excess Gibbs free energy model. An approach is proposed here to relate the Helmholtz excess free energy function at infinite pressure to its value at zero pressure so that the equation of state can reproduce the vapor–liquid equilibrium predicted by the G^E model at low temperature without seeking any help from additional parameters. A two-parameter cubic equation of state used previously by Twu and Coon [11] is considered here:

$$P = \frac{RT}{v - b} - \frac{a}{(v + ub)(v + wb)} \quad (6)$$

where P is the pressure, T is the absolute temperature, and v is the molar volume. The constants u and w are equation of state dependent (for the Soave–Redlich–Kwong equation [1]: $u = 0$, $w = 1$). The values of 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. (6) is a function of temperature and the parameter b is assumed to be a constant for pure components. The value of $a(T)$ at temperatures other than the critical temperature can be calculated from

$$a(T) = \alpha(T) a_c \quad (7)$$

where the alpha function, $\alpha(T)$, is a function only of reduced temperature, $T_r = T/T_c$. Since the prediction of pure component vapor pressure must be of high accuracy for accurate vapor–liquid calculations, we use the alpha correlation of Twu et al. [4]:

$$\alpha = T_r^{N(M-1)} e^{L(1 - T_r^{NM})} \quad (8)$$

Eq. (8) 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 data. Using the alpha correlation of Twu et al. [4] in the equation of state results in a very accurate prediction of vapor pressure for all chemical pure components. The L , M , and N parameters used to get the correct pure component vapor pressure for all pure components used in this paper are listed in Table 1.

Table 1

The L , M , and N parameters of the temperature-dependent α function given by Eq. (8) for pure components used with the SRK cubic equation of state

Component	T_c (K)	P_c (bar)	L	M	N
<i>n</i> -Pentane	469.70	33.70	0.379229	0.841706	1.82331
<i>n</i> -Hexane	507.85	30.31	0.158080	0.872819	3.84418
<i>n</i> -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

A cubic equation of state can be used to derive the Helmholtz free energy 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. (6) is given below:

$$\frac{\Delta A}{RT} = -\ln(Z - b^*) - \frac{1}{(w - u)} \frac{a^*}{b^*} \ln \left(\frac{Z + wb^*}{Z + ub^*} \right) \quad (9)$$

The parameters a^* and b^* in Eq. (9) are defined as:

$$a^* = Pa/R^2T^2 \quad (10)$$

$$b^* = Pb/RT \quad (11)$$

Z in Eq. (9) is the compressibility factor, which is the solution of the equation of state, Eq. (6), for the phase of interest:

$$Z^3 + [(u + w - 1)b^* - 1]Z^2 + [(uw - u - w)b^{*2} - (u + w)b^* + a^*]Z - (uwb^{*3} + uwb^{*2} + a^*b^*) = 0 \quad (12)$$

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

$$A^E = \Delta A - \sum_i^n x_i \Delta A_i \quad (13)$$

where x_i is the mole fraction of component i . Applying Eq. (13) to a van der Waals fluid and subtracting it from Eq. (13) gives:

$$A^E - A_{vdw}^E = \Delta A - \Delta A_{vdw} \quad (14)$$

Twu and Coon [11] used Eq. (14) to derive the following mixing rule for the cubic equation of state mixture a and b parameters at infinite pressure:

$$\frac{A_{\infty}^E}{RT} - \frac{A_{\infty, \text{vdw}}^E}{RT} = C_1 \left(\frac{a^*}{b^*} - \frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} \right) \quad (15)$$

with the constant C_1 being:

$$C_1 = -\frac{1}{(w-u)} \ln \left(\frac{1+w}{1+u} \right) \quad (16)$$

A_{∞}^E and $A_{\infty, \text{vdw}}^E$ in Eq. (15) are the excess Helmholtz energy at infinite pressure evaluated from a cubic equation of state using the complete mixing rules for its a and b parameters and using the van der Waals mixing rules for its a and b parameters (a_{vdw} and b_{vdw}), respectively.

If zero pressure, instead of infinite pressure, is applied to Eq. (14), an equation containing liquid volume is obtained:

$$\begin{aligned} \frac{A_0^E}{RT} - \frac{A_{0, \text{vdw}}^E}{RT} = & \ln \left[\left(\frac{v_{0, \text{vdw}}^* - 1}{v_0^* - 1} \right) \left(\frac{b_{\text{vdw}}}{b} \right) \right] - \frac{1}{(w-u)} \\ & \times \left[\frac{a^*}{b^*} \ln \left(\frac{v_0^* + w}{v_0^* + u} \right) - \frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} \ln \left(\frac{v_{0, \text{vdw}}^* + w}{v_{0, \text{vdw}}^* + u} \right) \right] \end{aligned} \quad (17)$$

A_0^E and $v_0^* = v_0/b$ are the excess Helmholtz energy and reduced liquid volume at zero pressure. As mentioned, the subscript vdw denotes that the properties are evaluated from the cubic equation of state using the van der Waals mixing rule for its a and b parameters. The zero pressure volume is obtained from Eq. (6) by setting pressure equal to zero and selecting the smallest root:

$$v_0^* = \frac{1}{2} \left\{ \left(\frac{a^*}{b^*} - u - w \right) - \left[\left(u + w - \frac{a^*}{b^*} \right)^2 - 4 \left(uw + \frac{a^*}{b^*} \right) \right]^{\frac{1}{2}} \right\} \quad (18)$$

Eq. (18) has a root as long as

$$\frac{a^*}{b^*} \geq (2 + u + w) + 2\sqrt{(u+1)(w+1)} \quad (19)$$

According to Eq. (19), the zero pressure mixing rule requires that the value of a^*/b^* for the pure components as well as for the mixture must exceed 5.82843 for SRK and 6.82843 for PR equation of state. Several extrapolation schemes for a^*/b^* at high temperatures have been proposed (e.g., Heidemann and Kokal [14]; Soave [15]; Michelsen [16]). Since extrapolation problem is not the focus of our efforts at this time, we suggest that Soave's methodology be used when extrapolating our mixing rule to high temperatures. Our objective in this paper is to propose a new methodology to reproduce accurately the incorporated G^E model from our new zero pressure mixing rule. The comparisons made later have been chosen so that extrapolation methodology is not relevant.

Eqs. (17) and (18) represent an exact model for a new mixing rule. However, because the equation of state parameter a^*/b^* and the zero pressure liquid volume are interrelated by Eqs. (17) and (18), the exact model does not permit explicit solution of Eq. (17) for a^*/b^* and an iterative technique is

required for the solution. If Eqs. (17) and (18) are used to solve for a^*/b^* , the resulting new mixing rule will give an exact match between the excess Helmholtz free energy of the equation of state at zero pressure and that of the incorporated excess Gibbs free energy model. Nevertheless, the non-explicit nature of the expression for the mixing rule becomes cumbersome in the evaluation of thermodynamic properties such as fugacity coefficients from the equation of state. This paper presents a methodology to overcome this obstacle to obtain an explicit expression for this new mixing rule.

A variety of alternatives have been proposed to simplify the exact model so that the equation of state parameters, a and b , can be explicitly expressed (Michelsen [8]; Dahl and Michelsen [9]; Novenario et al. [17]). However, these modifications of the exact model sacrifice to some extent the quality of the match between the equation of state and the G^E model. For example, the MHV1 model developed by Michelsen [8] can be alternately derived from our new mixing rule by assuming v_0^* is a constant (1.23547 for SRK and 1.22756 for PR), instead of solving for it from Eq. (18). This means that the MHV1 model assumes that the ratio of the zero pressure liquid volume to the close packing parameter b is the same for the mixture and for all pure components. This is the main reason why the MHV1 and MHV2 models perform poorly in reproducing the behavior of the G^E model when applied to systems either with components that are different in size or where the value of v_0^* of the system is not close to the fixed values given above.

In this paper, v_0^* will not be assumed to be constant. We propose instead that the ratio of the zero pressure liquid volume to the close packing parameter b of the system, v_0^* , be assumed to be the same as that of the van der Waals fluid, $v_{0\text{vdw}}^*$. Using Eqs. (3) and (4) for the parameters a and b in Eq. (18), $v_{0\text{vdw}}^*$ is ready to be calculated from the equation. The binary interaction parameters, k_{ij} and l_{ij} are not required in the proposal and both are set to zero in this work. Eq. (18) is used to calculate $v_{0\text{vdw}}^*$ for both the mixture and the pure components. Eq. (17) can then be simplified to

$$\frac{A_0^E}{RT} - \frac{A_{0\text{vdw}}^E}{RT} = \ln\left(\frac{b_{\text{vdw}}}{b}\right) + C_{v_0}\left[\frac{a^*}{b^*} - \frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*}\right] \quad (20)$$

with the constant C_{v_0} being:

$$C_{v_0} = -\frac{1}{(w-u)} \ln\left(\frac{v_0^* + w}{v_0^* + u}\right)_{\text{vdw}} \quad (21)$$

Since the equation of state parameters, a and b , are pressure independent, these two parameters can be cancelled out from Eqs. (15) and (20) to give the inter-relationship of A^E between infinite pressure and zero pressure as:

$$\frac{A_\infty^E}{RT} - \frac{A_{\infty\text{vdw}}^E}{RT} = \frac{C_1}{C_{v_0}} \left[\frac{A_0^E}{RT} - \frac{A_{0\text{vdw}}^E}{RT} - \ln\left(\frac{b_{\text{vdw}}}{b}\right) \right] \quad (22)$$

Using Eq. (5) and substituting Eq. (22) into Eqs. (1) and (2) results in a new and explicit mixing rule in terms of A_0^E at zero pressure:

$$b^* = \frac{b_{\text{vdw}}^* - a_{\text{vdw}}^*}{1 - \left[\frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} + \frac{1}{C_{v_0}} \left(\frac{A_0^E}{RT} - \frac{A_{0\text{vdw}}^E}{RT} - \ln\left(\frac{b_{\text{vdw}}}{b}\right) \right) \right]} \quad (23)$$

$$a^* = b^* \left[\frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} + \frac{1}{C_{v_0}} \left(\frac{A_0^E}{RT} - \frac{A_{0\text{vdw}}^E}{RT} - \ln \left(\frac{b_{\text{vdw}}}{b} \right) \right) \right] \quad (24)$$

As mentioned above, $A_{0\text{vdw}}^E$ in Eqs. (23) and (24) is the excess Helmholtz energy at zero pressure evaluated from a cubic equation of state using the mixing rules for its a_{vdw} and b_{vdw} parameters with both binary interaction parameters, k_{ij} and l_{ij} set to zero. The zero pressure volume $v_{0\text{vdw}}^* = v_{0\text{vdw}}/b$ is obtained from Eq. (18) by substituting a_{vdw} and b_{vdw} for the a and b parameters. Because A_0^E in Eqs. (23) and (24) is at the zero pressure, G^E models, such as the NRTL equation or the UNIFAC equation, can be directly incorporated into A_0^E .

There are some nice features of this new mixing rule. The new mixing rule reduces to the van der Waals mixing rule when A_0^E is equal to $A_{0\text{vdw}}^E$. The mixing rule satisfies the quadratic composition dependence of the second virial coefficient boundary condition. The most important is that the mixing rule is density dependent in an explicit form which allows the mixing rule to reproduce accurately the incorporated G^E model.

3. Incorporation of a UNIFAC/NRTL hybrid model in the new mixing rule

To make the CEOS totally predictive, the UNIFAC method can be used for the excess Helmholtz free energy expression A_0^E in Eqs. (23) and (24), since A_0^E is equal to G^E . If a correlative version of the CEOS is desired, a G^E model like NRTL can be used in the CEOS. We prefer a hybrid UNIFAC/NRTL method that we believe gives the benefits of both. The procedure we use is as follows. First, we incorporate the NRTL model shown in Eqs. (23) and (24) into the mixing rule as A_0^E :

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} \quad (25)$$

with τ_{ij} and G_{ij} defined as:

$$\tau_{ji} = \frac{A_{ji}}{T} \quad (26)$$

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

For any binary for which NRTL parameters have been obtained by fitting experimental data, we use those parameters directly in the mixing rule. For binaries where there are no NRTL parameters available, we generate them using UNIFAC. First, the activity coefficients over the entire range of concentration of the binary are generated from the UNIFAC model at the normal boiling point of the lower boiling component in the binary. Next, these calculated activity coefficients are used to regress the parameters A_{ij} , A_{ji} , and α_{ij} of the NRTL model. These values of A_{ij} , A_{ji} , and α_{ij} are then used in the mixing rule at all temperatures.

To test the predictive capabilities of this hybrid model, we have considered ten highly non-ideal binary mixtures which are traditionally described by liquid activity models. They are listed in Table 2. Even though NRTL parameters are available for these binaries, we have chosen to generate them from UNIFAC to show the results when using the CEOS in a predictive manner. This procedure is totally predictive and does not involve fitting any binary interaction parameters to the experimental data. In order to obtain liquid-like values for v_0^* at zero pressure from Eq. (18), we limit our analysis to systems with components and temperatures such that a^*/b^* is larger than the limiting value of 5.82843 for SRK. By doing this, we eliminate the need to include an extrapolation methodology into our comparisons.

The mixing rule for the parameter b as given by Eq. (23) forces the mixing rule to satisfy the quadratic composition dependence of the second virial coefficient. Alternatively, the conventional linear mixing rule could be chosen for the b parameter (i.e., ignoring the second virial coefficient boundary condition):

$$b = \sum_i \sum_j x_i x_j \left[\frac{1}{2} (b_i + b_j) \right] \quad (28)$$

We will examine the capability of the mixing rule for phase equilibrium prediction with and without the second virial coefficient constraint on the b parameter. We will also compare our new mixing rule with two of the most successful and widely used mixing rules, MHV1 (Michelsen [8]) and the mixing rule proposed by Wong and Sandler [10]. Wong and Sandler assumed that the excess Helmholtz free energy at infinite pressure can be approximated by the excess Gibbs free energy at low pressure:

$$A^E(T, x, P = \infty) = A^E(T, x, P = \text{low}) = G^E(T, x, P = \text{low}) \quad (29)$$

The Wong–Sandler approximation will be tested in this comparison to see how well the assumption in Eq. (29) stands. As stated before, one of our objectives in this paper is to test the ability of different mixing rules to reproduce the incorporated G^E model. In this work, we are going to perform rigorous tests of the capability of reproducing the G^E model using the equation of state combined with our new mixing rules. We use ‘WS’ to refer to the Wong–Sandler mixing rules. ‘TCB’ is used to represent the mixing rule developed by us in this work (Eqs. (23) and (24), and ‘TCB(0)’ to Eqs. (24) and (28). The zero in the TCB parenthesis means no second virial coefficient constraint. The accuracy of the reproducing activity coefficients of component i , γ_i (%) in terms of average absolute deviation percentage (AAD%), from the incorporated G^E model using these different mixing rules is given in Table 2. Similarly, the accuracy of the VLE prediction from the different mixing rules, which is also in terms of AAD% in bubble point pressure and k -values of components 1 and 2, is also presented in Table 2.

Examining the accuracy of reproducing activity coefficients as given in Table 2, the Wong–Sandler mixing rule gives the largest deviation for all the systems in this comparison. The inability to match the G^E derived from the equation of state with that from the incorporated G^E model invalidates the basic assumption behind the Wong–Sandler mixing rule. The predictions from the Wong–Sandler mixing rule without using any additional binary interaction parameters is unacceptable. Table 2 contains the results for the systems acetone–benzene and acetone–methanol. The zero pressure model, MHV1, reproduces closely the G^E model it is combined with for systems where the liquid volume of the components is close to the fixed value chosen by Michelsen [8]. It is not surprised that

Table 2

UNIFAC/NRTL interaction parameters and results of the prediction in terms of average absolute deviation percentage (AAD%) in activity coefficients, bubble point pressure and k -values

"Ethanol(1)/n-heptane(2) from 30.12 to 70.02°C; 1/2e/377, 379; 1/2c/457, 458

$A_{12} = 454.030$, $A_{21} = 650.045$, $\alpha_{12} = 0.4053$

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	24.71	24.71	16.82	12.86	25.81
MHV1	3.39	3.73	2.54	2.40	4.24
TCB	0.11	0.06	1.92	2.22	4.37
TCB(0)	0.08	0.05	1.90	2.24	4.40

"Ethanol(1)/water(2) from 24.99 to 120°C; 1/1b/93, 106, 107, 108

$A_{12} = 157.656$, $A_{21} = 587.394$, $\alpha_{12} = 0.6519$

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	19.28	16.97	10.69	12.37	12.24
MHV1	6.80	4.39	3.53	2.19	2.43
TCB	0.21	0.15	1.82	1.86	1.95
TCB(0)	0.16	0.12	1.85	1.83	1.93

"Methanol(1)/cyclohexane(2) from 25 to 55°C; 1/2a/242; 1/2c/208, 209

$A_{12} = 582.516$, $A_{21} = 600.610$, $\alpha_{12} = 0.3410$

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	25.13	25.33	18.99	15.06	23.07
MHV1	3.12	3.70	3.54	4.25	6.32
TCB	0.22	0.18	2.78	3.64	5.33
TCB(0)	0.17	0.14	2.77	3.68	5.38

"Methanol(1)/benzene(2) from 25 to 90°C; 1/2c/188; 1/2a/207, 210, 216, 217, 228

$A_{12} = 329.066$, $A_{21} = 609.043$, $\alpha_{12} = 0.4059$

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	20.45	19.73	14.39	14.82	15.19
MHV1	2.88	2.78	2.64	3.57	3.82
TCB	0.17	0.14	2.19	2.99	3.24
TCB(0)	0.13	0.11	2.16	3.00	3.23

"Acetone(1)/benzene(2) from 25 to 45°C; 1/3+4/194, 203, 208

$A_{12} = 147.481$, $A_{21} = 13.6647$, $\alpha_{12} = 0.5658$

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	4.06	4.61	2.27	2.68	4.26
MHV1	0.69	0.60	1.45	1.82	3.88
TCB	0.01	0.02	1.43	1.90	3.76
TCB(0)	0.01	0.01	1.42	1.90	3.75

"Acetone(1)/ethanol(2) from 32 to 48°C; 1/2a/323, 324, 325

$A_{12} = 128.070$, $A_{21} = 139.263$, $\alpha_{12} = 0.3889$

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	5.40	5.79	2.48	2.49	1.84
MHV1	1.78	1.41	2.32	2.94	4.68
TCB	0.01	0.01	1.45	1.87	3.73
TCB(0)	0.01	0.01	1.44	1.87	3.71

Table 2 (continued)

Acetone(1)/methanol(2) from 45 to 55°C; 1/2a/75, 80, 81 $A_{12} = 88.8477$, $A_{21} = 132.978$, $\alpha_{12} = 0.4102$

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	8.11	8.05	4.12	4.82	5.67
MHV1	0.74	0.45	0.49	1.04	0.98
TCB	0.00	0.00	0.45	0.95	0.93
TCB(0)	0.00	0.00	0.45	0.95	0.93

^aEthanol(1)/benzene(2) from 25 to 55°C; 1/2a/398, 407, 415, 417, 418, 421, 422 $A_{12} = 234.239$, $A_{21} = 514.157$, $\alpha_{12} = 0.3975$

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	14.98	13.56	9.83	12.12	9.48
MHV1	2.75	2.83	1.96	3.84	2.74
TCB	0.16	0.13	1.37	3.56	2.43
TCB(0)	0.12	0.10	1.37	3.57	2.44

^aMethanol(1)/water(2) from 24.99 to 100°C; 1/1b/29; 1/1/41, 49, 72, 73 $A_{12} = 33.6268$, $A_{21} = 265.775$, $\alpha_{12} = 0.7373$

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	7.81	6.71	2.28	3.35	3.94
MHV1	4.16	3.22	4.51	4.25	6.49
TCB	0.12	0.10	2.81	3.08	4.32
TCB(0)	0.09	0.08	2.84	3.09	4.36

^aMethanol(1)/n-hexane(2) from 25 to 45°C; 1/2c/219; 1/2a/252 $A_{12} = 647.116$, $A_{21} = 531.669$, $\alpha_{12} = 0.3330$

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	27.02	27.45	26.12	32.97	30.54
MHV1	2.37	3.95	4.84	6.25	5.34
TCB	0.10	0.06	4.16	5.68	4.86
TCB(0)	0.08	0.04	4.12	5.69	4.87

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

if the liquid volume of system is not close to the fixed constant, the G^E model is not reproduced by the equation of state using MHV1 mixing rule. These results are in agreement with a statement by Kalospiros et al. [13], although we have a different explanation for it. The results as shown in Table 2 illustrate that our new mixing rule reproduces the G^E model almost exactly. The errors in the reproduction of activity coefficients for these systems are minimal from our mixing rule.

For the VLE predictions, our new mixing rule gives consistent results and in general provides the best agreement between the experimental data and the predictions over the wide range of temperatures and pressures considered. Slightly higher deviations are found for MHV1. Again, the worst predictions are obtained from the Wong–Sandler mixing rule because of its inability to match the G^E model. The results for the methanol and *n*-hexane binary are not quite as good as the other binaries. The poor results are attributed to the inability of the UNIFAC model to describe satisfactorily the liquid phase for this mixture. If the NRTL parameters, A_{ij} , A_{ji} and α_{ij} , reported in the DECHEMA Chemistry Data Series for this binary are used directly in the mixing rule model instead of UNIFAC, the calculated results as shown in Table 3 are substantially improved.

Table 3

NRTL interaction parameters and results of the prediction in terms of average absolute deviation percentage (AAD%) in activity coefficients, bubble point pressure and k -values

^aMethanol(1)/n-hexane(2) from 25 to 45°C; I/2c/219; I/2a/252

$A_{12} = 823.172$, $A_{21} = 848.519$, $\alpha_{12} = 0.4388$ at 25°C

Direct calculations from NRTL parameters reported in DECHEMA (no regression)

Mixing rule	γ_1 (%)	γ_2 (%)	P (%)	k_1 (%)	k_2 (%)
WS	27.73	27.77	25.52	33.94	31.54
MHV1	2.47	4.12	3.13	1.99	1.85
TCB	0.12	0.05	1.82	1.23	1.13
TCB(0)	0.10	0.04	1.76	1.23	1.13

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

Finally, as we mentioned, we want to investigate the impact of the mixing rule with and without the second virial coefficient condition constraint on phase equilibrium prediction. Reviewing the results shown in Table 2, they show that our mixing rule either with or without second virial coefficient condition constraint yields almost identical results. This indicates that the second virial coefficient constraint has no effect on the phase equilibrium prediction. Theoretically, it would be nice to have the mixing rule satisfy the quadratic composition dependence of the second virial coefficient boundary condition. Practically, it is simpler just to use the conventional linear mixing rule for the b parameter. The same quality of phase behavior will be predicted from both cases.

4. Conclusion

We have successfully extended the Two-Coon Mixing Rule from infinite pressure to zero pressure. We demonstrate that CEOS/ A^E models such as the Wong–Sandler mixing rule do not reproduce the G^E models with which they are associated. We show why the zero pressure model does not reproduce exactly the G^E models at low pressure and reveal that approximate reproduction is feasible for MHV1 only for the systems with liquid volumes close to the assumed constant one. On the other hand, the new model we developed in this work accurately reproduces the activity coefficients of the G^E model. Due to this capability, the new mixing rule can be incorporated with the UNIFAC group contribution method into an equation of state to yield a completely predictive thermodynamic model for the prediction of high pressure vapor–liquid phase equilibrium.

List of symbols

a, b	Cubic equation of state parameters
a^*, b^*	Reduced parameters of a and b
A	Helmholtz free energy
A_{ij}, A_{ji}	NRTL binary interaction parameters
C_1	Infinite pressure function defined in Eq. (16)
C_{v_0}	Zero pressure function defined in Eq. (21)

G	Gibbs free energy
k_i	k value of component i defined as y_i/x_i
k_{ij}	Binary interaction parameter
l_{ij}	Binary interaction parameter
L, M, N	Parameters in the α function
P	Pressure
R	Gas constant
T	Temperature
u, w	Cubic equation of state constants
v	Molar volume
v_0^*	Reduced zero pressure liquid volume
x_i	Liquid mole fraction of component i
y_i	Vapor mole fraction of component i
Z	Compressibility factor

Greek letters

α	Cubic equation of state alpha function defined in Eq. (8)
α_{ij}	NRTL binary interaction parameters
γ_i	Activity coefficient of component i
Δ	Departure function

Subscripts

0	Zero pressure
∞	Infinite pressure
c	Critical property
i, j	Property of components i, j
ij	Interaction property between components i and j
vdw	van der Waals

Superscripts

*	Reduced property
E	Excess property

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