

Liquid activity coefficient model for CEOS/ A^E mixing rules

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Abstract

The current well-known excess Gibbs functions that combine with cubic equations of state (CEOS) all reduce to the ideal solution functions. A new class of excess Gibbs function, which reduces to the van der Waals one-fluid mixing rule, is introduced for application to various asymmetric, highly non-ideal chemical systems. The incorporation of this new excess Gibbs function into a cubic equation of state allows the CEOS/ A^E mixing rule to smoothly transition to the conventional van der Waals one-fluid mixing rules. It is well known that equations of state with the van der Waals mixing rules work very well for non-polar systems, it is, therefore, desirable that the composition dependent excess Gibbs free energy function reduce to that of the van der Waals fluid. Introducing this capability into a Gibbs energy model ensures the binary interaction parameters for the classical quadratic mixing rules available in many existing data banks for systems involving hydrocarbons and gases can be used directly in the new excess Gibbs function. The new liquid activity model is an excellent G^E function and is combined with an equation of state to handle non-ideal systems while still retaining the equation of state capability to handle non-polar systems in the accurate prediction of high pressure and high temperature phase equilibria. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cubic equations of state (CEOS) have seen widespread use in the petroleum and refining industries for the calculation of vapor–liquid equilibrium (VLE) ever since Soave [1] successfully developed a generalized α function for CEOS. To apply CEOS to more complex phase behavior, a more flexible composition-dependent mixing rule other than the van der Waals one-fluid mixing rule is needed.

The modern development of combining CEOSs with excess Helmholtz or excess Gibbs energy models has advanced the CEOS such that it is now an accepted and effective method for correlating and predicting phase equilibrium behavior of highly non-ideal systems. While conventional excess energy mixing rules

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have been successfully applied to strongly polar systems, the results obtained for non-polar systems are no better than the van der Waals one-fluid mixing rules, even though they use more binary parameters [2]. In comparison, systems containing non-polar components and light gases are usually well represented by a CEOS using van der Waals one-fluid mixing rules and only one or two parameters per binary.

In an effort to reduce the excess energy mixing rules to the conventional van der Waals mixing rules, Huron and Vidal [3] and Orbey and Sandler [4] modify the G^E model of NRTL, for example, to a different form. Since, the excess Gibbs energy model is now a modification of the original NRTL equation, the NRTL parameters reported in the DECHEMA Chemistry Data Series can no longer be used in the mixing rules. Another problem of modified activity coefficient models is the requirement that the new model at least give equal to or better correlative and predictive results than the original one.

This paper presents an infinite-pressure mixing rule that also includes an excess Gibbs energy function that uses existing NRTL parameters for highly non-ideal binary-pairs. However, in addition to using existing G^E databases, the activity coefficient model presented here also uses the binary-interaction-parameter k_{ij} of conventional van der Waals one-fluid mixing rules in the same mixture. This can be useful for systems where only some of the binary pairs require the use of a CEOS/ A^E mixing rule or an activity coefficient model, while other binary pairs can be described adequately by the van der Waals one-fluid mixing rules.

2. Infinite-pressure CEOS/ A^E mixing rules

The CEOS infinite-pressure mixing rules have been shown to have remarkable extrapolative powers. Many authors have demonstrated that parameters in activity coefficient models correlated at low temperatures can be used effectively to extrapolate to much higher temperatures. Twu and Coon [5] using a van der Waals mixture as the reference fluid derived the following infinite-pressure mixing rules for the CEOS mixture a and b parameters:

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

$$b^* = \frac{b_{\text{vdw}}^* - a_{\text{vdw}}^*}{1 - [(a_{\text{vdw}}^*/b_{\text{vdw}}^*) + (1/C_1)((A_{\infty}^E/RT) - (A_{\infty \text{vdw}}^E/RT))]} \quad (2)$$

The C_1 in both Eqs. (1) and (2) is the constant and is defined as follows:

$$C_1 = -\frac{1}{(w-u)} \ln \left(\frac{1+w}{1+u} \right) \quad (3)$$

where u and w are equation of state dependent constants used to represent a particular two-parameter CEOS (for the SRK equation: $u = 0$, $w = 1$ and for the PR equation: $u = -0.4142$, $w = 2.4141$).

In Eqs. (1) and (2), A_{∞}^E is the excess Helmholtz energy at infinite pressure. The subscript van der Waals in $A_{\infty \text{vdw}}^E$ denotes properties evaluated from a CEOS using the van der Waals mixing rules for its a and b parameters. Twu–Coon mixing rules reduce to the van der Waals mixing rules, if A_{∞}^E equals to $A_{\infty \text{vdw}}^E$. As mentioned previously, it is desirable to have a mixing rule using the same Gibbs free energy expression that can reduce to the classical van der Waals one-fluid mixing rule.

It is worth mentioning that we use the excess Helmholtz energy A^E approach to derive Eqs. (1) and (2). The equations can also be expressed in terms of excess Gibbs energy G^E , where A^E and G^E are related in the development below. The Helmholtz energy departure function, ΔA , is related to the excess Helmholtz energy, A^E , and the departure functions of the pure components i , ΔA_i , at the same temperature, pressure, and composition by the equation

$$A^E = \Delta A - \sum_i^n x_i \Delta A_i \quad (4)$$

A similar relation to Eq. (4) is true for the Gibbs free energy

$$G^E = \Delta G - \sum_i^n x_i \Delta G_i \quad (5)$$

To relate the Helmholtz energy of Eq. (4) to the Gibbs energy of Eq. (5), the following relationship between the Helmholtz energy departure function, ΔA , and the Gibbs energy departure function, ΔG , are needed

$$\Delta A = \Delta G - RT(Z - 1) \quad (6)$$

Eqs. (4)–(6) provide the connection between excess Helmholtz energy and excess Gibbs energy. Subtracting Eq. (5) from Eq. (4) gives

$$A^E - G^E = \Delta A - \Delta G - \sum_i^n x_i (\Delta A_i - \Delta G_i) \quad (7)$$

Using Eq. (6) two times in Eq. (7), once for the mixture and once for the pure component i , we have

$$A^E = G^E - RT \left(Z - \sum_i^n x_i Z_i \right) \quad (8)$$

Applying Eq. (8) to a van der Waals fluid and then subtracting it from Eq. (8), we get

$$\frac{A^E}{RT} - \frac{A_{\text{vdw}}^E}{RT} = \frac{G^E}{RT} - \frac{G_{\text{vdw}}^E}{RT} + (Z - Z_{\text{vdw}}) \quad (9)$$

In the limit of infinite pressure, $P \rightarrow \infty$, v approaches b and v_{vdw} approaches b_{vdw} . Also Z becomes Z_{vdw} , if the van der Waals mixing rule b_{vdw} is used for the b parameter. The last two terms in Eq. (9) cancel out, so that we get

$$\frac{A_{\infty}^E}{RT} - \frac{A_{\infty \text{vdw}}^E}{RT} = \frac{G_{\infty}^E}{RT} - \frac{G_{\infty \text{vdw}}^E}{RT} \quad (10)$$

The above derivation shows that the approach of using the excess Gibbs energy requires the b parameter to be b_{vdw} while using the excess Helmholtz energy approach releases the equation of state b parameter from its traditional linear mixing rule. This shows that the excess Helmholtz energy approach is a more concise way in the development of mixing rules than the excess Gibbs energy approach.

Our current infinite pressure mixing rule model assumes constant (pressure-independent) excess Helmholtz free energy to permit the use of an appropriate G^E correlation at low temperatures into the mixing rule. Any G^E model, such as the NRTL equation, can then be directly incorporated into our mixing rules for phase equilibrium calculations. To correct the approximation that the excess Helmholtz free energy at infinite pressure equal the excess Gibbs free energy at low pressure, the binary interaction parameter, k_{ij} is introduced as:

$$a_{\text{vdw}} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (11)$$

The conventional linear mixing rule meanwhile is used for the van der Waals b parameter as follows:

$$b_{\text{vdw}} = \sum_i \sum_j x_i x_j \left[\frac{1}{2} (b_i + b_j) \right] \quad (12)$$

Eq. (11) assumes $k_{ij} = k_{ji}$. However, they are generally not equal. To improve the accuracy and reproduction of the incorporated G^E model, the asymmetric van der Waals mixing rule for the a_{vdw} parameter is required

$$a_{\text{vdw}} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) + \sum_i x_i \left[\sum_j x_j (a_i a_j)^{1/6} (k_{ji} - k_{ij})^{1/3} \right]^3 \quad (13)$$

Eq. (13) has two adjustable parameters, k_{ij} and k_{ji} . The use of an asymmetric definition of k_{ij} in the mixing rule of Eq. (13) is similar to the asymmetric A_{ij} in the G^E mixing rule of the NRTL model. The reason for using an asymmetric A_{ij} is that there are two infinite dilution activity coefficients per binary and two parameters are required to match exactly the two infinite dilution activity coefficients. Eq. (13) contains one more parameter than Eq. (11). However, as pointed out by Wong et al. [6], if these two parameters could be derived from reported parameters of the activity coefficient model instead of additional data or a correlation, then k_{ij} and k_{ji} in Eq. (13) require no additional data or regression. Eq. (13) essentially has the same number of adjustable parameters as Eq. (11). If $k_{ij} = k_{ji}$, Eq. (13) reduces to the conventional van der Waals mixing rule Eq. (11).

Eq. (2) satisfies the second virial coefficient constraint, but unfortunately it is temperature dependent. Alternatively, a temperature independent, linear mixing rule can be used for the equation of state parameter b as follows:

$$b = \sum_i \sum_j x_i x_j \left[\frac{1}{2} (b_i + b_j) \right] (1 - l_{ij}) \quad (14)$$

For the same reason as introducing k_{ij} , the binary interaction parameter l_{ij} is introduced in b to correct the assumption made for the excess Helmholtz free energy at infinite pressure. We will test Eq. (14) against Eq. (2) in the phase equilibrium calculations.

3. A new liquid activity model

We now consider a new model for the excess Gibbs energy that allows our mixing rule to reduce to the van der Waals one-fluid mixing rule. To do this we first examine the term $A_{\infty \text{vdw}}^E$ in both Eqs. (1) and (2).

$A_{\infty \text{vdw}}^E$ can be derived from the equation of state for a van der Waals fluid at infinite pressure

$$\frac{A_{\infty \text{vdw}}^E}{RT} = C_1 \left[\frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} - \sum_i x_i \frac{a_i^*}{b_i^*} \right] \quad (15)$$

The equations for a_{vdw} and b_{vdw} are given by Eqs. (11) and (12). For algebraic simplicity, we limit the following discussion to binary mixtures, we obtain the following expression for the excess Helmholtz energy of a van der Waals fluid:

$$\frac{A_{\infty \text{vdw}}^E}{RT} = \frac{x_1 x_2 b_1 b_2 \delta_{12}}{(x_1 b_1 + x_2 b_2)} \quad (16)$$

where δ_{12} is the characteristic parameter of interaction between molecules 1 and 2.

$$\delta_{12} = -\frac{C_1}{RT} \left[\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2 + 2k_{12} \frac{\sqrt{a_1}}{b_1} \frac{\sqrt{a_2}}{b_2} \right] \quad (17)$$

Extending these relations to a multi-component mixture, Eqs. (16) and (17) become

$$\frac{A_{\infty \text{vdw}}^E}{RT} = \frac{1}{2} \sum_i \sum_j (b \delta_{ij}) \phi_i \phi_j \quad (18)$$

$$\delta_{ij} = -\frac{C_1}{RT} \left[\left(\frac{\sqrt{a_i}}{b_i} - \frac{\sqrt{a_j}}{b_j} \right)^2 + 2k_{ij} \frac{\sqrt{a_i}}{b_i} \frac{\sqrt{a_j}}{b_j} \right] \quad (19)$$

$$\phi_i = \frac{x_i b_i}{b} \quad (20)$$

It is interesting to note that Eq. (18) is also related to Eq. (15). Eq. (18) is the result of a van der Waals fluid satisfying the van der Waals one-fluid mixing rules. Note we mentioned that the excess Helmholtz free energy at infinite pressure is approximated by the excess Gibbs free energy at low pressure. Consequently, if we propose an expression in our mixing rule for the excess Helmholtz (or Gibbs) energy which reduces to Eq. (18), we will obtain the conventional van der Waals fluid mixing rules.

A general multi-component equation for a liquid activity coefficient model is now proposed for incorporation in the infinite-pressure mixing rules as follows:

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j^n x_j \tau_{ji} G_{ji}}{\sum_k^n x_k G_{ki}} \quad (21)$$

Eq. (21) appears to be similar to the NRTL equation, but there is a fundamental difference between them. NRTL assumes A_{ij} , A_{ji} , and α_{ij} are the parameters of the model, but our excess Gibbs energy model assumes τ_{ij} and G_{ij} are the binary interaction parameters. More importantly, any appropriate temperature-dependent function can be applied to τ_{ij} and G_{ij} . For example, to obtain the NRTL model, τ_{ij} and G_{ij} are calculated as usual from the NRTL parameters A_{ij} , A_{ji} and α_{ij}

$$\tau_{ji} = \frac{A_{ji}}{T} \quad (22)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (23)$$

In this way, the NRTL parameters reported in the DECHEMA Chemistry Data Series can be used directly in our mixing rules, there is no difference between NRTL and our model in the prediction of phase equilibrium calculations.

We also note Eq. (21) can recover the conventional van der Waals mixing rules when the following expressions are used for τ_{ij} and G_{ij} :

$$\tau_{ji} = \frac{1}{2}\delta_{ij}b_i \quad (24)$$

$$G_{ji} = \frac{b_j}{b_i} \quad (25)$$

Eqs. (24) and (25) are expressed in terms of CEOS parameters, a_i and b_i and the binary interaction parameter k_{ij} . Substituting Eqs. (24) and (25) into Eq. (21), Eq. (18) is thus obtained and subsequently our mixing rules (1) and (2), reduce to the classical van der Waals one-fluid mixing rules. The discussion above demonstrates that Eq. (21) is more generic in form than NRTL. Both the NRTL and van der Waals fluid parameters are special cases of our excess Gibbs free energy function.

It is important to emphasize that both van der Waals fluids and highly non-ideal mixtures can now be described by the same Gibbs excess energy model proposed here. More significantly, multi-component mixtures containing both types of binaries can be described in a unified framework. We can choose the appropriate expressions for τ_{ij} and G_{ij} from Eqs. (24) and (25) for binary pairs which are best described by van der Waals one-fluid mixing rules, while Eqs. (22) and (23) can be used for pairs which behave non-ideally. Therefore, the activity model is able to describe systems ranging from mixtures of simple hydrocarbons to highly non-ideal mixtures of organic chemicals and water over a broad range of temperatures and pressures in a consistent and unified framework.

4. Results

We have chosen the Twu et al. [7] form of the SRK CEOS and our activity model Eq. (21) here for illustration purposes. The equation for parameter a is a function of temperature. The value of $a(T)$ at temperatures other than the critical temperature can be calculated from

$$a(T) = \alpha(T)a_c \quad (26)$$

where the α function, $\alpha(T)$, is a function only of reduced temperature, $T_r = T/T_c$. We use the α correlation of Twu et al. [7]

$$\alpha(T) = T_r^{N(M-1)} e^{L(1-T_r^{NM})} \quad (27)$$

Eq. (27) 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. 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 for use with the SRK equation.

We want to investigate the impact of using different mixing rules for b parameter on phase equilibrium calculations. Since the Wong–Sandler (WS(b)) mixing rule has been shown to have exceptional success in phase equilibrium calculations, their mixing rule is selected and compared with ours. We label Eqs. (1), (2), (12), (13) and (21) the Twu–Sim–Tassone (TST(b)) mixing rule and label Eqs. (1), (14) and (21) the

Table 1
 L , M , and N parameters of Twu α function with the SRK CEOS

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

Twu–Sim–Tassone ($TST(b_{vdw})$) mixing rule. The ‘ (b) ’ in $WS(b)$ and $TST(b)$ indicates that the mixing rule satisfies the second virial coefficient constraint but is temperature dependent. The ‘ (b_{vdw}) ’ in $TST(b_{vdw})$ indicates that the temperature-independent van der Waals mixing rule b_{vdw} is used for the b parameter. It is worth noting that the Wong–Sandler mixing rule $WS(b)$ is a special case of our mixing rule $TST(b)$.

We have considered 12 highly non-ideal binary mixtures, which are traditionally described by liquid activity models. They are listed in Table 2. Since our mixing rule exactly reduces to the van der Waals one-fluid mixing rule, none of our tests are for mixtures of hydrocarbons that are known to be adequately described by that model. We will use only the activity coefficient parameters at the lowest isothermal temperature to predict high-pressure phase behavior for these non-ideal systems. Table 2 gives the values of these NRTL binary interaction parameters for these systems. The accuracy of reproducing the activity coefficients of component i , γ_i (%) in terms of average absolute deviation percentage (AAD%), from $WS(b)$, $TST(b)$ and $TST(b_{vdw})$ mixing rules is given in Table 2. Similarly, the accuracy of VLE predictions from these three mixing rules, which is also in terms of AAD% in the bubble point pressure and the K -values of component 1 and 2, is also presented in Table 2.

Examining the accuracy of reproducing activity coefficients as given in Table 2 shows that the result of reproducing G^E model behavior from the Wong–Sandler mixing rule is good, but in general is still not quite accurate enough. On the other hand, our mixing rule $TST(b)$ improves significantly the accuracy of reproducing activity coefficients over $WS(b)$ for almost all cases. Our model, $TST(b_{vdw})$, without temperature dependency, reproduces the G^E model behavior with similar accuracy as when using $WS(b)$.

The three mixing rules are also compared in the calculations of VLE. The binary interaction parameters, k_{ij} or l_{ij} , are derived from information obtained from the NRTL model itself. When the parameters are derived from the excess free energy model, the mixing rules can be considered containing the same number of parameters as the incorporated liquid activity coefficient model. Table 2 gives the results of binary interaction parameters for each binary and the accuracy of the prediction. Comparing the results shown in Table 2 indicate that all three mixing rules produce similarly high accuracy in predicting data covering wide ranges of temperature and pressure in the bubble point pressure and K -values of components for highly non-ideal systems.

The results also show that the mixing rule either with or without second virial coefficient condition constraint yields almost identical results. The second virial coefficient constraint has little effect on the phase equilibrium prediction. Theoretically, it would be nice to have a mixing rule that satisfies the

Table 2

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

Mixing rule	k_{12}	k_{21}	l_{12}	γ_1 (%)	γ_2 (%)	P (%)	K_1 (%)	K_2 (%)
Acetone(1)/water(2) from 100 to 250°C; I/1a/194 ($A_{12} = 68.4849$, $A_{21} = 746.618$, $\alpha_{12} = 0.2862$ at 100°C) ^a								
WS(b)	0.2751		2.98	4.17	3.01	4.44	3.31	
TST(b)	0.1412	0.2616		0.62	0.69	1.95	5.58	4.08
TST(b_{vdw})			0.3578	5.09	7.34	4.37	4.29	4.43
Ethanol(1)/ <i>n</i> -heptane(2) from 30.12 to 70.02°C; I/2e/377, 379; I/2c/457, 458 ($A_{12} = 521.746$, $A_{21} = 727.003$, $\alpha_{12} = 0.4598$ at 30.12°C) ^a								
WS(b)	0.3368			10.13	5.69	3.21	3.90	5.56
TST(b)	0.4812	0.1931		4.47	3.34	2.18	2.59	5.02
TST(b_{vdw})			0.2623	6.59	4.05	1.82	2.20	3.21
<i>n</i> -Pentane(1)/acetone(2) from –35 to 25°C; I/3 + 4/188, 189, 190 ($A_{12} = 485.086$, $A_{21} = 483.326$, $\alpha_{12} = 0.4683$ at –35°C) ^a								
WS(b)	0.2288			1.73	3.30	5.28	4.47	5.99
TST(b)	0.1882	0.2446		2.08	2.23	5.53	4.14	5.82
TST(b_{vdw})			0.1308	1.27	2.11	5.45	4.80	5.94
Ethanol(1)/water(2) from 24.99 to 120°C; I/1b/93, 106, 107, 108 ($A_{12} = 13.3878$, $A_{21} = 437.683$, $\alpha_{12} = 0.2945$ at 24.99°C) ^a								
WS(b)	0.2308			2.34	3.10	3.51	5.45	4.09
TST(b)	0.1202	0.2141		0.31	0.34	3.37	6.11	4.37
TST(b_{vdw})			0.2576	2.83	3.91	4.95	6.83	5.38
Methanol(1)/cyclohexane(2) from 25 to 55°C; I/2a/242; I/2c/208, 209 ($A_{12} = 644.886$, $A_{21} = 784.966$, $\alpha_{12} = 0.4231$ at 25°C) ^a								
WS(b)	0.3593			10.01	5.25	4.05	4.31	6.07
TST(b)	0.4893	0.2260		4.98	3.84	2.08	2.94	4.39
TST(b_{vdw})			0.2590	6.19	3.61	2.50	2.76	4.06
Methanol(1)/benzene(2) from 25 to 90°C; I/2c/188; I/2a/207, 210, 216, 217, 228 ($A_{12} = 441.228$, $A_{21} = 738.702$, $\alpha_{12} = 0.5139$ at 25°C) ^a								
WS(b)	0.2812			8.42	4.53	1.99	2.90	3.87
TST(b)	0.3925	0.1699		4.18	3.08	2.77	4.51	3.85
TST(b_{vdw})			0.1927	4.87	2.90	1.35	2.80	2.90
Acetone(1)/benzene(2) from 25 to 45°C; I/3 + 4/194, 203, 208 ($A_{12} = -35.4443$, $A_{21} = 193.289$, $\alpha_{12} = 0.3029$ at 25°C) ^a								
WS(b)	0.0567			0.50	0.45	0.82	1.06	1.84
TST(b)	0.0577	0.0428		0.04	0.04	0.79	1.01	1.63
TST(b_{vdw})			0.0266	0.16	0.15	0.80	1.03	1.69
Acetone(1)/ethanol(2) from 32 to 48°C; I/2a/323, 324, 325 ($A_{12} = 24.3880$, $A_{21} = 224.395$, $\alpha_{12} = 0.3007$ at 32°C) ^a								
WS(b)	0.0683			0.06	0.08	1.16	0.86	1.67
TST(b)	0.0616	0.0635		0.04	0.04	1.15	0.86	1.68
TST(b_{vdw})			0.0500	0.26	0.29	1.24	0.94	1.71

Table 2 (Continued)

Mixing rule	k_{12}	k_{21}	l_{12}	γ_1 (%)	γ_2 (%)	P (%)	K_1 (%)	K_2 (%)
Acetone(1)/methanol(2) from 45 to 55°C; I/2a/75, 80, 81 ($A_{12} = 31.5237$, $A_{21} = 180.554$, $\alpha_{12} = 0.3004$ at 45°C) ^a								
WS(b)	0.1052			0.86	1.02	0.86	1.15	1.47
TST(b)	0.0667	0.0969		0.08	0.09	0.73	0.89	0.97
TST(b_{vdw})			0.1012	0.84	1.01	0.84	1.15	1.45
Ethanol(1)/benzene(2) from 25 to 55°C; I/2a/398, 407, 415, 417, 418, 421, 422 ($A_{12} = 115.954$, $A_{21} = 584.473$, $\alpha_{12} = 0.2904$ at 25°C) ^a								
WS(b)	0.1941			4.90	3.64	2.26	5.22	3.06
TST(b)	0.2615	0.1230		1.06	0.90	1.44	3.83	2.98
TST(b_{vdw})			0.1179	2.87	2.22	1.65	4.13	2.63
Methanol(1)/water(2) from 24.99 to 100°C; I/1b/29; I/1/41, 49, 72, 73 ($A_{12} = -23.1150$, $A_{21} = 188.147$, $\alpha_{12} = 0.3022$ at 24.99°C) ^a								
WS(b)	0.0745			0.37	0.42	2.58	4.03	4.29
TST(b)	0.0326	0.0457		0.01	0.01	2.63	4.21	4.35
TST(b_{vdw})			0.1374	1.00	1.23	2.93	4.44	5.09
Methanol(1)/ <i>n</i> -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) ^a								
WS(b)	0.3954			11.95	5.61	5.20	5.98	5.08
TST(b)	0.5395	0.2406		7.11	5.37	2.78	3.38	2.94
TST(b_{vdw})			0.3190	8.34	4.55	3.77	4.41	3.80

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

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. It will not only predict the same quality of phase behavior, but also avoid any potential problems in the prediction of other thermodynamic properties at extremely high pressures.

5. Conclusions

It is extremely desirable to have a mixing rule that incorporates an excess Gibbs energy expression which transitions smoothly to the conventional van der Waals one-fluid mixing rules. This is important because the same mixing rule can be applied to all binaries, whether components are polars, non-polars, inorganic gases, or any combination of these. A new class of excess Gibbs free energy function is proposed in this work for this purpose. The incorporation of the proposed new excess Gibbs free energy function into a CEOS allows the CEOS/ A^E mixing rule to smoothly transition to the classical van der Waals one-fluid mixing rules. We demonstrate that the CEOS with the proposed excess Gibbs energy mixing rules can be applied with high accuracy to the prediction of phase equilibria using available parameters for the liquid activity coefficient model. Subsequent work will present a new excess Gibbs energy function for zero-pressure mixing rules.

List of symbols

a, b	cubic equation of state parameters
a^*, b^*	defined as Pa/R^2T^2 and Pb/RT , respectively
A	Helmholtz energy
C_1	constant at infinite pressure as defined in Eq. (3)
G	Gibbs energy
k_{ij}	binary interaction parameter
K_i	K -value of component i defined as y_i/x_i
L, M, N	parameters in the Twu's α function
P	pressure
R	gas constant
T	temperature
u, w	cubic equation of state constants
x_i	mole fraction of component i
Z	compressibility factor

Greek letters

α	cubic equation of state α function
δ_{ij}	characteristic of the interaction between molecules i and j
ϕ_i	volume fraction of component i as defined in Eq. (20)

Subscripts

∞	infinite pressure
i, j	property of component i, j
ij	interaction property between components i and j
vdw	van der Waals

Superscripts

*	reduced property
E	excess property

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