A Zero-Pressure Cubic Equation of State Mixing Rule for Predicting High Pressure Phase Equilibria Using Infinite Dilution Activity Coefficients at Low Temperature

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Abstract

The infinite dilution activity coefficients (γ_i^∞) of a solute in a solvent are important data in process separation calculations. These values reflect the degree of non-ideal solution behavior of the solute in the solvent. This paper investigates the use of infinite dilution activity coefficients in cubic equation of state mixing rules for the prediction of phase behavior at high pressures. A mixing rule recently developed by Twu and Coon (CEOS/A^E Mixing Rules Constrained by the vdW Mixing Rule and the Second Virial Coefficient, AIChE J., 42 (1996) 3212-3222) has been extended from infinite pressure to zero pressure. The methodology for extending the infinite-pressure Twu-Coon mixing rule was developed so that the zero-pressure Twu-Coon mixing rule reproduces the excess Gibbs free energy, as well as liquid activity coefficients of any activity models, with extremely high accuracy without requiring any additional binary interaction parameters. We compare the performance of this new mixing rule with the MHV1 and Wong-Sandler mixing rules for its ability to use γ_i^∞ in the prediction of high pressure phase behavior for strongly non-ideal systems.

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Introduction

The application of any cubic equation of state to systems containing highly non-ideal components requires an appropriate mixing rule for the equation of state parameter *a*. Huron and Vidal [1] pioneered linking the equation of state parameter *a* to the excess Gibbs free energy at infinite pressure. However, their mixing rule has not become widely used because the available excess Gibbs energy parameters at low pressure cannot be used in their mixing rule.

Because of that, several authors have proposed different approaches to use directly the existing liquid activity model parameters in equations of state. Among them, two models have been quite successful. One is a zero-pressure model by Michelsen [2] and Dahl and Michelsen [3] and the other is an infinite-pressure model by Wong and Sandler [4]. Both models can directly use available activity coefficient model parameters from low-pressure data in their mixing rules for predicting phase equilibria at high temperatures and pressures quite successfully. However, neither the zero-pressure model nor the infinite-pressure model can reproduce accurately the G^E model with which it is combined (Coutsikos et al. [5], Kalospiro et al. [6]).

A methodology has been developed to extend the infinite-pressure Twu-Coon mixing rule [7] to correctly reproduce the incorporated G^E model without introducing any additional parameters. Due to this capability, the available activity coefficient models at low pressure can be used directly in this new mixing rule. The activity model requires binary interaction parameters which are usually regressed from binary phase equilibrium data. Reliable VLE data are sometimes, however, not available for the system of interest. In that case, the activity

model parameters can be determined from γ_i^∞. Owing to a number of new techniques investigated in recent years, γ_i^∞ can be measured accurately and inexpensively. If the γ_i^∞ data are not available, group contribution methods such as UNIFAC can be used to estimate the necessary values. The γ_i^∞ can then be used to generate the parameters for the activity model, which then can be incorporated into the mixing rule for the calculation of real solution behavior over the whole composition range.

We compare the performance of the Wilson activity model on the prediction of phase equilibria for non-ideal mixtures using two γ_i^∞ in our new mixing rule, MHV1, and Wong-Sandler.

CEOS/A^E Mixing Rule

A two-parameter cubic equation of state is considered here:

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

where P is the pressure, T is the absolute temperature, and v is the molar volume. The constants u and w are equation of state dependent (for the Soave-Redlich-Kwong equation [8]: $u=0$, $w=1$). The parameter a in eqn.(1) 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, a_c, can be calculated from

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

The alpha function, $\mathrm{a}(T)$ in eqn.(2), 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 have chosen to use the alpha correlation of Twu et al. [9]:

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

Eqn.(3) has three parameters, L, M, and N which are unique to each component and are determined from the regression of pure component vapor pressure data. The values for the components used in this study are given in Table 1.

Twu and Coon [7] have related the excess Helmholtz free energy, A^E, with respect to a van der Waals fluid to the Helmholtz free energy departure function, ΔA, by the following:

$$A^E - A^E_{vdw} = \Delta A - \Delta A_{vdw} \tag{4}$$

Eqn.(4) was used by Twu and Coon [7] to derive the following mixing rule for the cubic equation of state mixture a and b parameters at infinite pressure:

$$\frac{A^E_\infty}{RT} - \frac{A^E_{\infty vdw}}{RT} = C_1\left(\frac{a^*}{b^*} - \frac{a^*_{vdw}}{b^*_{vdw}}\right) \tag{5}$$

with the C_1, a_{vdw} and b_{vdw} being:

$$C_1 = -\frac{1}{(w-u)}\ln\left(\frac{1+w}{1+u}\right) \tag{6}$$

$$a_{vdw} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \tag{7}$$

$$b_{vdw} = \sum_i \sum_j x_i x_j \left[\frac{1}{2}(b_i + b_j)\right] \tag{8}$$

$A^E_{¥}$ and $A^E_{¥vdw}$ in eqn.(5) 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 eqn.(4) is applied at zero pressure, instead of infinite pressure, an equation containing liquid volume is obtained:

$$\frac{A_0^E}{RT} - \frac{A_{0vdw}^E}{RT} = \ln\left[\left(\frac{v_{0vdw}^* - 1}{v_0^* - 1}\right)\left(\frac{b_{vdw}}{b}\right)\right] - \frac{1}{(w-u)}\left[\frac{a^*}{b^*}\ln\left(\frac{v_0^* + w}{v_0^* + u}\right) - \frac{a_{vdw}^*}{b_{vdw}^*}\ln\left(\frac{v_{0vdw}^* + w}{v_{0vdw}^* + u}\right)\right] \tag{9}$$

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 eqn.(1) by setting pressure equal to zero and selecting the smallest root:

$$v_0^* = \frac{1}{2}\left\{\left(\frac{a^*}{b^*} - u - w\right) - \left[\left(u + w - \frac{a^*}{b^*}\right)^2 - 4\left(uw + \frac{a^*}{b^*}\right)\right]^{\frac{1}{2}}\right\} \tag{10}$$

Eqn.(10) has a root as long as

$$\frac{a^*}{b^*} \geq (2 + u + w) + 2\sqrt{(u+1)(w+1)} \tag{11}$$

Eqns.(9) and (10) 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 eqns.(9) and (10), the exact model does not permit explicit solution of eqn.(9) for a^*/b^* and an iterative technique is required for the solution. If eqns.(9) and (10) 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 [2]; Dahl and Michelsen [3]). 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 [2] 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 eqn.(10). 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 model performs 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, $v_{0\,vdw}^*$. Using eqns.(7) and (8) for the parameters *a* and *b* in eqn.(10), $v_{0\,vdw}^*$ can be readily calculated from the equation. Eqn.(10) is used to calculate $v_{0\,vdw}^*$ for both the mixture and the pure components. Eqn.(9) can then be simplified to

$$\frac{A_0^E}{RT} - \frac{A_{0vdw}^E}{RT} = \ln\left(\frac{b_{vdw}}{b}\right) + C_{v_0}\left[\frac{a^*}{b^*} - \frac{a_{vdw}^*}{b_{vdw}^*}\right] \tag{12}$$

with the constant C_{v0} being:

$$C_{v_0} = -\frac{1}{(w-u)} \ln\left(\frac{v_0^* + w}{v_0^* + u}\right)_{vdw} \tag{13}$$

Since the equation of state parameters, a and b, are pressure independent, these two parameters can be canceled out from eqns.(5) and (12) to give the inter-relationship of A^E between infinite pressure and zero pressure as:

$$\frac{A_\infty^E}{RT} - \frac{A_{\infty vdw}^E}{RT} = \frac{C_1}{C_{v_0}}\left[\frac{A_0^E}{RT} - \frac{A_{0vdw}^E}{RT} - \ln\left(\frac{b_{vdw}}{b}\right)\right] \tag{14}$$

Substituting eqn.(14) into the mixing rule proposed by Twu and Coon [7] results in a new and explicit mixing rule in terms of A^E_0 at zero pressure:

$$b^* = \frac{b_{vdw}^* - a_{vdw}^*}{1 - \left[\frac{a_{vdw}^*}{b_{vdw}^*} + \frac{1}{C_{v_0}}\left(\frac{A_0^E}{RT} - \frac{A_{0vdw}^E}{RT} - \ln\left(\frac{b_{vdw}}{b}\right)\right)\right]} \tag{15}$$

$$a^* = b^*\left[\frac{a_{vdw}^*}{b_{vdw}^*} + \frac{1}{C_{v_0}}\left(\frac{A_0^E}{RT} - \frac{A_{0vdw}^E}{RT} - \ln\left(\frac{b_{vdw}}{b}\right)\right)\right] \tag{16}$$

As mentioned above, $A_0^E{}_{vdw}$ in eqns.(15) and (16) 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, as given in eqns.(7) and (8). The zero pressure volume $v_0^*{}_{vdw}=v_{0vdw}/b$ is obtained from eqn.(10) by substituting a_{vdw} and b_{vdw} for the a and b parameters.

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 $A_0^E{}_{vdw}$. The mixing rule satisfies the quadratic composition dependence of the second virial coefficient boundary condition. The most

important aspect 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.

Incorporation of the Wilson Activity Model into the New Mixing Rule

Since A_0^E in eqns.(15) and (16) is at zero pressure, its value is identical to the excess Gibbs free energy G^E. Therefore, any activity model such as the Wilson equation can be used directly for the excess Helmholtz free energy expression A_0^E in these two equations.

For a solution of *n* components, Wilson's equation is:

$$\frac{G^E}{RT} = -\sum_i^n x_i \ln\left[\sum_j^n x_j \Lambda_{ij}\right] \tag{17}$$

where

$$\Lambda_{ij} = \left(\frac{v_j}{v_i}\right) exp\left(-A_{ij}/T\right) \tag{18}$$

and T is temperature in kelvin. In Wilson's derivation, G^E is related to the pure-component molar volume v_i, which is listed in Table 1. Wilson's equation has two adjustable parameters, A_{ij} and A_{ji}. These two adjustable parameters per binary pair can be uniquely determined from two infinite dilution activity coefficients.

These values of A_{ij} and A_{ji} are then used at all temperatures. Table 2 gives the values of these Wilson binary interaction parameters converted from the γ_i^∞ for the selected systems. In this work, we have considered eight binary highly non-ideal mixtures which are traditionally described by liquid activity models. They are listed in Table 2. In order to obtain liquid-like values for v_0^* at zero pressure from eqn.(10), 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 as given by eqn.(11).

The mixing rule for the parameter *b* as given by eqn.(15) 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):

$$b = \sum_i \sum_j x_i x_j \left[\frac{1}{2} \left(b_i + b_j \right) \right] \tag{19}$$

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 [2]) and the mixing rule proposed by Wong and Sandler [4]. 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:

$$A^E(T, x, P=¥) = A^E(T, x, P=low) = G^E(T, x, P=low) \tag{20}$$

The Wong-Sandler approximation will be tested in this comparison to see how well the assumption in eqn.(20) 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 (eqns.15 and 16), and 'TCB(0)' to eqns.(16) and (19). The zero in the TCB parenthesis means no second virial coefficient constraint. The accuracy of reproducing the activity coefficients of component *i*, g_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 component 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, closely reproduces 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 [2]. It is not surprising that if the liquid volume of the system is not close to the fixed constant, the G^E model is not reproduced by the equation of state using the MHV1 mixing rule. These results are in agreement with a statement by Kalospiro et al. [7], although we have a different explanation for it. The results shown in Table 2 illustrate that our new mixing rule reproduces the G^E model almost exactly. The errors in the reproduction of the activity coefficients for these systems are minimal from our mixing rule.

For VLE predictions, our new mixing rule gives consistent results and in general provides good agreement between the experimental data and the predictions over a wide range of temperatures and pressures using only information on the infinite dilution activity coefficients. It was somewhat surprising that good agreement was also obtained from MHV1, although it

cannot reproduce accurately the incorporated liquid activity coefficients. This unexpected result from MHV1 might come from some mutual cancellation of errors, but we do not know at this time. Again, the worst predictions are obtained from the Wong-Sandler mixing rule because of its inability to match the G^E model.

Finally, as we mentioned, we want to investigate the impact on phase equilibrium prediction of the mixing rule with and without the second virial coefficient condition constraint. Reviewing the results shown in Table 2, they show that our mixing rule yields almost identical results either with or without second virial coefficient condition constraint. 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.

Conclusion

This work shows that the γ_i^∞ are useful for the calculation of real solution behavior over the whole composition range. The Wilson equation with the two parameters determined from two infinite dilution activity coefficients adequately represents the vapor-liquid equilibria for the entire composition range.

We have successfully extended the Twu-Coon Mixing Rule from infinite pressure to zero pressure. We have demonstrated 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 models do not reproduce exactly the G^E models at low pressure and reveal that

approximate reproduction is feasible for MHV1 only for systems with liquid volumes close to the assumed constant value. On the other hand, the new model we developed in this work accurately reproduces the activity coefficients of the G^E model.

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Table 1

The *L*, *M*, and *N* parameters of the temperature-dependent a function given by eqn.(3) for pure components used with the SRK cubic equation of state and their molar volumes

Component	T_c(K)	P_c(bar)	L	M	N	*v*(cc/mol)
n-pentane	469.70	33.70	0.379229	0.841706	1.82331	116.10
n-hexane	507.85	30.31	0.158080	0.872819	3.84418	131.79
n-heptane	540.16	27.36	0.340339	0.844963	2.38332	147.58
cyclohexane	553.58	40.73	0.245880	0.845046	2.25895	108.74
benzene	562.16	48.98	0.163664	0.860016	2.98498	89.33
acetone	508.20	47.01	0.479844	0.870627	1.79010	74.06
methanol	512.64	80.97	0.690551	0.911298	1.96941	40.80
ethanol	513.92	61.48	1.07646	0.964661	1.35369	58.78
water	647.13	220.55	0.413297	0.874988	2.19435	18.14

Table 2
Wilson Interaction Parameters and Results of the Prediction in terms of Average Absolute Deviation Percentage (AAD%) in Activity Coefficients, Bubble point Pressure and K-values

[a]ethanol(1)/n-heptane(2) from 30.12 to 70.02 C; I/2e/377, 379; I/2c/457, 458

A_{12}=1000.13, A_{21}=208.890 (g_1^{∞} = 23.98, g_2^{∞} = 12.39)

mixing rule	γ_1(%)	γ_2(%)	P(%)	k_1(%)	k_2(%)
WS	17.81	16.35	12.32	9.76	18.60
MHV1	3.41	3.76	1.10	1.07	1.86
TCB	0.10	0.05	0.91	1.07	1.65
TCB(0)	0.07	0.04	0.89	1.09	1.68

[a]methanol(1)/cyclohexane(2) from 25 to 55 C; I/2a/242; I/2c/208, 209

A_{12}=1073.87, A_{21}=333.799 (g_1^{∞} = 33.08, g_2^{∞} = 20.64)

mixing rule	γ_1(%)	γ_2(%)	P(%)	k_1(%)	k_2(%)
WS	17.02	15.11	15.46	12.32	18.33
MHV1	3.15	3.59	3.33	2.49	3.42
TCB	0.17	0.13	4.21	3.08	4.20
TCB(0)	0.13	0.10	4.23	3.03	4.15

[a] methanol(1)/benzene(2) from 25 to 90 C; I/2c/188; I/2a/207,210,216,217,228

A_{12}=965.095, A_{21}=141.820 (g_1^{∞} = 23.79, g_2^{∞} = 8.79)

mixing rule	γ_1(%)	γ_2(%)	P(%)	k_1(%)	k_2(%)
WS	15.70	13.46	9.27	9.53	9.65
MHV1	3.04	2.90	4.23	6.10	5.08
TCB	0.18	0.14	3.55	5.23	4.32
TCB(0)	0.14	0.11	3.51	5.25	4.31

[a] acetone(1)/benzene(2) from 25 to 45 C; I/3+4/194, 203, 208

A_{12}=208.602, A_{21}=-52.0233 (g_1^{∞} = 1.69, g_2^{∞} = 1.51)

mixing rule	γ_1(%)	γ_2(%)	P(%)	k_1(%)	k_2(%)
WS	3.65	3.66	2.34	2.03	4.04
MHV1	0.73	0.58	0.83	1.06	1.73
TCB	0.01	0.01	1.03	1.03	1.71
TCB(0)	0.01	0.01	0.78	1.03	1.71

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

Table 2(continued)
Wilson Interaction Parameters and Results of the Prediction in terms of Average Absolute Deviation Percentage (AAD%) in Activity Coefficients, Bubble point Pressure and K-values

acetone(1)/ethanol(2) from 32 to 48 C; I/2a/323, 324, 325

A_{12}=121.982, A_{21}=132.022 (g_1^{∞} = 2.26, g_2^{∞} = 1.95)

mixing rule	γ_1(%)	γ_2(%)	P(%)	k_1(%)	k_2(%)
WS	4.25	4.26	3.17	2.71	2.34
MHV1	1.75	1.37	1.34	1.78	2.49
TCB	0.01	0.01	1.23	0.83	1.58
TCB(0)	0.01	0.01	1.23	0.83	1.57

[a] acetone(1)/methanol(2) from 45 to 55 C; I/2a/75, 80, 81

A_{12}=-33.5257, A_{21}=250.052 (g_1^{∞} = 1.94, g_2^{∞} = 1.78)

mixing rule	γ_1(%)	γ_2(%)	P(%)	k_1(%)	k_2(%)
WS	3.11	3.62	2.39	2.50	3.44
MHV1	0.74	0.45	0.65	1.01	0.96
TCB	0.00	0.00	0.71	0.95	1.00
TCB(0)	0.00	0.00	0.71	0.95	1.00

[a]ethanol(1)/benzene(2) from 25 to 55 C; I/2a/398, 407, 415, 417, 418, 421, 422

A_{12}=668.863, A_{21}=71.8375 (g_1^{∞} = 10.05, g_2^{∞} = 4.47)

mixing rule	γ_1(%)	γ_2(%)	P(%)	k_1(%)	k_2(%)
WS	12.40	10.33	10.72	13.42	10.50
MHV1	2.62	2.60	2.60	4.26	3.13
TCB	0.13	0.10	3.40	4.84	3.73
TCB(0)	0.10	0.08	3.41	4.83	3.72

[a]methanol(1)/n-hexane(2) from 25 to 45 C; I/2c/219; I/2a/252

A_{12}=1166.31, A_{21}=438.080 (g_1^{∞} = 39.17, g_2^{∞} = 35.78)

mixing rule	γ_1(%)	γ_2(%)	P(%)	k_1(%)	k_2(%)
WS	17.18	14.37	16.49	20.77	19.05
MHV1	2.44	4.06	2.72	2.72	2.53
TCB	0.11	0.05	2.40	3.93	3.64
TCB(0)	0.09	0.04	2.45	3.94	3.65

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