

# Reformulation of Wong-Sandler Mixing Rule for Cubic Equations of State

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*The cubic equation of state mixing rule of Wong and Sandler is reformulated in a way that eliminates one of its parameters and so that it can go smoothly from activity coefficient-like behavior to the classical van der Waals one-fluid mixing rule merely by variation of its parameters. The parameters in the reformulated mixing rule can be obtained from correlation of vapor-liquid equilibrium data or from the two infinite dilution activity coefficients for each binary pair in the mixture. When these activity coefficients are estimated from the UNIFAC group contribution model, the mixing rule becomes completely predictive. The correlative and completely predictive forms of this mixing rule are tested here and shown to be accurate for five difficult binary systems and one ternary mixture over large ranges of temperature and pressure.*

## Introduction

The estimation of the equilibrium phase behavior of complex mixtures over broad ranges of temperature and pressure is an important problem in chemical process design. Equations of state are powerful tools for addressing this problem. In particular, cubic equations are widely used due to their algebraic simplicity and, in many cases, their accuracy. There are two requirements for these equations to be successful: they must predict the saturation pressure of pure substances accurately, and mixing rules must be available that correctly extend these equations to multicomponent mixtures.

There has been significant improvement in the accuracy of cubic equations of state for the prediction of pure component properties in the last two decades (Sandler et al., 1993). The extension of equations of state to describe phase behavior for a broad range of multicomponent mixtures had been more difficult due to limited applicability of the van der Waals (vdW) one-fluid mixing and combining rules that are commonly used

where

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

Here  $a_i$  and  $b_i$  are the pure component parameters in the cubic equation of state, and  $k_{ij}$  is the concentration-independent binary interaction parameter usually obtained from correlation.

In 1992 Wong and Sandler introduced a mixing rule that provides a theoretically correct connection between equations of state and the excess-free-energy (activity coefficient) models and allows the correlation of vapor-liquid equilibrium data for a wide variety of mixtures over large ranges of pressure and temperature. It was found that with this mixing rule the excess-free-energy (activity coefficient) parameters available in the DECHEMA Chemistry Data Series tables (DECHEMA, 1977) obtained from low pressure data could be used directly for the prediction of phase behavior at much higher temperatures and pressures (Wong et al., 1992). Also it has been shown (Orbey et al., 1993) that the UNIFAC group contribution model (Fredenslund et al., 1975) could be combined with this new mixing rule for the accurate prediction of

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad \text{and} \quad b_m = \sum_i \sum_j x_i x_j b_{ij} \quad (1)$$

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high temperature, high pressure phase behavior, thereby removing the low pressure restriction from the UNIFAC and other group contribution models.

In the Wong-Sandler (1992) rule the basic equations (which we leave unchanged here) for the mixture parameters of an equation of state,  $a_m$  and  $b_m$ , are

$$b_m = \frac{\sum \sum x_i x_j \left( b - \frac{a}{RT} \right)_{ij}}{1 - \frac{A^E}{CRT} - \sum x_i \frac{a_i}{RTb_i}} \quad (3a)$$

and

$$\frac{a_m}{b_m} = \sum x_i \frac{a_i}{b_i} + \frac{A^E}{C}, \quad (4a)$$

which, for later reference, we note can also be written as

$$b_m - \frac{a_m}{RT} = \sum_i \sum_j x_i x_j \left( b - \frac{a}{RT} \right)_{ij} \quad (3b)$$

and

$$\frac{A^E}{C} = \frac{a_m}{b_m} - \sum_i x_i \frac{a_i}{b_i}, \quad (4b)$$

where  $A^E$  is a Helmholtz excess-free-energy term,  $a$  and  $b$  are equation-of-state parameters,  $R$  is the gas constant,  $T$  is absolute temperature, and  $C$  is a constant dependent on the equation of state selected;  $(1/\sqrt{2})\ln(\sqrt{2}-1) = -0.62323$  for the modified Peng-Robinson (Stryjek and Vera, 1986) equation used here. The parameters in this mixing rule are those of the excess-free-energy model,  $A^E$ , and the binary interaction parameter  $k_{ij}$

$$\left( b - \frac{a}{RT} \right)_{ij} = \frac{\left[ \left( b - \frac{a}{RT} \right)_i + \left( b - \frac{a}{RT} \right)_j \right]}{2} (1 - k_{ij}). \quad (5)$$

Since this mixing and combining rule was introduced, the nature of its parameters has been the focus of interest and some confusion. The role of those that come from the excess-free-energy model is clear. The binary interaction parameter was first thought of as an independent parameter associated with the second virial coefficient. In subsequent studies (Wong et al., 1992; Orbey et al., 1993), we found that  $k_{ij}$  could also be obtained from excess-free-energy-model parameters and therefore does not contain any additional information. This observation suggests that with a suitable reformulation, this parameter could be eliminated, which we do here.

A desirable characteristic of a mixing rule that includes an excess-free-energy expression is that it go smoothly to the conventional vdW one-fluid mixing rules for some values of its parameters. This is useful because in multicomponent mixtures it frequently occurs that only some of the binary

pairs form highly nonideal mixtures requiring mixing rules such as those described earlier, while other binary pairs in the same mixture can be adequately described by the classical vdW one-fluid mixing rule. Therefore, it is advantageous to have a mixing rule using a single free-energy expression that with a suitable selection of its parameters can reduce to the conventional van der Waals one-fluid mixing rule.

Here, while leaving the basic equations (Eqs. 3a and 4a) unchanged, we slightly reformulate other aspects of the Wong-Sandler mixing rule to address both these issues. The new mixing rule contains two parameters instead of three (if a two-parameter activity coefficient model is used for  $A^E$ ), and with a suitable choice of parameters it reduces to the classical vdW one-fluid mixing rule. We also show that the parameters in the mixing rule can be obtained in a number of ways, including correlation, prediction, or determination from the two infinite dilution activity coefficients for each pair of components. When infinite dilution activity coefficients are obtained from a model such as UNIFAC, the mixing rule is completely predictive. We show here that this mixing rule is capable of both correlating and predicting the vapor-liquid equilibrium of various complex binary mixtures very accurately over wide ranges of temperature and pressure and that it can be useful for accurate predictions of multicomponent vapor-liquid equilibria.

## Reformulated Model

In reformulating the mixing rule we retain the basic equations (Eqs. 3a and 4a or 3b and 4b), but rewrite the cross second virial term given in Eq. 5 as

$$\left( b - \frac{a}{RT} \right)_{ij} = \frac{(b_i + b_j)}{2} - \frac{\sqrt{a_i a_j} (1 - k_{ij})}{RT}, \quad (6)$$

which is necessary to ensure that the vdW one-fluid mixing and combining rules with the usual definition of the binary interaction coefficient will be recovered.

We now consider the forms of the excess Helmholtz free energy that allow the Wong-Sandler mixing rule to reduce smoothly to the vdW one-fluid model. To do this we first examine the special case on the vdW one-fluid model for which  $a_m$  and  $b_m$  are given by Eq. 1. Also using that  $b_{ij} = (b_i + b_j)/2$  from Eq. 2 and for algebraic simplicity, limiting the following discussion to binary mixtures (though the results are more generally applicable) we obtain the following expression for the excess Helmholtz free energy

$$A^E = \frac{Cx_1x_2}{(x_1b_1 + x_2b_2)} \left( 2a_{12} - a_1 \frac{b_2}{b_1} - a_2 \frac{b_1}{b_2} \right) = \frac{\delta x_1x_2}{x_1b_1 + x_2b_2} \quad (7)$$

where the definition of  $\delta$  is evident from the preceding expression. We need to stress that Eq. 7 is the result only for the special case of a fluid satisfying the vdW one-fluid mixing and combining rules. Consequently, if we use any expression in the Wong-Sandler mixing rule for the excess Helmholtz (or Gibbs) free energy, which reduces to Eq. 7 for some values of

its parameters, we will obtain the conventional vdW one-fluid mixing rules.

One example of a Helmholtz free-energy expression of this form is the following variation of the Wohl equation

$$A^E = \frac{\beta_{12}x_1x_2}{x_1b_1 + x_2b_2} + \frac{\beta_{112}x_1^2x_2}{(x_1b_1 + x_2b_2)^2} + \frac{\beta_{122}x_1x_2^2}{(x_1b_1 + x_2b_2)^2} + \dots \quad (8)$$

In the limit of  $\beta_{112} = \beta_{122} = \dots = 0$  we recover the van Laar activity coefficient expression and also the vdW one-fluid mixing rules with

$$k_{12} = 1 - \frac{1}{2\sqrt{a_1a_2}} \left[ a_1 \frac{b_2}{b_1} + a_2 \frac{b_1}{b_2} + \frac{\beta_{12}}{C} \right]. \quad (9)$$

Another possibility is the modified NRTL expression for the  $A^E$  term:

$$\frac{A^E}{RT} = \sum_i x_i \left[ \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \right] \quad (10)$$

with

$$G_{ji} = b_j \exp(-\alpha_{ij} \tau_{ji}) \quad (11)$$

where  $b_j$  is the volume parameter in the equation of state for species  $j$ . This modified NRTL form was suggested earlier by Huron and Vidal (1979) for the excess Gibbs free energy for use in their model. In above formalism, we have four parameters:  $\alpha_{12} = \alpha_{21}$ ,  $\tau_{12}$ ,  $\tau_{21}$ , and  $k_{12}$ . By setting  $\alpha_{12} = 0$ , one obtains

$$\frac{A^E}{RT} = \frac{x_1x_2(b_1\tau_{12} + b_2\tau_{21})}{x_1b_1 + x_2b_2}. \quad (12)$$

The usual vdW one-fluid mixing rule with the single binary interaction parameter  $k_{ij}$  in Eq. 2 is then given by

$$k_{12} = 1 - \frac{1}{2\sqrt{a_1a_2}} \left[ a_1 \frac{b_2}{b_1} + a_2 \frac{b_1}{b_2} + \frac{RT}{C} (b_1\tau_{12} + b_2\tau_{21}) \right]. \quad (13)$$

Equations 9 and 13 are of little practical interest. They are presented here merely to demonstrate that when used in the Wong-Sandler mixing rule, the Wohl expansion and the modified NRTL equation reduce to the vdW one-fluid mixing rules in certain parameter limits. Further, in these special cases, the vdW one-fluid binary interaction parameter can be obtained in terms of the Helmholtz free-energy parameters. In the Appendix we consider the derivation of a variation to the vdW one-fluid model from the preceding equations.

We will use only the modified NRTL model here to predict and correlate phase behavior. However, to reduce the

number of parameters in the model, two cases will be considered. For binary pairs describable by the vdW one-fluid model, we merely set  $\alpha_{12} = 0$ , and determine the value of the sum  $(b_1\tau_{12} + b_2\tau_{21})$ , or choose it to give the known value of the binary interaction coefficient from Eq. 13. For binary pairs that form highly nonideal mixtures, we set  $k_{12} = 0$  and after some preliminary trials found that we could choose  $\alpha_{12} = 0.1$  for all mixtures. In this mode there are only two adjustable parameters in the model,  $\tau_{12}$  and  $\tau_{21}$ . It is important to note that both vdW one-fluid mixtures and highly nonideal mixtures can now be described by the same free-energy model, but with different choices of the Helmholtz free-energy parameters. Consequently, multicomponent mixtures containing both types of binaries can be described in a unified framework.

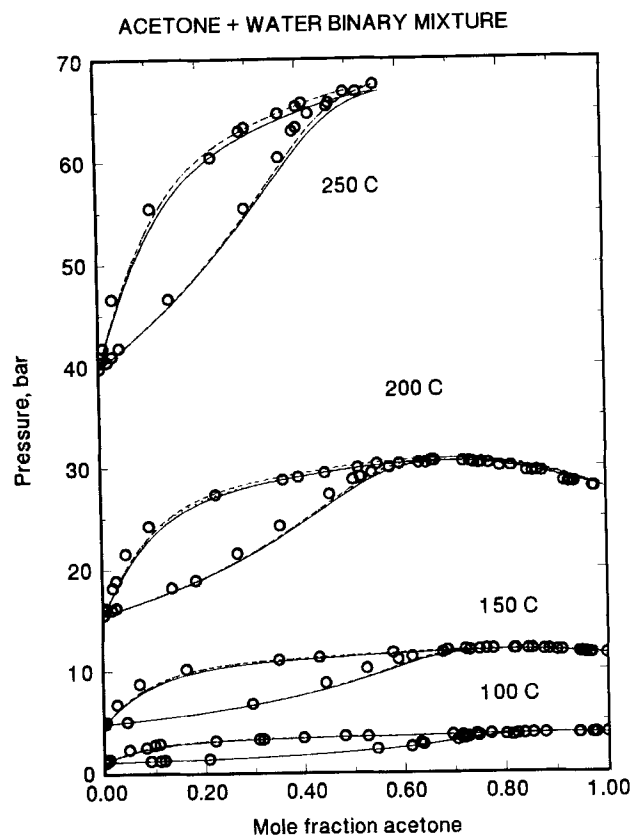
The vdW one-fluid mixing rules cannot be obtained if, for example, the UNIQUAC or Wilson excess-free-energy models are used directly in the reformulated mixing rule presented here; these models do not reduce to Eq. 7. However, they can be used indirectly, as will be evident from the discussion of the use of the UNIFAC model (Fredenslund et al., 1977) below. Therefore, we can view the vdW one-fluid mixing rule as a special case of the more general Wong-Sandler mixing rule that can be derived from it in certain circumstances. More importantly, we can choose an expression for  $A^E$  that for some parameter choices behaves like the vdW one-fluid mixing rules, while for other choices behaves quite differently and is therefore able to describe systems ranging from mixtures of simple hydrocarbons to very nonideal mixtures of organic chemicals and water over broad ranges of temperature and pressure in a unified framework.

There are several choices for evaluating the two parameters in the reformulated mixing rule for nonideal mixtures. The first is to correlate vapor-liquid equilibrium data over the whole concentration range. The second is to solve the two relations obtained from Eq. 10

$$\tau_{ji} = \ln \gamma_i^\infty - \tau_{ij} \frac{b_i}{b_j} \exp(-\alpha_{ij} \tau_{ij}) \quad (14)$$

using known values of the infinite dilution activity coefficients of each species in the other. A third method, which requires no experimental data, is to obtain these infinite dilution activity coefficients from a predictive model such as UNIFAC. To predict the behavior of a multicomponent mixture for highly nonideal binary pairs, we set  $\alpha_{12} = 0.1$  and  $k_{12} = 0$ , obtain the infinite dilution activity coefficients from UNIFAC, and then evaluate the binary parameters  $\tau_{12}$  and  $\tau_{21}$  from Eq. 14. For pairs of components in this mixture that are describable by the vdW one-fluid mixing rule,  $\alpha_{12}$  is set to zero, and the sum  $(b_1\tau_{12} + b_2\tau_{21})$  is calculated from Eq. 13 using an available value for the parameter  $k_{12}$ . This does not result in a unique solution for  $\tau_{12}$  and  $\tau_{21}$ . Therefore, we have used

$$\tau_{ji} = \frac{C}{RT} \left[ \frac{\sqrt{a_i a_j} (1 - k_{ij})}{b_{ij}} - \frac{a_i}{b_i} \right]. \quad (15)$$



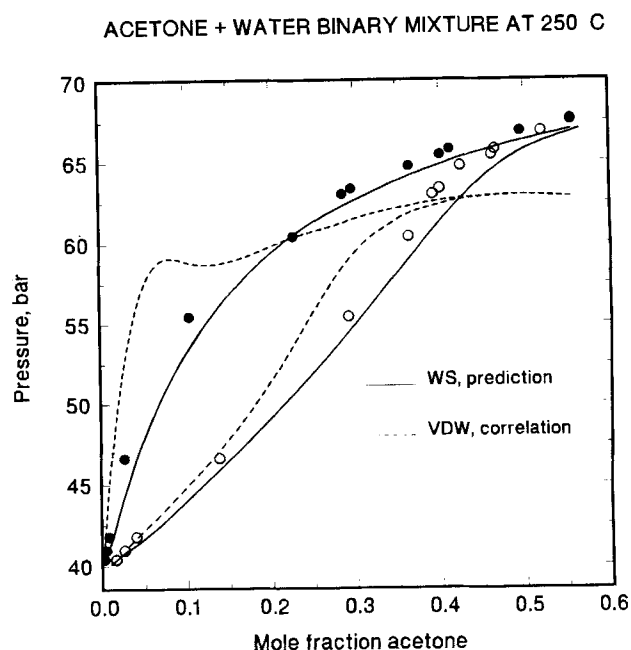
**Figure 1. Vapor-liquid equilibrium of the acetone + water binary mixture.**

The circles are the experimental data mentioned in the text; the solid lines are the predictions using the Wong-Sandler mixing rule and UNIFAC predictions for the infinite dilution activity coefficients at 25°C; the dashed lines are the result of a two-parameter correlation of the lowest temperature isotherm and then extrapolation to the higher temperatures; and the dotted line is a two-parameter correlation of each isotherm.

## Application to Binary Mixtures

To test the method, we have investigated five binary non-ideal mixtures of varying complexity. For all the systems studied we set  $\alpha_{12} = 0.1$  and  $k_{12} = 0$  and used the completely predictive (zero parameter) approach described earlier, plus two forms of the correlative method. (Since as we have shown, the reformulated mixing rule exactly reduces to the vdW one-fluid model, none of our tests are for mixtures of hydrocarbons that are known to be adequately described by that model.) The results are shown in Figures 1 to 6. In all cases here, as in our previous work, we have used the Stryjek-Vera (1986) form of the Peng-Robinson (1976) equation of state.

Figure 1 shows the vapor-liquid equilibrium (VLE) results for acetone + water system compared with the experimental measurements of Griswold and Wong (1952). Here and in the other figures, except Figure 2, the solid lines are predictions at all temperatures using the equation of state and UNIFAC predictions for the infinite dilution activity coefficients only at 25°C. We will refer to this as method 1. The dashed lines result from determining the model parameters by the correlation of the lowest temperature vapor-liquid



**Figure 2. Vapor-liquid equilibrium of the acetone + water binary mixture.**

The circles are the experimental data; the solid lines are the predictions using the Wong-Sandler mixing rule and UNIFAC predictions for the infinite dilution activity coefficients at 25°C; the dashed lines result from the one-parameter van der Waals one-fluid mixing rule correlation of the data at 250°C.

equilibrium data set and making predictions at all higher temperatures; we refer to this as method 2. The dotted lines are the correlations that result from determining the model parameters by the correlation along each isotherm; this is method 3. The first general observation here, and with the other systems considered below, is that very good agreement with experiment is obtained by all three methods. It is noteworthy that method 1, which uses UNIFAC predictions at 25°C, and method 2, which uses data only along the lowest temperature isotherm, result in good predictions at temperatures as high as 250°C. As to be expected, method 3 results (two-parameter correlation at each temperature) are slightly better than the predictions of zero-parameter method 1 and the extrapolation of the two-parameter method 2. In Figure 2 we show two different results for this system at 250°C. One is the zero-parameter prediction of the present model based on the UNIFAC estimates of the infinite dilution activity coefficients at 25°C, and the second is the van der Waals one-fluid mixing rule correlation with its single parameter determined by correlating vapor-liquid equilibrium data at 250°C.

The results for the 2-propanol + water binary system are presented in Figure 3. The points are data of Barr-David and Dodge (1959), and the lines are the results of the present model. An excellent representation of the data up to 300°C and 125 bar was obtained by both correlation (2 parameters at each temperature) and prediction (0 adjustable parameters). The results of correlating only the lowest isotherm are also quite good, though somewhat less accurate. Results for the methanol + benzene (Butcher and Medani, 1968) system are presented in Figure 4. A reasonably good representation

## 2-PROPANOL + WATER BINARY MIXTURE

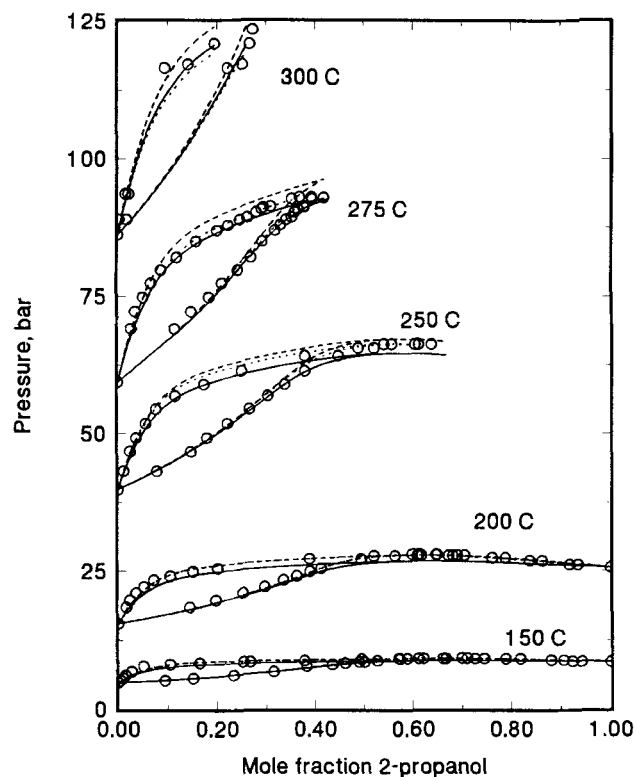


Figure 3. Vapor-liquid equilibrium of the 2-propanol + water binary mixture.

The legend is as in Figure 1.

of VLE behavior is found with any of the three methods. The results for the methanol + water system (Griswold and Wong, 1952) are shown in Figure 5, where excellent correlations and predictions of the VLE behavior from 25°C and subatmospheric pressures to 250°C and 70 bar is observed. Finally, the results for the acetone + methanol binary system (Griswold and Wong, 1952) in the temperature range of 25 to 200°C are presented in Figure 6. Again, very good correlations and predictions are obtained.

Some general conclusions can be drawn from these results. First, the reformulation of the Wong-Sandler mixing rule has had no deleterious effect on its accuracy, while having the advantage of now being simply reducible to the vdW one-fluid rules, if needed. Second, as with the original form of the mixing rule, the parameters here are only very slightly dependent on temperature, which allows extrapolations to be made over wide ranges of temperature. Third, even though any form of the excess-free-energy model can be used in this mixing rule, only when the modified NRTL model (used here) or the Wohl expansion are used will the model reduce to the van der Waals one-fluid mixing rule by an appropriate choice of parameters. However, as is also shown here, the UNIFAC and other models can be used indirectly by the matching of infinite dilution activity coefficients. Finally, the method we have presented here is the best we know of for the complete prediction of elevated pressure binary vapor-liquid equilibria.

## METHANOL + BENZENE BINARY MIXTURE

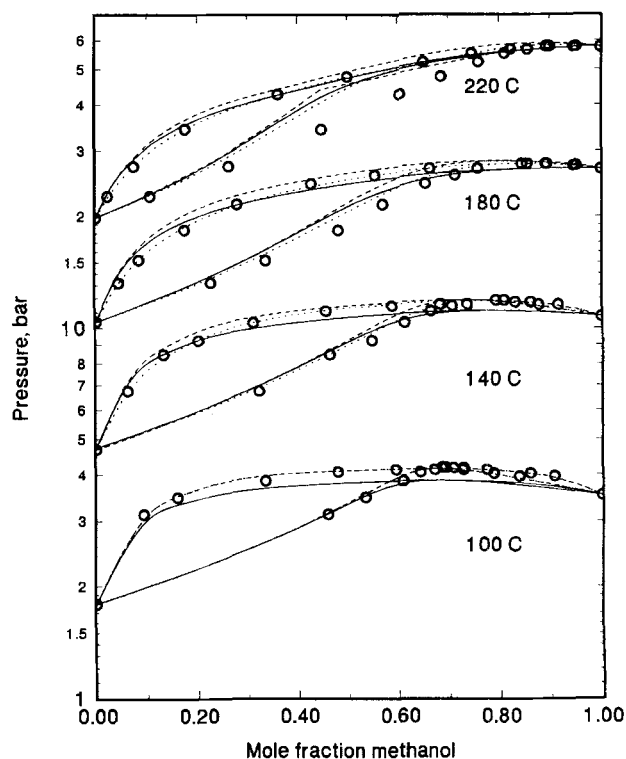


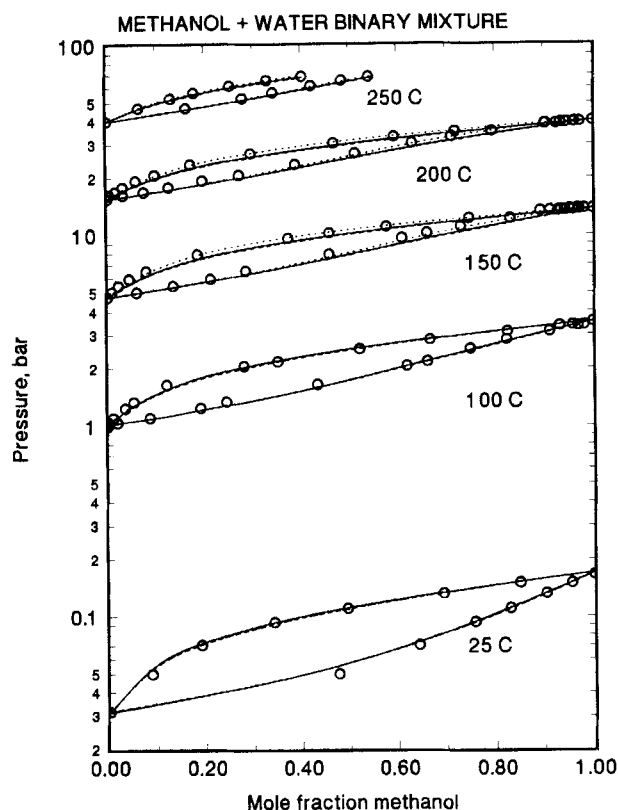
Figure 4. Vapor-liquid equilibrium of the methanol + benzene binary mixture.

The legend is as in Figure 1.

## Application to a Ternary Mixture

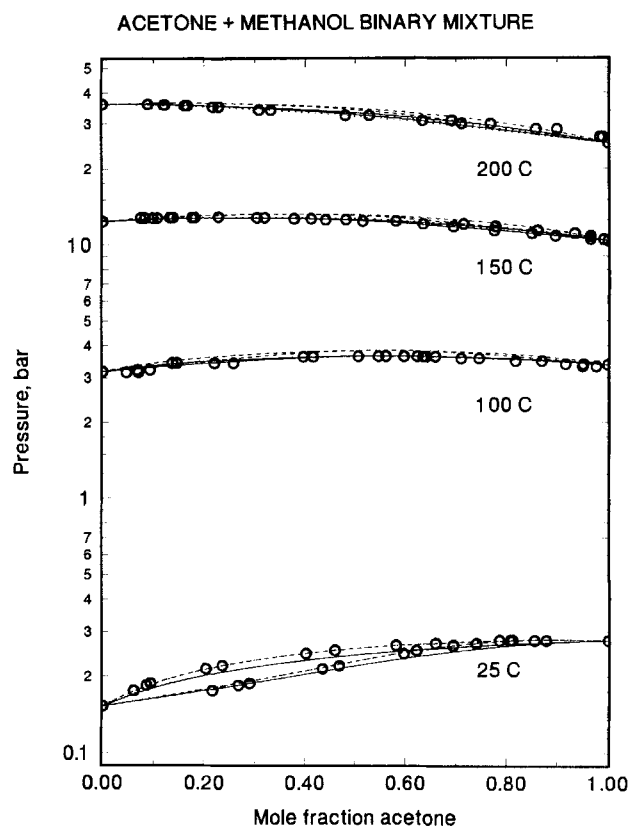
Griswold and Wong (1952) report VLE data for a ternary mixture composed of some of the binary systems studied here. We use the data reported for an acetone + methanol + water system at 250°C to demonstrate the effectiveness of the reformulated mixing rule for the prediction of ternary mixture behavior. We carried out isothermal bubble point calculations using the prediction model presented here for all of the 57 ternary data points reported by Griswold and Wong. The results are reported in Table 1. The present model, without correlating a single parameter to binary or ternary VLE data (only UNIFAC group contribution predictions at 25°C were used), is shown to accurately predict the ternary vapor-liquid behavior for this mixture.

For comparison, we have also performed VLE calculations with the van der Waals one-fluid mixing rule with the binary parameters fit to experimental total pressure data for each binary system at 25°C. These results are also presented in Table 1. This latter approach compares poorly with the predictive model presented here; the average absolute deviation in pressure is about 13% with the van der Waals one-fluid approach, whereas the present model predicts pressures with an average accuracy of 2%. The mole fraction predictions are also found to be better with the model proposed here. The superiority of the new model results from the fact that the parameters in the Wong-Sandler mixing rule are virtually in-



**Figure 5. Vapor-liquid equilibrium of the methanol+water binary mixture.**

The legend is as in Figure 1.



**Figure 6. Vapor-liquid equilibrium of the acetone+methanol binary mixture.**

The legend is as in Figure 1.

dependent of temperature and pressure, while the binary interaction parameters of the classical van der Waals rule depend more strongly on temperature for such nonideal systems. To further illustrate this point, we correlated the vapor-liquid equilibrium data for each of the binary systems in the acetone + water + methanol system at 250°C using van der Waals one-fluid mixing rule (for the acetone + methanol binary we used a 200°C isotherm, since there were no data at 250°C) fitting the binary interaction parameter to the total pressure of the mixture. Next, using the van der Waals one-fluid rule and these correlated parameters we recalculated the ternary phase equilibrium at 250°C. These results are also presented in Table 1. In this case results are of course much better than in the vdW one-fluid calculations with parameters obtained at 25°C, and close to the results of the predictive model presented here, but not better.

The reason that the predictive approach presented here is better than the standard vdW one-fluid correlation method, which uses the binary VLE data at the temperature of interest, is a result of the quality of the fitting of the constituent binary mixtures. Even though the van der Waals one-fluid mixing rule is satisfactory for correlating the data for the methanol + water and acetone + methanol binaries, its correlation of the acetone + water binary is poor, as shown in Figure 2. In contrast, the prediction (not correlation) by the present model captures the essential behavior for all binaries, including the acetone + water mixture, over a wide range of

**Table 1. % Average Absolute Deviations\* in Ternary Phase Equilibrium Calculations for Acetone + Methanol + Water System at 250°C**

	AAD Pressure	Vapor-Phase Mole Fractions		
		AAD Acetone	AAD Methanol	AAD Water
This work	2.00	6.73	7.75	5.20
vdW ( $k_{12}$ fit to 25°C)	13.21	25.47	21.16	6.88
vdW ( $k_{12}$ fit to 250°C)	2.47	8.44	8.79	3.06

$$\text{*Percent average absolute deviation} = \frac{100}{N} \sum_{n=1}^N \frac{|(m_{n,\text{exp}} - m_{n,\text{cal}})|}{m_{n,\text{exp}}}$$

temperatures. This is reflected in the predictions for the ternary system; as the mole fraction of methanol in the ternary mixture decreases, the system more closely resembles the acetone + water binary system, leading to greater errors in VLE calculations with the vdW one-fluid model.

## Conclusions

In 1992 Wong and Sandler reported a mixing-combining rule for two-parameter cubic equations of state that was shown to correlate complex systems with high accuracy. The

predictive capabilities of this mixing rule were later demonstrated (Wong et al., 1992; Orbey et al., 1993).

In this work we have reformulated this mixing rule to eliminate one of the parameters, and in a way that it can be reduced to the van der Waals one-fluid mixing rule with the appropriate choice of parameters. As shown here, this reformulation does not compromise the quality of the VLE predictions or correlation made with the model. Further, the parameters in this reformulated model remain essentially independent of temperature, as was the case with the original mixing rule.

We have also demonstrated that the parameters of the mixing rule can be evaluated from two infinite-dilution activity coefficients, or from the correlation of complete VLE data. When these activity coefficients are obtained from the UNIFAC group contribution model at 25°C, as we have done here, the method is completely predictive over a large temperature range, eliminating the need to fit parameters to VLE data for systems that are adequately describable by UNIFAC. We have also shown our model to be capable of predicting complex binary and multicomponent phase equilibrium with high accuracy. On the other hand, it is not necessary to give up the accumulated binary interaction information available for the van der Waals one-fluid mixing rule for those binary pairs for which that rule is applicable; the mixing rule presented here permits the use of that information without any computational difficulty. Most importantly, multicomponent mixtures consisting of both highly nonideal binary pairs and binary pairs for which the van der Waals one-fluid mixing rules can be used can now be described in a consistent way using a single model.

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## Notation

- $a$  = equation-of-state energy parameter
- $A$  = molar Helmholtz free energy
- $b$  = equation-of-state excluded volume parameter
- $B$  = second virial coefficient
- $C$  = numerical constant dependent on equation of state
- $G$  = local composition factor in NRTL model
- $k$  = binary interaction parameter
- $P$  = pressure
- $R$  = gas constant
- $T$  = temperature
- $V$  = molar volume
- $x$  = mole fraction

## Greek letters

- $\alpha$  = parameter in local composition factor of NRTL model
- $\beta$  = Wohl expansion parameter
- $\gamma$  = activity coefficient
- $\delta$  = parameter in Eq. 7
- $\lambda$  = parameter in Eq. A2
- $\tau$  = parameter in local composition factor of NRTL model

## Subscripts and Superscripts

- $i, j$  = molecular species or term in expansion
- $m$  = mixture property
- $E$  = excess property on mixing
- $\infty$  = infinite dilution property

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## Appendix

In the article we have shown that if we set

$$A^E = \frac{B_{12}x_1x_2}{x_1b_1 + x_2b_2}, \quad (\text{A1})$$

we recover the usual van der Waals (vdW) one-fluid mixing rules. It is of interest to consider the mixing-rule implications of other excess-free-energy models. For example, simple extension of Eq. A1 is

$$A^E = \frac{x_1 x_2 (\beta_{12} + \lambda_{12} x_1)}{x_1 b_1 + x_2 b_2} \quad (\text{A2})$$

Using this expression we again obtain the van der Waals one-fluid mixing rule, but with the binary interaction parameter  $k_{12}$  in the following form

$$k_{12} = K_{12} - (K_{12} - K_{21})x_1 \quad (\text{A3})$$

where

$$K_{12} = 1 - \frac{1}{2\sqrt{a_1 a_2}} \left[ \frac{\beta_{12}}{C} + a_1 \frac{b_2}{b_1} + a_2 \frac{b_1}{b_2} \right] \quad (\text{A4})$$

and

$$K_{21} = 1 - \frac{1}{2\sqrt{a_1 a_2}} \left[ \frac{\beta_{12} - \lambda_{12}}{C} + a_1 \frac{b_2}{b_1} + a_2 \frac{b_1}{b_2} \right] \quad (\text{A5})$$

Equation A3 is the combining rule proposed by Panagiotopoulos and Reid (1986) and Adachi and Sugie (1986). Related combining rules have been suggested by Sandoval et al. (1989) and Schwartzentruber and Renon (1989a,b). From this analysis we see the free-energy model that underlies these combining rules. In a similar fashion, the mixing and combining rule implications of other excess-free-energy models can be found.

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