A Theoretically Correct Mixing Rule for Cubic Equations of State

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A new mixing rule developed for cubic equations of state equates the excess Helmholtz free energy at infinite pressure from an equation of state to that from an activity coefficient model. Use of the Helmholtz free energy insures that the second virial coefficient calculated from the equation of state has a quadratic composition dependence, as required by statistical mechanics. Consequently, this mixing rule produces the correct low- and high-density limits without being density-dependent.

As a test, the mixing rule is used for ternary mixtures of cyclohexane + benzene + water, ethanol + benzene + water and carbon dioxide + n-propane + water, and all the constituent binaries. The new mixing rule and a simple cubic equation of state can be used for the accurate correlation of vapor-liquid and liquid-liquid equilibria for binary mixtures. Using the parameters obtained from binary systems, the phase behavior of ternary mixtures can be predicted. Also, unlike previous empirical mixing rules, this theoretically based mixing rule is equally applicable and accurate for simple mixtures containing hydrocarbons and inorganic gases and mixtures containing polar, aromatic and associating species over a wide range of pressures. This mixing rule makes it possible to use a single equation of state model with equal accuracy for mixtures usually described by equations of state and for those traditionally described by activity coefficient models. It is the correct bridge between these two classes of models.

Introduction

Cubic equations of state are used widely for phase equilibrium calculations. To use such equations to model complex-phase behavior of highly nonideal mixtures, however, mixing rules other than the commonly employed van der Waals one-fluid mixing rules are required. Several authors (Panagiotopoulos and Reid, 1986a; Adachi and Sugie, 1986; Sandoval et al., 1989; Schwartzentruber et al., 1989) have proposed various modified forms of the van der Waals mixing rules that use composition-dependent binary interaction parameters. While such mixing rules have been used successfully for some highly nonideal mixtures, they are not generally applicable; since in the low-density limit they are inconsistent with the statistical mechanical result that the second virial coefficient must be a quadratic function of composition. Further, these rules may fail for simple mixtures (Shibata and Sandler, 1988).

To correct these problems, attempts have been made to develop density-dependent mixing rules (for example, Luedecke and Prausnitz, 1985; Panagiotopoulos and Reid, 1986b) so that the correct low-density limit is recovered. Such an approach, however, is *ad hoc* and does not preserve the cubic nature of equation of state when used for mixtures. Moreover, as pointed out by Michelsen and Kistenmacher (1990), some of the new mixing rules that have been proposed lead to inconsistencies when a component is split into two or more identical fractions. There have been ongoing efforts to correct such

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deficiencies (Schwartzentruber and Renon, 1991; Mathias et al., 1991), but with little success.

An alternative approach for developing mixing rules was proposed by Huron and Vidal (1979). This method involves equating the excess Gibbs free energy at infinite pressure calculated from an equation of state to that of an excess Gibbs free energy (activity coefficient) model for liquids. In order that the excess Gibbs free energy at infinite pressure computed from an equation of state be finite, Huron and Vidal had to require that the excess volume at infinite pressure be zero; otherwise, the $P\underline{V}^E$ term becomes infinite. Consequently, a linear mixing rule for the excluded volume parameter b_m had to be used. It was pointed out by Sheng et al. (1992) that such an assumption is not necessary if one equates excess Helmholtz free energies instead. This allows a wider choice for the mixing rule for the equation of state parameter b_m.

The Huron-Vidal mixing rule does not satisfy the requirement that the second virial coefficient be a quadratic function of composition, and therefore is inconsistent with statistical mechanical theory. Here we show that by the simple expedient of considering the Helmholtz free energy, we can develop a new class of density-independent mixing rules, in which the energy parameter a_m and the excluded volume parameter b_m of any cubic equation of state are determined to give the correct excess Helmholtz energy at infinite pressure and, simultaneously, the correct quadratic composition dependence of the second virial coefficient. Consequently, this new class of mixing rules produce results that are correct at both the low-density and high-density limits without being density-dependent.

Theory

For simplicity, we present the derivation of the new mixing rule here for the van der Waals equation of state. The derivation of the new mixing rule and the fugacity coefficient equation for the Peng-Robinson equation is given in the Appendix; a similar derivation can be used for other two-parameter cubic equations of state.

The van der Waals equation of state is given by:

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2} \tag{1}$$

To apply this equation to mixtures, the equation of state parameters a_m and b_m are made functions of compositions using mixing rules. For example, the traditional van der Waals "one-fluid" mixing model is:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \qquad b_m = \sum_i \sum_j x_i x_j b_{ij} \tag{2}$$

Further, the following combining rules are generally assumed:

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \qquad b_{ij} = \frac{(b_i + b_j)}{2} \tag{3}$$

where k_{ij} is an interaction parameter characteristic of each binary pair. The modification proposed by Panagiotopoulos and Reid (1986) was to make k_{ij} composition-dependent resulting in:

$$a_m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - k_{ij} + x_j l_{ij}) \tag{4}$$

While mixing rules should lead to a quadratic dependence of the second virial coefficient on composition, there is no other theoretical restriction on their temperature, density or composition dependence. However, there is an advantage to mixing rules being independent of density since this preserves the cubic nature of the equation of state. If we expand the equation as a virial series, the relation between the second virial coefficient $B(T)$ and the equation of state parameters is:

$$B(T) = b - \frac{a}{RT} \tag{5}$$

Since, from statistical mechanics, the composition dependence of the second virial coefficient is quadratic:

$$B_m(T) = \sum_i \sum_j x_i x_j B_{ij}(T) \tag{6}$$

we must have that

$$b_m - \frac{a_m}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \tag{7}$$

with $[b - a/(RT)]_{ij}$ being the composition-independent cross second virial coefficient of the equation of state. A sufficient, but not necessary, condition for satisfying Eq. 7 is the van der Waals one-fluid model of Eq. 2. Traditionally this solution has been used at all densities. However, Eqs. 2 are only one solution to Eq. 7; other solutions are possible, which is the subject of this article.

As a disgression, for later reference, we note that:

$$b_m = \frac{\displaystyle\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \dfrac{F(x)}{RT}} \tag{8}$$

and

$$a_m = b_m F(x) \tag{9}$$

where $F(x)$ is an arbitrary function of composition vector x, is also a solution of Eq. 7.

Many other algebraic solutions are possible, for example,

$$b_m = \sum_i \sum_j x_i x_j b_{ij} + F(x) \quad a_m = \sum_i \sum_j x_i x_j a_{ij} + RTF(x) \tag{10}$$

though they may be devoid of any physics.

The cross second virial coefficient of Eq. 7 can be related to those of the pure components by:

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \dfrac{a_i}{RT}\right) + \left(b_j - \dfrac{a_j}{RT}\right)}{2}(1 - k_{ij}) \tag{11}$$

where here k_{ij} is a second virial coefficient binary interaction parameter.

The Helmholtz free energy departure function, which is the difference between the molar Helmholtz free energy of pure species i and the ideal gas at the same temperature and pressure, is:

$$\underline{A}_i(T,P)-\underline{A}_i^{IG}(T,P)=\left(-\int_{V=\infty}^{V_i}P\,d\underline{V}\right)-\left(-\int_{\underline{V}=\infty}^{\underline{V}=\frac{RT}{P}}\frac{RT}{\underline{V}}\,d\underline{V}\right) \qquad (12)$$

for the van der Waals fluid this becomes:

$$\underline{A}_i(T,P)-\underline{A}_i^{IG}(T,P)=-RT\ln\left[\frac{P(\underline{V}_i-b_i)}{RT}\right]-\frac{a_i}{\underline{V}_i} \qquad (13)$$

Similarly, the mixture Helmholtz free energy departure function, which is the difference between the molar Helmholtz free energy of a mixture, $\underline{A}_m$, and that of the same mixture as an ideal gas, $\underline{A}_m{}^{IGM}$, at the same temperature, pressure, and composition is:

$$\underline{A}_m(T,P,x)-\underline{A}_m^{IGM}(T,P,x)=-RT\ln\left[\frac{P(\underline{V}_m-b_m)}{RT}\right]-\frac{a_m}{\underline{V}_m} \qquad (14)$$

Finally, the excess Helmholtz free energy for mixing at constant temperature and pressure, $\underline{A}^E(T,P,x)$, is:

$$\begin{aligned}\underline{A}^E(T,P,x)&=\underline{A}_m(T,P,x)-\underline{A}_m^{IM}(T,P,x)=\\&=\underline{A}_m(T,P,x)-\sum_i x_i\underline{A}_i(T,P)-RT\sum_i x_i\ln x_i=\\&=\underline{A}_m^{IGM}(T,P,\mathrm{x})-RT\ln\left[\frac{P(\underline{V}_m-b_m)}{RT}\right]-\frac{a_m}{\underline{V}_m}\\&\quad-\sum_i x_i\underline{A}_i^{IG}(T,P)+RT\sum_i x_i\ln\left[\frac{P(\underline{V}_i-b_i)}{RT}\right]+\sum_i\frac{x_ia_i}{\underline{V}_i}\\&\quad-RT\sum_i x_i\ln x_i=-\frac{a_m}{\underline{V}_m}+\sum_i x_i\frac{a_i}{\underline{V}_i}-RT\ln\left[\frac{P(\underline{V}_m-b_m)}{RT}\right]\\&\quad+RT\sum_i x_i\ln\left[\frac{P(\underline{V}_i-b_i)}{RT}\right]\end{aligned} \qquad (15)$$

since

$$\underline{A}_m^{IGM}(T,P,x)-\sum_i x_i\underline{A}_i^{IG}(T,P)=RT\sum_i x_i\ln x_i \qquad (16)$$

Expressions for the excess Helmholtz free energy of liquid mixtures have usually been derived using lattice models with the assumption that there are no free sites on the lattice. This is approximately equivalent to the assumption that in a liquid solution the molecules are so closely packed that there is no free volume. This limit in an equation of state is:

$$\begin{aligned}\lim_{P\to\infty}\underline{V}_i&=b_i\\\lim_{P\to\infty}\underline{V}_m&=b_m\end{aligned} \qquad (17)$$

Therefore, if we equate the excess Helmholtz free energy at infinite pressure from an equation of state to that of a liquid solution model we have:

$$\underline{A}_\infty^E(x)=-\frac{a_m}{b_m}+\sum_i x_i\frac{a_i}{b_i} \qquad (18)$$

Equation 18 is analogous to the relation found by Huron and Vidal (1979), but since they used the excess Gibbs free energy at infinite pressure they had to make the additional assumption on the b parameter of Eq. 3.

Equations 7 and 18 completely define a_m and b_m in terms of $\underline{A}_\infty^E(x)$ (the high-density term) and k_{ij} (the low-density term). These equations can be solved to obtain

$$b_m=\frac{\sum_i\sum_j x_ix_j\left(b-\frac{a}{RT}\right)_{ij}}{1+\left(\frac{\underline{A}_\infty^E(x)}{RT}\right)-\sum_i x_i\left(\frac{a_i}{b_iRT}\right)} \qquad (19)$$

and

$$\frac{a_m}{b_m}=\sum_i x_i\frac{a_i}{b_i}-\underline{A}_\infty^E(x) \qquad (20)$$

Note that Eqs. 19 and 20 are in the form of Eqs. 8 and 9 with

$$F(x)=\sum_i x_i\frac{a_i}{b_i}-\underline{A}_\infty^E(x) \qquad (21)$$

Therefore, these mixing rules produce a second virial coefficient which has a quadratic composition dependence, and at low densities these mixing rules predict fugacities similar to a virial equation truncated at the second virial coefficient. At high density, however, the Helmholtz free energy of the solution is that of the chosen liquid activity coefficient model described by $\underline{A}_\infty^E(x)$, and could be of either a random or local composition form. Consequently, we have obtained a mixture equation of state model that is correct at both the low- and high-density limits without postulating a density-dependent mixing rule.

It should be noted that the mixing rule suggested by Huron and Vidal (1979) is, in effect, the zeroth-order truncation of a series expansion of Eqs. 19 and 20 with respect to $(1/T)$ and with k_{ij} set equal to zero. However, since both the excluded volume parameter b and the second virial coefficient are of the order (a/RT), the proper composition dependence for the second virial coefficient cannot be preserved unless the expansion is carried beyond the first-order term. In fact, there is no need to expand Eqs. 19 and 20 with respect to temperature.

If, instead of our mixing rule, the van der Waals one-fluid mixing model is used, the form of excess Helmholtz free energy of the liquid has then been dictated to be:

$$\underline{A}^E_\infty(\underline{x}) = \sum x_i \frac{a_i}{b_i} - \frac{\sum\sum x_i x_j a_{ij}}{\sum\sum x_i x_j b_{ij}} \tag{22}$$

Alternatively, if one uses this excess Helmholtz free energy expression in our mixing rule, the van der Waals one-fluid mixing rule is recovered at all densities. However, the mixing rule developed here allows a much more flexible choice of liquid solution model so that, if necessary, local composition effects at high density can be represented accurately. Further, the approach developed here is theoretically correct and can be easily extended to other two-parameter cubic equations of state. For example, the expressions of mixture parameters and fugacities of components derived for the Peng-Robinson equation of state (Peng and Robinson, 1975) are given in the Appendix.

Results and Discussion

In this section we demonstrate the applicability of the mixing rule we have developed by examining experimental vapor-liquid, liquid-liquid and vapor-liquid-liquid equilibrium data for several binary and ternary systems at both low pressures and high pressures, some of which have presented difficulty in other equation of state studies. The systems considered range from almost ideal to highly nonideal mixtures and include some systems that are traditionally described by equations of state, and others for which activity coefficient models are used. It should be noted that since we can always choose Eq. 22 for $\underline{A}^E_\infty$ our mixing rule can never be worse than the one-constant van der Waals one-fluid model and therefore will describe simple hydrocarbon systems quite well. In addition, as we show below, our mixing rule is also applicable to mixtures that previously could not be accurately described by an equation of state.

In the following, we will use models for the excess Helmholtz free energy, which are normally used for the excess Gibbs free energy. The relation between the two is:

$$\underline{G}^E = \underline{A}^E + P\underline{V}^E \tag{23}$$

Excess Gibbs free energy (activity coefficient) models are used generally as low pressure, and $\underline{V}^E$ is usually small, so that the difference between $\underline{G}^E$ and $\underline{A}^E$ is small. Further, if one examines the derivation of $\underline{G}^E$ models, it is evident that it is really a model for $\underline{A}^E$ which has been derived. Also, due to the absence of the $P\underline{V}^E$ term, $\underline{A}^E$ is much less pressure-dependent than $\underline{G}^E$. Indeed, to an excellent approximation we have that:

$$\underline{G}^E(T,x,P=low) = \underline{A}^E(T,x,P=low) = \underline{A}^E(T,x,P=\infty) \tag{24}$$

Therefore, in what follows, we will use the same functional form for $\underline{A}^E$ at infinite pressure as is now used for $\underline{G}^E$ at low pressures. It needs to be emphasized that it is the composition dependence of $\underline{A}^E$ which is important; it is not necessary that for the liquid phase of any specific mixture to be stable over the whole composition range $0<x<1$ to use our mixing rule.

The parameters in our mixing rule are cross virial coefficient interaction coefficient and the coefficients in the expression used for the excess Helmholtz free energy. Thus, for example, there are three parameters per binary if the Wilson model is used, and four parameters (including α) if the NRTL model is used.

In the following examples, we have used the Stryjek and Vera (1986) modification of the Peng-Robinson (1975) equation of state. To get the correct pure-component vapor pressures, the equation of state constants for all pure components were computed using the correlations of Stryjek and Vera (1986). For demonstration, the NRTL model was used in our calculations here, though any other $\underline{A}^E$ (or $\underline{G}^E$) model could be used as well. Interaction parameters were obtained by regression of data for binary mixtures at the temperatures of interest; their values and the results of the correlations are given in Table 1. In all cases, the ternary results reported here are predictions using parameters fit to binary data only.

Due to the so-called Michelsen-Kistenmacher (1990) syndrome, in which a mixing rule is not invariant to the subdivision of a component in two or more identical components, mixing rules that use two asymmetric binary interaction parameters, such as the density-independent Panagiotopoulos-Reid mixing rule (1986a) here called BIP2, perform poorly for ternary mixtures containing two similar components. This has been shown by Mathias et al. (1991) using the specific example of the solubility of water in mixtures of cyclohexane and benzene. Cyclohexane and benzene are very similar, and the solubility of water changes almost linearly with the composition of the mixed solvent. With parameters determined from binary data, however, the BIP2 mixing rule predicts a maximum in the solubility of water as a function of mixed solvent composition as show in Figure 1, while liquid-liquid predictions for this ternary system using the mixing model proposed in this work agree well with experimental data. The fact that our mixing rule does not suffer from the so-called Michelsen-Kistenmacher syndrome is evident from its derivation.

Another system considered here is the binary mixture of ethanol and benzene. When parameters are adjusted to obtain agreement with experimental VLE data for the ethanol-benzene mixture near the two high dilution ends near room temperature, the Panagiotopoulos-Reid mixing rule predicts the formation of a heterogeneous azeotrope and liquid-liquid phase separation at higher pressures. Experimental data, however, show that ethanol and benzene are completely miscible at this temperature. Figure 2 shows that our mixing rule results in much better agreement with experiment, including the prediction of a homogeneous azeotrope.

Mathias et al. (1991) have shown that mixing rules with two asymmetric binary interaction parameters, such as that of Panagiotopoulos and Reid, fail to predict a plait point for the ternary system ethanol + benzene + water (experimental data reported in Sørenson and Arlt, 1980c), nor will their proposed empirical modification that rectifies the Michelsen-Kistenmacher syndrome. This is probably due to the poor correlation of the ethanol + benzene data, which results from using those mixing rules. Figure 3 shows that our model correctly predicts a liquid-liquid plait point, though the predicted phase envelope is larger than that found experimentally and contains less water. It also shows the results of the NRTL activity coefficient model prediction using reported parameters obtained from binary

Table 1. Binary Data Sources, Parameters and Average Absolute Deviation in K Values

			NRTL					BIP2		
System	Type	T[K]	k_{ij}	α_{ij}	τ_{ij}	τ_{ji}	AD K %	k_{ij}	k_{ji}	AD K %
cyclohexane + water[a]	LLE	298	0.71	0.20	7.72	9.56	1.4	−0.14	0.45	1.5
benzene + water[b]	LLE	298	0.52	0.20	5.37	6.04	2.6	−0.12	0.29	7.6
benzene + ethanol[c]	VLE	298	0.21	0.36	2.55	0.34	1.8	0.05	0.12	6.2
ethanol + water[d]	VLE	298	0.28	0.30	0.03	1.48	3.3	−0.14	−0.07	7.4
propane + methanol[e]	VLE	313	0.16	0.45	4.03	1.85	2.0	0.04	0.09	3.9
carbon dioxide + propane[f]	VLE	344	0.40	0.30	1.02	−0.15	1.2	0.18	0.18	4.3
		311	0.35	0.30	1.12	−0.16	2.4	0.14	0.14	3.3
		278	0.37	0.30	1.26	−0.18	2.3	0.14	0.11	2.3
carbon dioxide + methanol[g]	VLE	313	0.38	0.29	0.64	0.27	3.1	0.05	0.08	7.7

[a] Sørensen and Arlt (1980a).
[b] Sørensen and Arlt (1980b).
[c] Gmehling and Onken (1977).
[d] Gmehling et al. (1988).
[e] Galivel-Solastiouk et al. (1986).
[f] Reamer et al. (1951).
[g] Ohgaki and Katayama (1976).

vapor-liquid and liquid-liquid equilibrium data (Gmehling and Onken, 1977; Gmehling et al., 1988; Sørensen and Arlt, 1980a,b). The equation of state model using our mixing rule gives predictions that are similar to, if not slightly better than, those obtained from the activity coefficient approach. The shortcoming of classical activity coefficient models, especially in the plait point region, is well documented in the literature (for example, dePablo and Prausnitz, 1988). Since our mixing rule uses a classical activity coefficient model to describe the nonideality of the high-density phase, it is not surprising to observe similar behavior.

Schwartzentruber et al. (1987) have pointed out that erroneous liquid-phase splitting is generally predicted when equation of state models with various mixing rules are used to

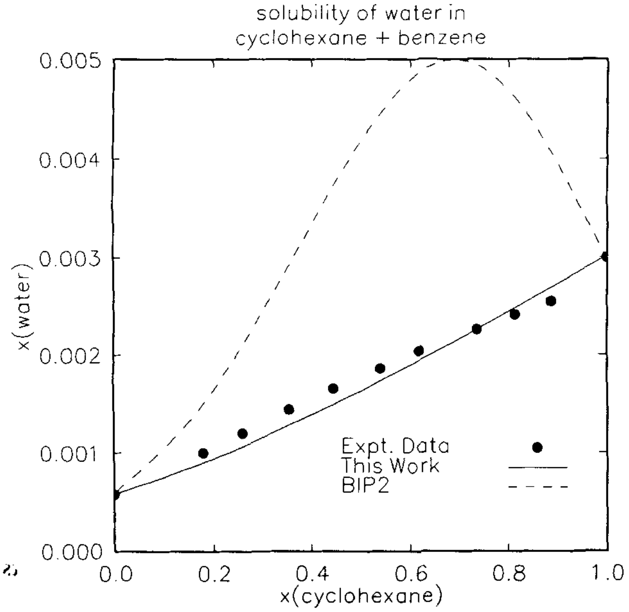

Figure 1. Comparison of measured and predicted water solubility in the benzene and cyclohexane mixture at 298 K.

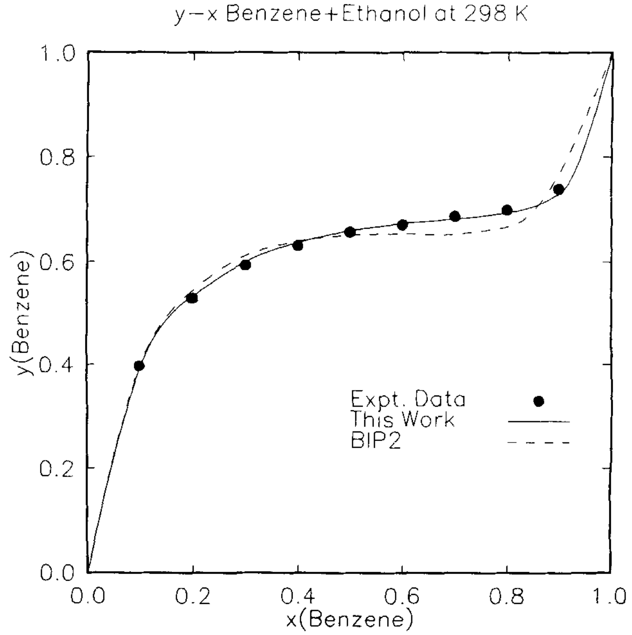

Figure 2. Measured and correlated x-y curves for the benzene-ethanol system at 298 K.

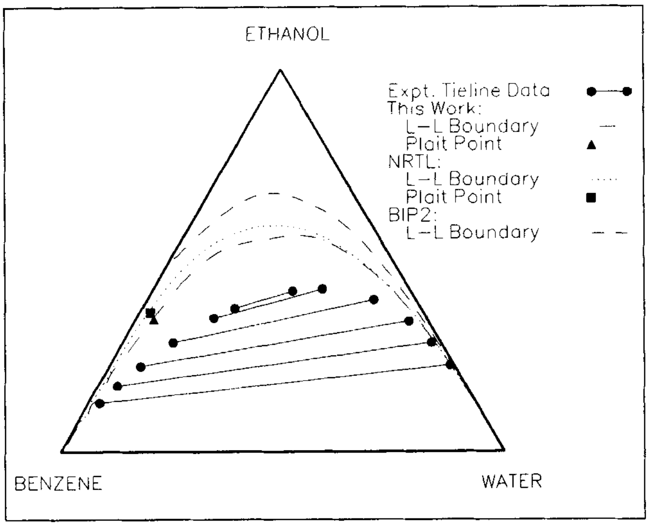

Figure 3. Measured tie lines for the benzene-ethanol-water system at 298 K and predicted phase boundaries and plait points using our mixing rule, the NRTL model, and the Pangiotopoulos-Reid model (which does not predict a plait point).

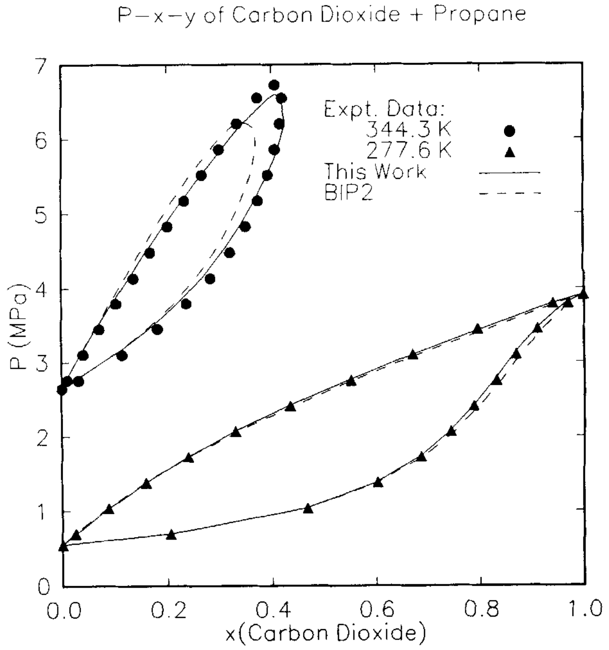

Figure 5. Measured and correlated *P-x-y* curves for the carbon dioxide-propane mixture at 277.6 and 344.3 K.

correlate vapor-liquid equilibrium data for the propane-methanol binary mixture at 313.1 K. The experimental data of Galivel-Solastiouk et al. (1986) in Figure 4 show this system to be highly nonideal. In particular, the bubble point pressure first rises sharply and then abruptly levels off as propane is added to methanol. Schwarzentruber et al. (1987) found that for this system the Huron-Vidal mixing model incorrectly predicts liquid-liquid immiscibility. Figure 4 shows that a simple asymmetric mixing model such as BIP2 gives similar erroneous results. A modified version of the asymmetric mixing rule proposed by Schwarzentruber et al. (1987) avoids the prediction of liquid-liquid separation, but produces a homogeneous azeotrope with a maximum in bubble point pressure near the propane end. There, however, is no evidence in the experimental data that supports the existence of such an azeotrope. On the other hand, our mixing rule predicts the correct phase behavior, in good agreement with the experimental data, without showing false local maxima and minima in the bubble point pressure curve.

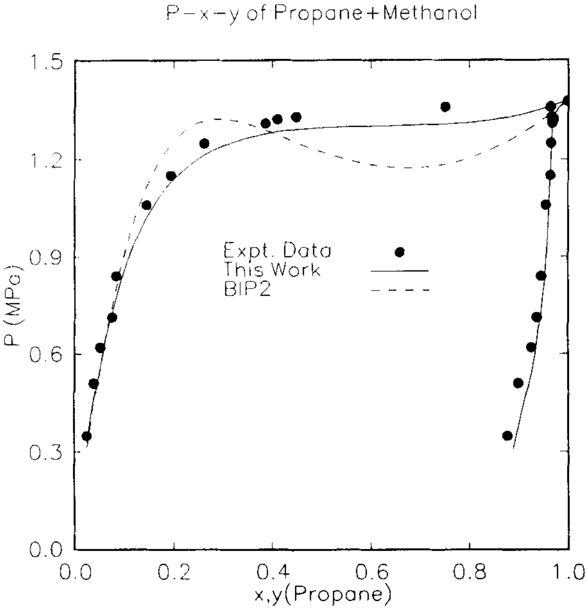

Figure 4. Measured and correlated *P-x-y* curves for the propane-methanol mixture at 298 K.

Shibata and Sandler (1979) have pointed out that some mixing models useful for complex mixtures are unsatisfactory for simple mixtures such as the inorganic gases (nitrogen and carbon dioxide) with hydrocarbons, especially near the critical point of the mixture. To examine the performance of our mixing rule for such systems we have correlated the experimental data for carbon dioxide + propane reported by Reamer et al. (1951) using the mixing rule developed here and, for comparison, the BIP2 model. Figure 5 shows that the difference between the two models is negligible at temperatures below the critical temperature of carbon dioxide (for example, 277.6 K). However, at 344.3 K, the BIP2 model predicts a critical pressure for the binary mixture that is substantially lower than that found experimentally, while the performance of our mixing model near the critical region is much better.

We next compared the predictions of our mixing rule with the vapor-liquid equilibrium data for the ternary system carbon dioxide + propane + methanol of Galivel-Solastiouk et al. (1986). In this calculation the vapor-liquid equilibrium data of Ohgaki and Katayama (1976) were used to obtain the interaction parameters for the carbon dioxide + methanol binary system; the other binary mixtures have been discussed above. The experimental data and the predictions using our new mixing rule and the BIP2 model at 313.1 K for both 1.21 MPa and 1.71 MPa are compared in Figures 6a and 6b, respectively.

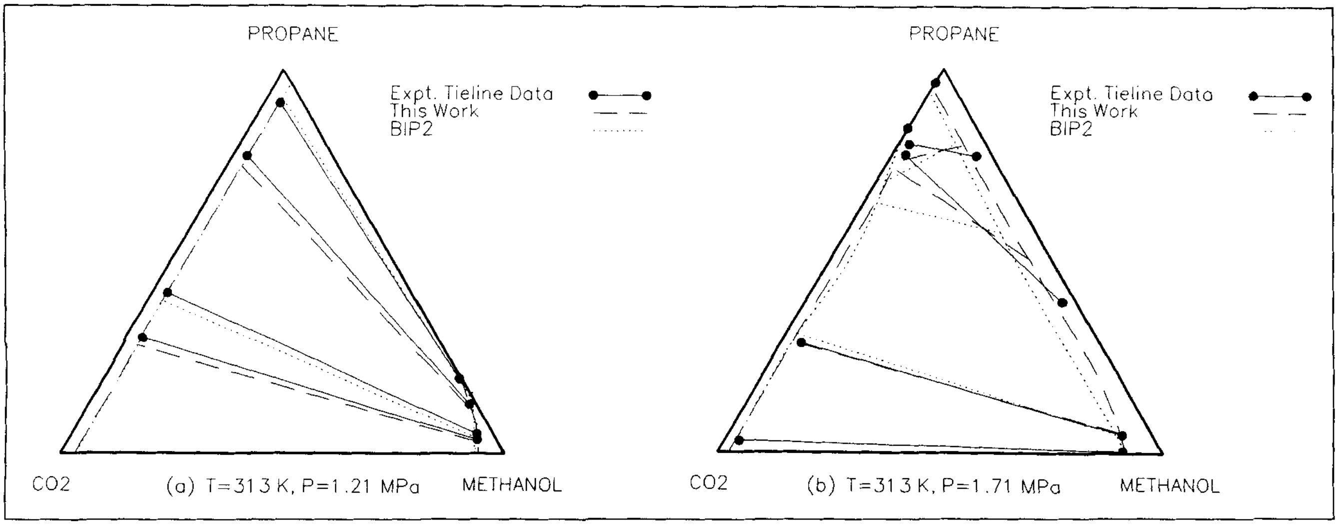

Figure 6. Measured and predicted phase boundaries and tie lines for the carbon dioxide-propane-methanol system at 313 K: (a) $P = 1.21$ MPa; (b) $P = 1.71$ MPa.

Note that in Figure 6a, since the predictions of the two models are similar, only one prediction is shown for each tie line. However, both model predictions are shown in Figure 6b.

At 313.1 K, carbon dioxide is a supercritical fluid, while methanol is a liquid at both pressures. The vapor pressure of propane is about 1.3 MPa, so that at 1.21 MPa mixtures of carbon dioxide and propane are gaseous and completely miscible, while vapor-liquid equilibrium exists in the carbon dioxide + methanol and propane + methanol binaries. The equilibrium vapor- (essentially carbon dioxide and propane) and liquid- (essentially methanol) phase boundaries run smoothly between the binary limits as shown in Figure 6a. The phase boundaries and tie lines calculated by the two mixing models are virtually indistinguishable and agree well with experimental data.

At 1.71 MPa, pure propane is a liquid, propane and methanol form completely miscible liquid mixtures, and vapor-liquid-phase splitting occurs in the carbon dioxide + propane and carbon dioxide + methanol binary mixtures. Therefore, the vapor- and liquid-phase boundaries extend from the carbon dioxide + methanol boundary to the carbon dioxide + propane boundary, rather than the propane + methanol boundary as was the case at the lower pressure. Both mixing models correctly predict this feature of the phase diagram, since they are correct for each of the binary systems. Our mixing model, however, produces a liquid-phase boundary that is in better agreement with the experimental data than the BIP2 model. Note from the experimental data in Figure 6b that as the propane concentration is increased, the tie lines change rapidly in slope, starting by being parallel to the CO_2-methanol axis, shifting toward the propane-methanol axis, and then changing direction to end on the CO_2-propane axis. The region, in which the tie lines change slope abruptly, is difficult to predict with any model to a high degree of accuracy. Nonetheless, our model is able to reproduce these characteristics and certainly much better than the BIP2 model.

For mixtures, which vary from slightly to highly nonideal, the mixing rule developed is very good for both correlation and prediction of phase behavior. It is useful to comment on the values and behavior of the parameters that we have found in this work. We note that the values of the parameters in the free energy model are quite similar to those found when the same model is used directly in an activity coefficient (γ-ϕ) calculation of phase behavior. This provides hope that a group contribution method such as UNIFAC (Fredenslund et al., 1975) can be incorporated directly into our mixing rule making it largely predictive. We are now exploring this possibility.

From our derivation, the binary interaction parameter, k_{ij}, describes second virial coefficient behavior. Consistent with this, we have found that the value of k_{ij} is relatively independent of the free energy model used, provided the expression used for $\underline{A}^E_\infty$ provides a reasonable description of the system under study. Further, we note from Table 1 that the values of the k_{ij} parameter are large, as is to be expected from second virial coefficient behavior for nonideal systems. For example, using the data in Dymond and Smith (1980), k_{ij} for the carbon dioxide-propane mixture at about 315 K is 0.32, which compares favorably with the value of 0.35 reported in Table 1. However, from second virial coefficient data k_{ij} should be 0.70 for the carbon-dioxide–methanol system, while we find a value of 0.38 from our correlation of VLE data. This difference may be the result of the generally poor accuracy of second virial coefficient data for the alcohols and/or the inability of cubic equations of state to predict quantitatively accurate second virial coefficients. It is noteworthy, however, that while the values of the parameter k_{ij} may appear large, at first glance, they are consistent with observed virial coefficient behavior. This is as it should be, since in our development, k_{ij} is a binary interaction parameter for the second virial coefficient.

Conclusions

A goal of applied thermodynamicists has been to replace activity coefficient models for mixtures with equations of state. Among the reasons for this are: (1) to avoid the use of standard states and hypothetical phase conditions; (2) to have models which can be used at high pressures and close to a vapor-liquid critical point; and (3) to have models that cover a wide range of temperature and pressure with few parameters. While simple equations of state with suitably adjusted parameters are able to describe the PVT and VLE behavior of pure components, success with nonideal mixtures has been limited. Good predictions, or at least correlations, are obtained for simple mixtures (mixtures of inorganic gases and hydrocarbons), while poor results are generally obtained with mixtures containing, for example, polar fluids. Since the pure components are described reasonably well, these failures are due to the models used to obtain the mixture equation of state parameters. Consequently, many empirical, *ad hoc* mixing rules have been derived. Usually, the mixing rules are complicated, perhaps are even density-dependent, apply to only certain classes of mixtures, and/or violate the low-density quadratic composition boundary condition.

In contrast, here we have derived a theoretically correct mixing rule for cubic equations of state (though the procedure is applicable to other equations of state as well), which applies to all mixtures. A unique feature of this mixing rule is that, while it is independent of density when combined with an equation of state, it converges to the activity coefficient model prescribed by the user at high density and at low densities to a virial equation of state with a second virial coefficient that is quadratic in composition. We need to emphasize that it is not the mixing rule alone that produces this density dependence, since the mixing rule is density-independent, but rather the combination of the mixing rule and the equation of state.

This mixing rule provides a unified and consistent way of combining equations of state and excess free energy models to encompass mixtures that previously could only be described by one or the other. Further, not only is the model theoretically correct, but as we have shown here, it is reasonably accurate in describing both simple and complex phase behavior of binary and ternary systems for the diverse systems we have considered. Since we have complete freedom in choosing the expression $\underline{A}^E_\infty$, our mixing rule can be used to describe a wide variety of mixtures and phase behavior, and most importantly, systems that could not previously be described by equations of state.

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Notation

a = equation of state "energy" parameter
$\underline{A}$ = molar Helmholtz free energy
b = equation of state "excluded volume" parameter
B = second virial coefficient
C = numerical constant defined in Eq. A4
D = summation term defined in Eq. A9
F = arbitrary function
g = local composition factor for the NRTL model in Eq. A18
G = molar Gibbs free energy
k = binary interaction coefficient
l = binary interaction coefficient
P = pressure
Q = quadratic sum of second virial coefficients, Eq. A8
R = gas constant
T = temperature
$\underline{V}$ = molar volume
x = mole fraction
x = mole fraction vector

Greek letters

α = NRTL model parameter, Eq. A17
τ = NRTL model binary interaction parameter, Eq. A17
φ = fugacity coefficient
γ = activity coefficient

Superscripts

E = excess property
IG = ideal gas
IGM = ideal gas mixture
IM = ideal mixture

Subscripts

i, j = molecular species
m = mixture
∞ = infinite pressure state

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Appendix

Peng and Robinson (1975) proposed the following modification of the van der Waals equation of state:

$$P=\frac{RT}{(\underline{V}-b)}-\frac{a(T)}{\underline{V}^2+2b\underline{V}-b^2} \tag{A1}$$

If the compressibility factor $P\underline{V}/(RT)$ is expanded in a virial series, the expression for the second virial coefficient is the same as Eq. 5. The Helmholtz free energy departure function for the Peng-Robinson equation at a given temperature, pressure and composition is:

$$\frac{(\underline{A}-\underline{A}^{IGM})}{RT}=-\ln\left[\frac{P(\underline{V}-b)}{RT}\right]+\frac{a}{2\sqrt{2}bRT}\ln\left[\frac{\underline{V}+(1-\sqrt{2})b}{\underline{V}+(1+\sqrt{2})b}\right] \tag{A2}$$

In the limit of pressure going to infinity this becomes:

$$\lim_{P\to\infty}\frac{(\underline{A}-\underline{A}^{IG})}{RT}=\frac{a}{bRT}C \tag{A3}$$

with the constant C being:

$$C=\frac{1}{\sqrt{2}}\ln(\sqrt{2}-1) \tag{A4}$$

Therefore, the excess Helmholtz free energy at infinite pressure $\underline{A}^E_\infty/(RT)$ is:

$$\frac{\underline{A}^E_\infty}{CRT}=\frac{a_m}{b_mRT}-\sum_i x_i\frac{a_i}{b_iRT} \tag{A5}$$

Using the same development as earlier, we obtain the following expressions for equation of state parameters a_m and b_m:

$$b_m=\frac{Q}{(1-D)} \tag{A6}$$

and

$$\frac{a_m}{RT}=Q\frac{D}{(1-D)} \tag{A7}$$

with Q and D defined as:

$$Q=\sum_i\sum_j x_ix_j\left(b-\frac{a}{RT}\right)_{ij} \tag{A8}$$

and

$$D=\sum_i x_i\frac{a_i}{b_iRT}+\frac{\underline{A}^E_\infty}{CRT} \tag{A9}$$

The thermodynamic properties of a mixture can now be calculated. The fugacity coefficient is computed from:

$$\ln\varphi_i=\int_{\underline{V}}^{\infty}\left[\frac{1}{RT}\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}-\frac{1}{\underline{V}}\right]d\underline{V}-\ln\left(\frac{P\underline{V}}{RT}\right) \tag{A10}$$

For the Peng-Robinson equation of state and an arbitrary set of mixing rules for a_m and b_m, we have:

$$\ln\varphi_i=-\ln\left[\frac{P(\underline{V}-b_m)}{RT}\right]+\frac{1}{b_m}\left(\frac{\partial nb_m}{\partial n_i}\right)\left(\frac{P\underline{V}}{RT}-1\right)+\frac{1}{2\sqrt{2}}\left(\frac{a_m}{b_mRT}\right)\left[\frac{1}{a_m}\left(\frac{1}{n}\frac{\partial n^2a_m}{\partial n_i}\right)-\frac{1}{b_m}\left(\frac{\partial nb_m}{\partial n_i}\right)\right]\ln\left[\frac{\underline{V}+b_m(1-\sqrt{2})}{\underline{V}+b_m(1+\sqrt{2})}\right] \tag{A11}$$

The partial derivatives of a_m and b_m are:

$$\frac{\partial nb_m}{\partial n_i}=\frac{1}{(1-D)}\left(\frac{1}{n}\frac{\partial n^2Q}{\partial n_i}\right)-\frac{Q}{(1-D)^2}\left(1-\frac{\partial nD}{\partial n_i}\right) \tag{A12}$$

and

$$\frac{1}{RT}\left(\frac{1}{n}\frac{\partial n^2a_m}{\partial n_i}\right)=D\frac{\partial nb_m}{\partial n_i}+b_m\frac{\partial nD}{\partial n_i} \tag{A13}$$

with the partial derivatives of Q and D given by:

$$\left(\frac{1}{n}\frac{\partial n^2Q}{\partial n_i}\right)=2\sum_j x_j\left(b-\frac{a}{RT}\right)_{ij} \tag{A14}$$

and

$$\frac{\partial nD}{\partial n_i}=\frac{a_i}{b_i RT}+\frac{\ln\gamma_{\infty i}}{C} \tag{A15}$$

with

$$\ln\gamma_{\infty i}=\frac{1}{RT}\frac{\partial n\underline{A}^E_\infty}{\partial n_i} \tag{A16}$$

Though any free energy model could have been used, we used the NRTL model (Renon and Prausnitz, 1965) here for $\underline{A}^E_\infty/(RT)$:

$$\frac{\underline{A}^E_\infty}{RT}=\sum_i x_i\left(\frac{\sum_j x_j\tau_{ji}g_{ji}}{\sum_k x_k g_{ki}}\right) \tag{A17}$$

with

$$g_{ij}=\exp(-\alpha_{ij}\tau_{ij}) \qquad (\alpha_{ij}=\alpha_{ji}) \tag{A18}$$

In this case, the partial derivatives of $\underline{A}^E_\infty/(RT)$ with respect to the mole number of each species, which is the logarithm of the species activity coefficient, is given by:

$$\ln\gamma_{\infty i}=\frac{\sum_j x_j\tau_{ji}g_{ji}}{\sum_k x_k g_{ki}}+\sum_j\frac{x_j g_{ij}}{\sum_k x_k g_{kj}}\left(\tau_{ij}-\frac{\sum_l x_l\tau_{lj}g_{lj}}{\sum_k x_k g_{kj}}\right) \tag{A19}$$

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