

A Flexible Mixing Rule Satisfying the Ideal-Solution Limit for Equations of State

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While the ideal solution is an important reference for the thermodynamic modeling of mixtures, the one-fluid approach for equations of state (EOSs) fails to meet this limit. In this work we present additional evidence supporting this fact. A conceptually new treatment previously proposed for EOSs that meets the ideal solution limit at zero values for the interaction parameters is further developed here. A flexible composition dependence is proposed to cover the entire spectrum from symmetrical to highly asymmetrical, highly nonideal, mixtures. The new composition dependence gives the ideal solution limit, and it accounts for the effect of density on the excess properties of nonideal mixtures. The model treats vapor and liquid phases using a single formalism. For vapor–liquid equilibrium calculations, the new mixing rule can be considered as a hybrid between the well-known φ - φ and γ - φ approaches.

Introduction

The one-fluid approach assumes that the equation of state (EOS) for the mixture is formally identical with the EOS for the pure compounds and that for a mixture the EOS parameters depend on the pure compound parameters, the composition, and additional interaction parameters. Wilczek-Vera and Vera¹ observed that the extension of equations of state (EOSs) to mixtures, using the conventional one-fluid approach, gives expressions which are unable to represent the simple case of an ideal solution over the entire composition range. In a recent publication,² we reinforced such a conclusion through a rigorous derivation for the case of one of the simplest forms of the virial EOS. On the other hand, activity coefficient models, such as the Wilson or the NRTL equations,³ are applicable to nonideal mixtures and satisfy the ideal solution limit at particular values of the interaction parameters. However, these liquid-phase models can be used only if the effect of density on the excess properties can be neglected. A conceptually new approach recently proposed² accounts for the effect of density on the excess properties of nonideal mixtures while keeping the desirable feature of giving the ideal solution limit for null interaction parameters. However, phase equilibria calculation results showed² that for highly nonideal systems the mixture molar volume required a more flexible composition dependence. The purpose of the present study is to propose such a flexible composition dependence and to present some additional evidence to support the hypothesis of the impossibility of representing ideal solutions using the one-fluid approach.

Ideal Solution

For the ideal solution the mixture molar volume $v^{\text{id.sol}}$ is a linear mole fraction weighed average of the pure

compound molar volumes v_i . Thus, for any composition \mathbf{x} and for any value of the pressure, between zero and the pressure of the mixture P , at the system temperature T :

$$v^{\text{id.sol.}} = \sum_{i=1}^N x_i v_i \quad \{\text{at } T, \text{ for any } \mathbf{x} \text{ and pressure } \in (0, P)\} \quad (1)$$

The i th element of vector \mathbf{x} is x_i , the mole fraction of component i in the mixture, and N is the number of components. All expressions for the thermodynamic properties of the ideal solution can be derived from eq 1, commonly known as Amagat's law.

From exact thermodynamics, the fugacity coefficient of component q in a mixture, $\hat{\varphi}_q$, is given by

$$\ln \hat{\varphi}_q = \frac{1}{RT} \int_0^P \left(\bar{v}_q - \frac{RT}{P} \right) dP \quad (2)$$

where \bar{v}_q is the partial molar volume of component q in the mixture and R is the universal gas constant. From eq 1 it is clear that for an ideal solution the partial molar volume of component q , $\bar{v}_q^{\text{id.sol.}}$, is equal to the pure compound volume v_q at any pressure from zero pressure to the mixture pressure and at any composition \mathbf{x} . Thus, the fugacity coefficient of component q in an ideal solution is equal to the fugacity coefficient of the pure compound q , φ_q , at the same pressure P and temperature T of the ideal solution.

$$\ln \hat{\varphi}_q^{\text{id.sol.}} = \ln \varphi_q \quad (3)$$

Because the activity coefficient of component q , in the Lewis sense, is equal to the fugacity coefficient of component q in the mixture ($\hat{\varphi}_q$) divided by the pure compound fugacity coefficient (φ_q), eq 3 implies that for an ideal solution the activity coefficient is unity.¹ It is important to note that, by definition, the ideal solution at fixed temperature and composition obeys Amagat's law at all pressures between zero and the pressure of

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the system. If Amagat's law is satisfied at a particular pressure, not necessarily the system is ideal.³

Virial EOS and the Ideal Solution Limit

A simple form of the truncated virial EOS is

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} \quad (4)$$

where z is the compressibility factor and B is the mixture (or pure-compound) second virial coefficient. In a previous publication² we demonstrated that the representation of ideal solutions by eq 4 would force the cross second virial coefficients B_{ij} to depend on pressure. This clearly violates the restrictions that must be met by the coefficients of the virial expansion written in terms of the inverse molar volume. Hence, eq 4 cannot represent ideal solutions even when its deviation from Amagat's law may be rather small. From this result we inferred² that commonly used EOSs, such as the cubic EOSs, cannot represent ideal solutions. These semiempirical models have mathematical forms more complex than that of eq 4.

The virial EOS, expanded in terms of pressure and truncated after the second virial coefficient term, is simpler than eq 4. Because of its extreme simplicity, this form is able to meet the ideal solution limit.² However, such simplicity implies a very limited range of practical applicability.

EOSs of Common Use

In this work we concentrate on the case of the well-known Peng–Robinson EOS (PR-EOS),⁴ as a typical example of a cubic EOS. The PR-EOS and its variants have found widespread application in practical calculations. The PR-EOS has the form

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2} \quad (5)$$

where a and b are respectively the energetic and the covolume parameters for the mixture. For mixtures, a and b should be functions of composition and temperature only. The original PR-EOS⁴ uses a conventional quadratic mixing rule for a and a linear mixing rule for b .

It would be desirable to find expressions for a and b such that eq 5 gives a mixture volume matching eq 1 at any temperature, pressure, and composition. We identify as $a^{\text{id.sol.}}$ and $b^{\text{id.sol.}}$ the ideal solution expressions for a and b . The parameters $a^{\text{id.sol.}}$ and $b^{\text{id.sol.}}$ should depend at most on composition and temperature but not on pressure, density, or phase identity. To search for possible expressions of $a^{\text{id.sol.}}$ and $b^{\text{id.sol.}}$, we do not impose an a priori composition dependence on a and b .

As a first step in the search for $a^{\text{id.sol.}}$ and $b^{\text{id.sol.}}$, we study a particular case. We impose an ideal solution behavior on a binary system. Hence, we write eq 1 for a binary mixture, introduce the result into eq 5, and obtain a relationship connecting $a^{\text{id.sol.}}$ and $b^{\text{id.sol.}}$. Thus, we write

$$a^{\text{id.sol.}} = \left(-P + \frac{RT}{v_1x_1 + v_2x_2 - b^{\text{id.sol.}}} \right) [(v_1x_1 + v_2x_2)^2 + 2b^{\text{id.sol.}}(v_1x_1 + v_2x_2) - (b^{\text{id.sol.}})^2] \quad (6)$$

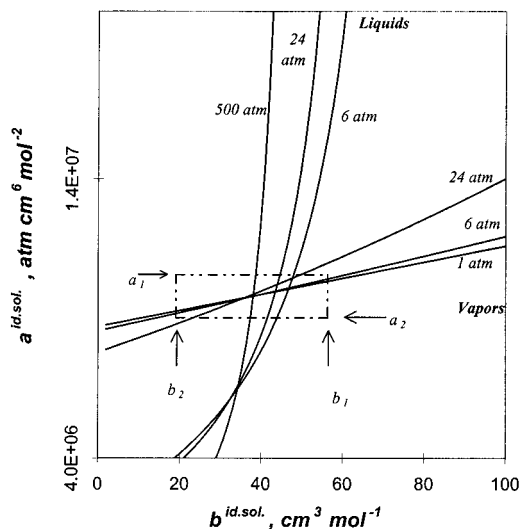


Figure 1. Relation between the PR-EOS a and b at ideal solution conditions for the system propane (1)–water (2) at 340 K. $x_1 = x_2 = 0.5$.

where v_1 and v_2 are respectively the molar volume of pure component 1 and the molar volume of pure component 2 at T and P . At fixed pressure, temperature, composition, and phase identity, eq 6 defines a curve $a^{\text{id.sol.}}$ vs $b^{\text{id.sol.}}$. Figure 1 shows a set of such curves, for different pressures and phase identities. Figure 1 corresponds to an equimolar mixture of propane (1) and water (2), at a temperature $T = 340$ K. The pure-compound parameters a_1 and a_2 were obtained from the DIPPR⁵ experimental vapor pressures tables using the method of Soave.⁶ We used the DIPPR⁵ critical temperatures and pressures to compute the critical values of a_1 , a_2 , b_1 , and b_2 . For reference we included in Figure 1 a window defined by the values of b_1 and b_2 and of a_1 and a_2 at $T = 340$ K. At the scale of Figure 1 it appears that the curves corresponding to a vapor phase have a common intersection point inside the pure compounds a – b window and that the three liquid-phase curves have a common intersection point outside the a – b window. However, these common intersection points do not really exist, as could be seen using proper axis scales. If it were possible to find a reference ideal solution mixing rule for the propane (1)–water (2) system, dependent at most on temperature and composition, a common intersection point should exist for all six curves of Figure 1. In other words, Figure 1 tells that the only way to define reference ideal solution mixing rules for the propane (1)–water (2) system would be to let the parameters $a^{\text{id.sol.}}$ and $b^{\text{id.sol.}}$ be both pressure-dependent and phase-identity-dependent. Hence, for this system, we conclude that mixing rules for a and b , depending only on temperature and composition, cannot satisfy the ideal solution limit, at all temperatures, pressures, and phase identities. Although, rigorously, this conclusion is only valid for the propane (1)–water (2) system, this particular case also supports the hypothesis of the impossibility of representing ideal solutions, in a range of conditions, through EOSs using the one-fluid approach. A clear implication comes from this hypothesis: mixing rules which combine excess Gibbs energy (g^E) models with EOSs will not, in general, recover the ideal solution behavior at conditions at which the imported liquid-phase model gives a zero value for g^E .

After presenting the above additional evidence on the impossibility of representing ideal solutions using EOSs

in a conventional way, we focus on the formulation of a flexible composition dependence for a mixing rule for EOSs. This formulation, based on our previous work,² is useful for highly nonideal mixtures and meets the ideal solution limit for zero values of interaction parameters.

Basic Concepts

From exact thermodynamics for a homogeneous mixture, it can be shown that the partial derivative of the molar excess Gibbs energy g^E with respect to the absolute pressure P , at constant temperature and composition, is equal to the excess molar volume v^E . Hence, we write

$$\left(\frac{\partial g^E}{\partial P}\right)_{T,x} = v^E \quad (7)$$

Here the word "excess" implies the difference between the properties of the real fluid and the properties of the ideal solution compared at the same temperature, pressure, and composition. The fluid can be a vapor mixture or a liquid mixture.

Excess Gibbs energy models for liquid mixtures, e.g., Wilson or NRTL,³ ignore the effect of pressure on g^E . Hence, from eq 7, these models necessarily give zero excess volume v^E ; i.e., they consider a nonideal mixture to have an ideal solution volumetric behavior.

The conceptually new approach we previously proposed² considers nonzero values for v^E , thus making the excess Gibbs energy g^E pressure-dependent according to eq 7. This approach² accounts for pressure, temperature, and composition effects on v^E . The fundamental concept of this approach² consists of the formulation of an expression for the excess volume in terms of composition and of the pure-compound molar volumes v_i . The excess volume v^E depends on pressure indirectly, i.e., through the pressure dependence of the molar volumes of the pure compounds. A particular v_i is related to temperature and pressure according to a particular EOS. Different pure compounds may be represented using different EOSs. The most important feature of this approach² is that it recovers the ideal solution behavior when the binary parameters are set equal to zero.

New Form of the Ideal-Solution-Based EOS Approach (ISB-EOS)

For highly asymmetric nonideal mixtures, treated with the new ISB-EOS approach, we propose the following expression for the excess molar volume v^E :

$$v^E = \frac{\sum_{j=1}^N x_j x_j \epsilon_{jj} \Lambda_{jj}}{\sum_{i=1}^N \Lambda_{ii} x_i} = v - v^{\text{id.sol.}} \quad (8)$$

where v is the molar volume of the mixture and ϵ_{ij} , which depends on pressure through volumetric information of the pure compounds i and j , has units of molar volume and relates linearly to the excess molar volume v^E . The binary parameter Λ_{ji} is dimensionless and characteristic of the ji pair. If the values of all Λ_{ji} parameters are equal to unity, the excess volume given by eq 8 becomes quadratic in composition:

$$v^E = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \epsilon_{ji} \quad \text{for all } \Lambda_{lk} = 1 \quad (9)$$

For values of Λ_{ji} different from unity, the composition dependence of eq 8 is more flexible than a quadratic dependence. Equation 8 is a pair-based model and overcomes the limitations of a quadratic dependence without resorting to ternary parameters. It is convenient to define Λ_{ji} as the exponential of the parameter λ_{ji} . Hence, we write

$$\Lambda_{ij} = \exp(-\lambda_{ij}) \quad (10)$$

The parameter λ_{ij} is also dimensionless and sets the value of Λ_{ij} . The convenience of using λ_{ij} as the independent variable, instead of Λ_{ij} , is that for any finite value of λ_{ij} the variable Λ_{ij} is positive. Thus, the right-hand side of eq 8 cannot become undefined because of a null denominator when adjusting the parameters λ_{ij} . The appearance of the variable Λ_{mn} in both the numerator and denominator of eq 8 reduces the instabilities associated with the exponential function of eq 10 when adjusting λ_{mn} . Although not explored in this work, Λ_{ij} might be considered to be temperature-dependent with λ_{ij} proportional to $(RT)^{-1}$.

Integrating eq 7, between zero pressure and the system pressure P , using eq 8 for the excess volume, we obtain the following expression of the excess Gibbs energy g^E :

$$\frac{g^E}{RT} = \frac{\sum_{j=1}^N x_j x_j \tau_{jj} \Lambda_{jj}}{\sum_{i=1}^N \Lambda_{ii} x_i} \quad (11)$$

where τ_{ij} is the value of the integral of ϵ_{ij} from zero pressure up to the pressure of the system, over the product RT :

$$\tau_{lk} = \frac{1}{RT} \int_0^P \epsilon_{lk} dP \quad (12)$$

To obtain eq 11, we have used the boundary condition $g^E = 0$ at the limit of infinite volume or, equivalently, $P = 0$. Notably, eq 11 can also be written as

$$\frac{g^E}{RT} = \frac{\sum_{j=1}^N x_j \tau_{jj} \Lambda_{jj}}{\sum_{i=1}^N \Lambda_{ii} x_i} \quad (13)$$

Equation 13 has the same formal composition dependence as the NRTL model³ for g^E . The essential difference with the NRTL model is that in eq 13 τ_{ji} is not only a function of temperature but also a function of pressure. Hence, while the original NRTL model³ gives a zero excess volume, because of the fact that it considers that the excess Gibbs energy is independent of pressure in eq 7, when eq 13 is combined with eq 7, a nonzero excess volume, given by eq 8, is obtained.

Definition of the Variable ϵ_{ij}

The next step is to define the dependence of ϵ_{ij} on pressure through pure compound volumes and binary

parameters. In this work we set ϵ_{ij} to have the following form:

$$\epsilon_{ij} = A_{ij}[(v_i - v_j) - F(v_i^B - v_j^B)] \quad (14)$$

where A_{ij} is a dimensionless binary parameter which may depend on temperature but not on pressure or composition and v_i^B is the virial molar volume of pure compound i , at the temperature T and pressure P of the system, calculated as explained below. The pure compound i molar volume, v_i , at T and P , is calculated from a pure compound EOS; F is a variable that controls the behavior of the model at low density, and its value can be either zero or unity. By construction, the relationship between the mixture volume and any of the pure compound v_i 's or v_i^B 's is linear. In fact, eq 14 is simpler and has a better pressure dependence than the expression used in our previous work.²

Calculation of Pure Compound Virial Molar Volumes

We calculate the virial molar volume v_i^B for pure compound i , at the T and P of the system, using the simplest form of the virial EOS expanded in terms of pressure and truncated after the second virial coefficient term:

$$v^B = \frac{RT}{P} + B \quad (15)$$

For consistency, the value of B_i that we use in eq 15 is not the experimental value of the second virial coefficient at T but the value predicted by the EOS used for the pure compound i . For the purposes of evaluating the second virial coefficient from volumetric data, it is preferable to use its definition as the infinite volume limit of the product $v(z - 1)$. For the purposes of this work, in which the analytical form of the EOS is known, we use the equivalent exact definition of the second virial coefficient B :

$$B = \lim_{v \rightarrow \infty} \left[-v^2 \frac{\partial z}{\partial v} \right]_T \quad (16)$$

where z is the compressibility factor obtained from the EOS chosen for representing the particular pure compound. For the PR-EOS,⁴ for example, eq 16 results in the following expression for B_i :

$$B_i = b_i - a_i/RT \quad (17)$$

For noncubic EOSs, the EOS of compound i also sets the value of B through eq 16. In any case, using the value of the particular EOS second virial coefficient in eq 15, instead of the experimental value, guarantees that all v_i tend to v_i^B as the density is reduced. Hence, for $F = 1$, ϵ_{ij} (eq 14) tends to zero at low density, forcing v^E to be zero at low pressure (eq 8). For $F = 0$ such a restriction is not imposed.

Liquid-Volume Sensitivity with Respect to Pressure

The mixture molar volume is a function of the binary variables ϵ_{ij} , as dictated by eq 8. In turn, the binary variables ϵ_{ij} are a function of the pure compound molar volumes and virial volumes according to eq 14. For the liquid mixture, the pure compound liquid molar volumes

are quite insensitive to pressure while the virial volumes depend on pressure according to eq 15. Thus, to see the effect of pressure on the ϵ_{ij} variables and on the liquid mixture molar volume, from eq 15, we write

$$v_i^B - v_j^B = \left(\frac{RT}{P} + B_i \right) - \left(\frac{RT}{P} + B_j \right) = B_i - B_j \quad (18)$$

Because the pure compound second virial coefficients depend only on temperature, eq 18 shows that the difference $v_i^B - v_j^B$ is independent from pressure. This is a major advantage of the present treatment with respect to the form used in our previous work.² In some cases, the form used previously resulted in a strong pressure dependence for the mixture liquid molar volume and limited the variation of the binary parameter to a narrow range, beyond which negative values for the mixture volume were obtained. The new formulation represented by eq 14 removes the problem of high sensitivity of the mixture liquid volume with respect to pressure.

Expression for Variable τ_{rj}

From eqs 2, 12, and 14, we obtain

$$\tau_{rj} = A_{rj} \ln \left[\frac{\varphi_r \left(\frac{\varphi_j^B}{\varphi_r^B} \right)^F}{\varphi_j} \right] \quad (19)$$

where φ_j is the fugacity coefficient of the pure compound j at the temperature and pressure of the system and φ_j^B is the pure compound virial fugacity coefficient arising from eqs 2 and 15, i.e.,

$$\varphi_j^B = \exp(B_j P/RT) \quad (20)$$

To obtain eq 19, we added and subtracted the term RT/P , where necessary in eq 14, to obtain expressions in terms of pure compound fugacity coefficients. As shown below, this leads to an expression for the fugacity coefficient of a given component in the mixture $\hat{\varphi}_q$ (or for the activity coefficient), which is a function of the pure compound fugacity coefficients.

The particular form we have adopted for the relationship between ϵ_{ij} and the pure volumes v_i , v_j , v_i^B , and v_j^B (eq 14) is somewhat arbitrary. However, to obtain a solution for the integral of eq 12 in terms of pure compound fugacity coefficients, ϵ_{ij} must depend linearly on differences between pure compound molar volumes as we propose in eq 14.

Binary Parameters and Limits

The binary parameters of the model are A_{ij} and λ_{ij} . Both parameters are dimensionless and may be considered to be functions of temperature but not a function of pressure or composition. We observe that eq 8 meets the following limits:

(a) The molar volume of the mixture gives a total volume, which is a homogeneous function of first degree in the numbers of moles.

(b) For zero values of all binary parameters A_{ij} , the excess volume is zero and hence the ideal solution behavior is recovered. If the binary parameter A_{ij} is made temperature-dependent, then it should vanish as the temperature tends to infinity, so that the ideal solution is recovered at high temperature.

(c) If all λ_{ij} values are set to zero, then the excess volume has a quadratic composition dependence.

(d) The proper limit of the pure compound is met independently of the values of A_{ij} and λ_{ij} used. We set then

$$A_{ij} = 0 \quad (21)$$

and

$$\lambda_{ij} = 0 \quad (22)$$

(e) Equation 8 satisfies the restriction of invariance of the molar volume of the mixture.⁷

(f) Virial conditions are defined here as the conditions of temperature and pressure for which all pure compound EOSs, of the components of the mixture, tend to the virial EOS (eq 15). At virial conditions, for $F = 1$, all variables ϵ_{ij} tend to zero, giving a zero excess volume; i.e., the volume of the mixture is given by eq 1. Combining eq 1 with eq 15 for the pure compound virial volumes, it can be shown that the mixture also behaves according to eq 15, giving the following expression for the mixture second virial coefficient, which thus corresponds to an ideal virial mixture:

$$B_{\text{mix}} = \sum_{i=1}^N \sum_{j=1}^N x_i x_j B_{ij} \quad (23)$$

with

$$B_{ij} = \frac{B_i + B_j}{2} \quad (24)$$

Although for $F = 0$, and for nonzero λ_{ij} values, the mixture at low density does not behave as a virial mixture, it properly approaches the ideal gas limit, as discussed below. If all λ_{ij} values are zero and $F=0$, then, at virial conditions, the mixture behaves according to eq 15 with a mixture second virial coefficient given by eq 23 with the following expression for B_{ij} :

$$B_{ij} = \frac{B_i + B_j}{2} + A_{ij}(B_i - B_j) \quad (25)$$

In this case the expression for the mixture second virial coefficient, i.e., eq 23 coupled with eq 25, corresponds to a nonideal virial mixture.

(g) The study of eq 8 for a binary system for which $\lambda_{ij} = \lambda_{ji} = 0$, i.e., a mixture for which the volume shows a quadratic composition dependence, shows that it is convenient to set

$$A_{ij} = -A_{ji} \quad \text{if } \lambda_{ij} = \lambda_{ji} = 0 \quad (26)$$

If for a given binary either λ_{ij} or λ_{ji} are different from zero or both parameters are different from zero, then A_{ij} and A_{ji} can be independent, because the composition dependence for the binary ij is not quadratic. The maximum possible number of adjustable parameters to represent a binary mixture is then four: A_{ij} , A_{ji} , λ_{ij} , and λ_{ji} .

(h) Ideal gas conditions are those at which all pure compound EOSs tend to the ideal gas law. At ideal gas conditions all ϵ_{ij} variables tend to zero, regardless of the value of F , and hence the mixture also behaves as an ideal gas. In fact, at ideal gas conditions the virial EOS, eq 15, also tends to the ideal gas law.

In the present work we do not impose any special limit at infinite pressure. This makes it possible to remove the restriction of the existence of a strictly positive covolume b_i for each of the pure compound EOSs and the covolume may be zero, as in the case of some EOSs. The boundary condition at infinite volume and the effect of the potential existence of finite volume roots at a pressure equal to zero are discussed further in the appendix.

Within the context of the present work, for each pure compound, the method requires having an EOS able to represent the liquid–vapor transition at subcritical temperatures. However, the method could also be used for modeling the volumetric behavior of gas mixtures. For instance, the pure compounds could be represented using eq 4, and eq 8 can be used for the mixture. For pure compounds, eq 4 gives more accurate pure compound volumes and fugacities than eq 15. In this case, the modeling of the gas mixture would be based on a reference term, which corresponds to the (reasonable) isometric mixing of the pure gaseous components, in contrast with the conventional use of eq 4 for mixtures.

Fugacity and Activity Coefficients

The activity coefficient of component q , in the Lewis convention, is obtained through differentiation of g^E (eq 11) with respect to the number of moles of compound q .

$$\ln \gamma_q = \frac{\sum_{j=1}^N x_j \tau_{jq} \Lambda_{jq}}{\sum_{l=1}^N \Lambda_{lq} X_l} + \sum_{j=1}^N \frac{x_j \Lambda_{qj}}{\sum_{l=1}^N \Lambda_{lj} X_l} \left(\tau_{qj} - \frac{\sum_{r=1}^N x_r \tau_{rj} \Lambda_{rj}}{\sum_{l=1}^N \Lambda_{lj} X_l} \right) \quad (27)$$

Using the fact that the activity coefficient of component q is equal to the fugacity coefficient of component q in the mixture ($\hat{\varphi}_q$) divided by the pure compound fugacity coefficient (φ_i), we write

$$\ln \hat{\varphi}_q = \ln \varphi_q + \frac{\sum_{j=1}^N x_j \tau_{jq} \Lambda_{jq}}{\sum_{l=1}^N \Lambda_{lq} X_l} + \sum_{j=1}^N \frac{x_j \Lambda_{qj}}{\sum_{l=1}^N \Lambda_{lj} X_l} \left(\tau_{qj} - \frac{\sum_{r=1}^N x_r \tau_{rj} \Lambda_{rj}}{\sum_{l=1}^N \Lambda_{lj} X_l} \right) \quad (28)$$

From eqs 19 and 28, we see that $\hat{\varphi}_q$ depends on the composition, binary parameters, pure compound fugacity coefficients, φ_i , and pure compound virial fugacity coefficients, φ_i^B . For zero values of all A_{ij} 's, the ideal values of the partial molar volume and of the fugacity coefficient of component q in the mixture (eq 3) are obtained, because ϵ_{ij} and τ_{ij} vanish when A_{ij} is equal to zero. In this latter case the activity coefficient γ_q is equal to unity for each component.

Note that, in contrast with conventional theories for liquid solutions, the activity coefficient γ_q given by eq 27 depends not only on temperature, composition, and binary parameters but also on pressure and phase

Table 1. Sample Values of Parameter A_{12} for the Simplest Variant of the Present Model

system	pressure range (atm)	temp (K)	ref 2		this work	
			A_{12} value ^a	AAD % ^{a,b}	A_{12} value ^c	AAD % ^c
1-propanol (1)–2-methyl-1-propanol (2)	0.207–0.326	343.15	0	0.29	0	0.29
benzene (1)–octane (2)	0.191–0.853	348.15	0.1025	1.19	0.1162	0.96
<i>n</i> -hexane (1)–benzene (2)	0.515–0.758	333.15	0.6224	0.65	0.6308	0.60
propylene (1)–propane (2)	23.3–27.8	338.71	0.1441	0.04	0.1440	0.03

^a $A_{21} = -A_{12}$. ^b AAD % = average absolute value percent relative deviation in the calculated bubble pressure. ^c $F = 0$, $\lambda_{12} = \lambda_{21} = 0$, and $A_{21} = -A_{12}$.

identity, through the pure compound fugacity coefficients and pure compound virial fugacity coefficients (eq 19).

Equations 27 and 28 can be used for phase equilibrium calculations. For the case of vapor–liquid equilibrium, the necessary condition of equilibrium is

$$\hat{\phi}_i^V y_i = \hat{\phi}_i^L x_i \quad i = 1, N \quad (29)$$

For calculating a vapor–liquid equilibrium at given temperature T and pressure P , the liquidlike and vaporlike fugacity coefficients and virial fugacity coefficients of the pure compounds at T and P are calculated first. Then, the remaining iteration variables are only the phase compositions. For a particular assumption of the liquid-phase composition, $\hat{\phi}_i^L$ is calculated using the liquidlike pure compound fugacity coefficients computed in the previous step. Similarly, for a particular assumption of the vapor-phase composition, $\hat{\phi}_i^V$ is calculated using the vaporlike pure compound fugacity coefficients calculated previously. There is no need to calculate the mixture volume (eq 8) during the iterative solution of the set of eq 29. However, when the calculation converges, it is advisable to calculate the molar volumes of the phases, using eq 8, to make sure that they are not negative.

Results

For this discussion we identify our previously proposed model² as the ZBV1 model. The simplest possible form of the present model is obtained by setting $F = 0$ and $\lambda_{ij} = \lambda_{ji} = 0$. In such a case the composition dependence is quadratic (eq 9) and the condition $A_{ij} = -A_{ji}$ (eq 26) is used. The variable ϵ_{ij} then becomes

$$\epsilon_{ij}|_{F=0} = A_{ij}(v_i - v_j) \quad (30)$$

The choice of $F = 0$, $\lambda_{ij} = \lambda_{ji} = 0$, and $A_{ij} = -A_{ji}$ makes the present model different from the ZBV1 model only in the expression for ϵ_{ij} . The ZBV1 ϵ_{ij} expression had a more complex form than eq 30 because of an additional term. Such a term depended on the pure compound volumes, virial molar volumes, second virial coefficients, and covolume parameters. The ZBV1 model did not allow cancellation of the virial contribution.

In this study we tested first the effect of the simplification that the choice of $F = 0$, $\lambda_{ij} = \lambda_{ji} = 0$, and $A_{ij} = -A_{ji}$ introduces with respect to the ZBV1 model,² for the cases where the ZBV1 model gives a very good correlation of vapor–liquid equilibrium data. Those cases correspond to Figures 1–7 of ref 2, i.e., to the systems 1-propanol (1)–2-methyl-1-propanol (2), benzene (1)–octane (2), *n*-hexane (1)–benzene (2), propylene (1)–propane (2), and ethylene (1)–ethane (2). The experimental database and the EOS for the pure compounds used here are the same than those used in a previous work.² For these cases, the new model produces a

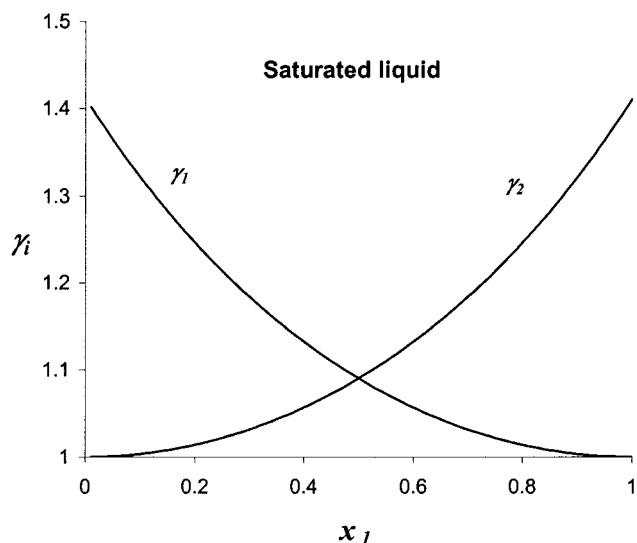


Figure 2. Predicted activity coefficients for the saturated liquid phase of the system benzene (1)–octane (2) at 348.15 K as a function of the liquid-phase composition. $A_{12} = -A_{21} = 0.1162$, $F = 0$, and $\lambda_{12} = \lambda_{21} = 0$.

correlation of results with a quality indistinguishable from that obtained with the ZBV1 model. The pressure vs composition graphs or the relative volatility vs composition graphs are not reproduced here because they are practically identical with Figures 1–7 of the previous publication.² For this test, we adjusted one parameter per isotherm. The resulting A_{12} values differ only slightly from those previously reported for the ZBV1 model, as illustrated for some systems in Table 1, where we also report for both cases the corresponding average error in the calculated bubble pressure. As can be seen in Table 1, both models represent equally well the bubble pressure.

As shown in Table 1, the parameter A_{12} equals zero for the system 1-propanol (1)–2-methyl-1-propanol (2). Hence, the liquid and vapor phases are considered to be ideal. In this case the experimental information used by the model was only the pure compound critical temperatures and pressures and the pure compound saturation pressures at the system temperature.

Figure 2 shows the predicted activity coefficients as a function of the liquid-phase composition x_1 , for the saturated liquid phase of the system benzene (1)–octane (2) at 348.15 K, using $F = 0$, $\lambda_{ij} = \lambda_{ji} = 0$, and $A_{ij} = -A_{ji}$. Figure 2 illustrates that the simplest form of this model is normally associated with a symmetrical pattern for the activity coefficients of the saturated phases. The ZBV1 model representation of the vapor–liquid equilibrium of the system *n*-hexane (1)–ethanol (2) at 313.15 K was not satisfactory.² Figure 3 compares the results obtained with the ZBV1 model and with the present model for this system. In comparison with the ZBV1 model, the present model represents better the data, at

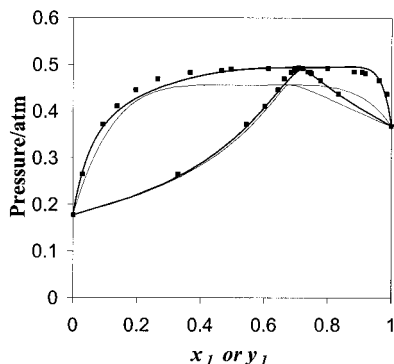


Figure 3. Vapor-Liquid equilibrium for the system hexane (1)-ethanol (2) at 313.15 K. Experimental data are as in ref 2. Thick line: present model with $A_{12} = 0.7006$, $A_{21} = -1.284$, $F = 1$, and $\lambda_{12} = \lambda_{21} = -1.107$. Thin line: ZBV1 model.²

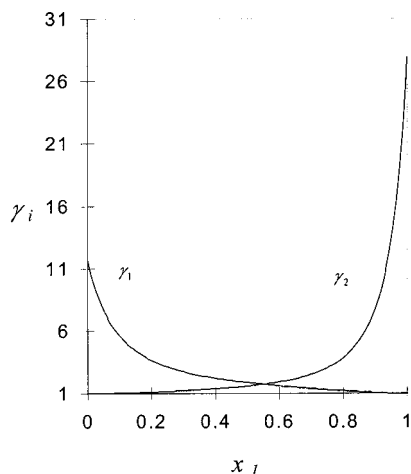


Figure 4. Predicted saturated liquid-phase activity coefficients for the system hexane (1)-ethanol (2) at 313.15 K.

the cost of using two additional parameters. Because $F = 1$, the correlation presented in Figure 3 satisfies the virial limit for the mixture.

Figure 4 shows the predicted saturated liquid-phase activity coefficients, as a function of the liquid-phase composition, for the system hexane (1)-ethanol (2) at 313.15 K. These activity coefficients correspond to the hexane (1)-ethanol (2) liquid at its bubble pressure. The low correlation error shown in Figure 3 could only be achieved with the high asymmetry of the activity coefficients depicted in Figure 4. In fact, the present work was motivated by the search for a modification of the ZBV1 model,² to make possible the representation of highly asymmetric systems such as hexane (1)-ethanol (2).

Figures 5 and 6 show results for the vapor-liquid equilibrium of the high-pressure azeotropic system carbon dioxide (1)-ethane (2) at 250 K. The model produces the results shown in Figures 5 and 6 using a single binary parameter. In this case the excess volume composition dependence is quadratic, and hence the activity coefficients of the saturated phases show symmetry. The results can be improved using more parameters, i.e., a nonquadratic composition dependence. In such a case the resulting activity coefficients show asymmetry.

Of special interest is the system diethylamine (1)-methanol (2), which presents two azeotropes at 398.58 K.⁸ Figure 7 shows the experimental and the present model bubble pressure as a function of the liquid-phase

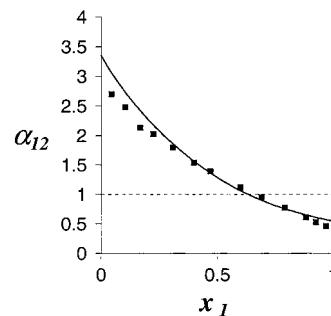


Figure 5. Relative volatility for the system carbon dioxide (1)-ethane (2) at 250 K as a function of the liquid-phase composition. Experimental data are as in ref 2. Solid line: present model with $F = 0$, $A_{12} = -A_{21} = 1.855$, and $\lambda_{12} = \lambda_{21} = 0$.

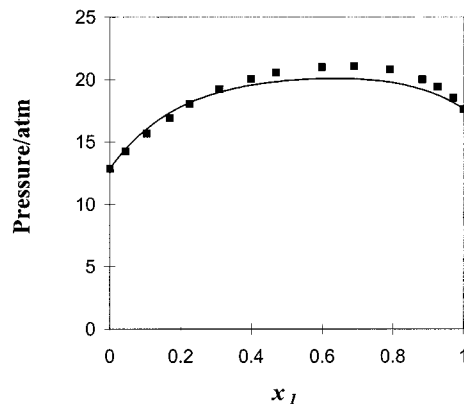


Figure 6. Bubble pressure for the system carbon dioxide (1)-ethane (2) at 250 K as a function of the liquid-phase composition. Experimental data are as in ref 2. Solid line: present model with $A_{12} = -A_{21} = 1.855$, $F = 0$, and $\lambda_{12} = \lambda_{21} = 0$.

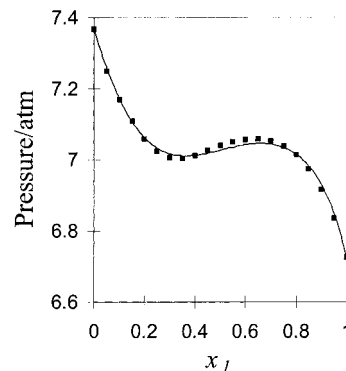


Figure 7. Bubble pressure for the diazeotropic system diethylamine (1)-methanol (2) at 398.58 K. ■: experimental data.⁸ Solid line: present model with $A_{12} = -4.951$, $A_{21} = -5.274$, $F = 1$, and $\lambda_{12} = \lambda_{21} = 1$.

composition. This system shows minimum and maximum pressure azeotropes. The correlation is satisfactory using three parameters. Figure 8 shows the distribution coefficient of diethylamine (1) as a function of its liquid-phase mole fraction. The curve intersects the unity line twice at nontrivial composition values. The fit of the distribution coefficient is also satisfactory. Figure 9 shows the predicted saturated liquid-phase activity coefficients for diethylamine (1)-methanol (2) at 398.58 K. Although the system does not follow a quadratic mixing rule, this does not imply a high degree of non-ideality; i.e., the activity coefficients differ moderately from unity. From Figure 9, the system diethylamine (1)-methanol (2) shows a special type of symmetry: the curves seem to be symmetrical with respect to the point

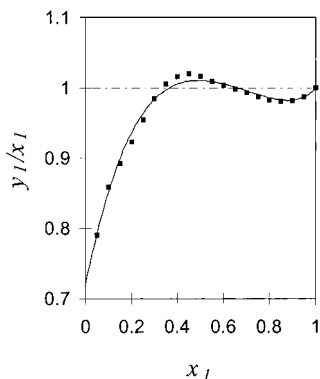


Figure 8. Distribution coefficient for the diazeotropic system diethylamine (1)–methanol (2) at 398.58 K. ■: experimental data.⁸ Solid line: present model with $A_{12} = -4.951$, $A_{21} = -5.274$, $F = 1$, and $\lambda_{12} = \lambda_{21} = 1$.

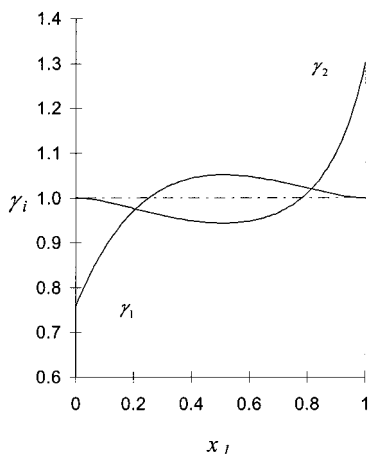


Figure 9. Predicted saturated liquid-phase activity coefficients for the diazeotropic system diethylamine (1)–methanol (2) at 398.58 K. $A_{12} = -4.951$, $A_{21} = -5.274$, $F = 1$, and $\lambda_{12} = \lambda_{21} = 1$.

located at $x_1 = 0.5$ and $\gamma = 1$. Polyazeotropy does not necessarily imply high nonideality.

For all systems studied it was possible to find a liquidlike volume and a vaporlike volume for each pure compound at the system temperature and pressure, using the PR-EOS⁴ with the energy parameter adjusted to give an exact reproduction of the pure compound experimental vapor pressure. When one of these roots does not exist, an extrapolation scheme has to be used to obtain acceptable values of the fugacity coefficients. This problem has not been addressed in the present work.

In this work we have made no attempt to predict the binary parameters from pure compound properties. The present approach should be seen as a method to extend to higher pressures the use of the ideal solution as a reference system for the calculation of thermodynamic properties that can normally be obtained with the conventional one-fluid approach for EOSs. In its present state of development, the model presented here is not continuous in the vicinity of the gas–liquid critical point of a mixture, and hence it should not be used at conditions close to those of the critical gas–liquid state. This discontinuity seems to be present even in the event of having available extrapolation schemes to find proper values of the phase volumes when necessary. However, the calculation of liquid–liquid critical points as well as the representation of gas–gas equilibria seems possible.

Conclusions

In this work we have presented additional evidence supporting the hypothesis of the impossibility to represent ideal solutions for EOSs using the one-fluid approach. If this hypothesis is generally true, the clear conclusion is that approaches that combine EOSs and models of the excess Gibbs energy (g^E) for liquids cannot give the ideal solution limit when $g^E = 0$ for the imported liquid model. To overcome such a drawback, we have proposed here a modeling approach that, as in a previous work,² uses EOSs and meets the ideal solution limit at zero values for the interaction parameters. In this work we have introduced a more flexible composition dependence into the model, making it possible to treat from symmetrical to highly asymmetrical systems, without ignoring the effect of density on the excess properties. The representation of the binary vapor–liquid equilibrium we have obtained here is satisfactory for all systems studied.

Appendix: Discussion of the Boundary Condition for g^E at Infinite Volume ($P = 0$)

In the limiting condition of very large volume, at constant temperature, the pressure decreases toward zero as the system approaches ideal gas behavior at infinite volume. Because the ideal gas mixture is an ideal solution, all of the excess properties of the system tend toward zero. This limiting behavior, used to obtain eq 11 of the text, should not be confused with the evaluation of excess functions at $P = 0$ for liquid mixtures using a pressure-explicit EOS able to represent the liquid and vapor properties. These EOSs usually exhibit liquid-type volume roots at subcritical temperatures at $P = 0$. For the sake of discussion, we consider the case that the temperature is such that for every pure compound the corresponding EOS gives a liquidlike root at zero pressure. From eqs 19 and 20 it can be shown that as pressure tends to zero the liquid τ_{rj} tends to

$$\tau_{rj}|_{\text{liq}, P=0} = A_{rj} \ln[P\varphi_r/P\varphi_j] \quad (\text{A-1})$$

The ratio $P\varphi_r/P\varphi_j$ is equal to the ratio of the fugacity of the liquid pure compound r over the fugacity of the liquid pure compound j , both computed at zero pressure. It can be shown⁹ that this ratio has a finite value which generally leads to a nonzero excess energy at zero pressure for the (liquid) mixture using eq 11. Hence, as is the case for EOSs coupled to one-fluid mixing rules, eq 11 is able to generate a nonzero excess Gibbs energy at zero pressure, if pure compound zero-pressure liquid roots exist either naturally or because of extrapolation schemes. However, the mixing rule gives a zero excess Gibbs energy for zero pressure at infinite volume, as required. Following standard pure compound EOS thermodynamics, we use the equivalence between the fugacity coefficients calculated with volume-explicit or pressure-explicit EOSs⁹, i.e.,

$$\ln \varphi_q = \frac{1}{RT} \int_0^P \left(v_q - \frac{RT}{P} \right) dP = \int_{v_q}^{\infty} \frac{(z_q - 1)}{v_q} dv_q + (z_q - 1) - \ln z_q \quad (\text{A-2})$$

For pressure-explicit EOSs, the calculation of the fugacity coefficient using the right-hand side of eq A-2 avoids

any confusion with respect to liquidlike volume roots. At infinite volume, the pure compound fugacity coefficients are all unity and, according to eq 19 of the text, the τ_{ij} factors are all zero and eq 13 gives a zero excess Gibbs energy.

A related topic, which is normally associated with the departure from ideal gas behavior at low pressures, is the deviation from ideal behavior caused either by self-association or by cross-association (solvation) of the molecules. Self-association should be taken into account by the pure compound EOS that is used for the self-associating component. Thus, the mixing rule is not related to this effect. Cross-association in nonideal mixtures, on the other hand, is accounted for by the interaction parameters. However, cross-association in ideal mixtures does not require interaction parameters (e.g., first system of Table 1). An interesting case is that of a mixture of carboxylic acids. These substances are known to strongly self-associate even in the gas phase at very low pressure. The present model takes this effect into account first by the EOSs chosen for the pure carboxylic acids. Such EOSs should be able to represent well not only the vapor pressure curve but also the important departure from the ideal gas law, for the pure compound volume, at very low pressure and density. The use of proper EOSs for the pure carboxylic acids implies that the gaslike mixture volume, given by eq 8 of the text, will differ considerably from the ideal gas volume at low pressures. This will be so even if the computed values of ϵ_{ij} (eq 14) are small for the pairs of carboxylic acids. Hence, at gaslike densities and at nonzero very low pressures, the model is able to represent the departure from the ideal gas law. If the interactions in the mixture of carboxylic acids are similar to those in the pure fluids, the mixture will be ideal and will depart from the ideal gas law at densities where nonassociating systems do not. However, because of the ideality of the mixture, the boundary condition $g^E = 0$ will still be appropriate. For the case of carboxylic acids forming nonideal mixtures, the association effects will be accounted for by the pure compound EOSs and by the interaction parameters. In this case the system has nonideal mixture and nonideal gas nature up to very low densities. However, even systems of carboxylic acids reach full dissociation at extremely low densities, and hence, even for such systems, the boundary condition $g^E = 0$ is adequate.

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List of Symbols

a = energetic parameter
 A_{ij} = binary parameter
 b = covolume parameter
 B = second virial coefficient

g = molar Gibbs energy
 F = factor to control the low-density behavior
 n = number of moles
 N = number of components
 P = absolute pressure
 R = universal gas constant
 T = absolute temperature
 x_i = liquid mole fraction of component i
 y_i = vapor mole fraction of component i
 z = compressibility factor

Greek Letters

α_{ij} = relative volatility of component i with respect to component $j = y_i x_j x_i^{-1} y_j^{-1}$
 λ_{ij} = binary parameter
 γ = activity coefficient
 v = molar volume
 φ = fugacity coefficient

Superscripts

B = virial
E = excess property
id.sol. = ideal solution
L = liquid phase
V = vapor phase
 \wedge = in the mixture
- = partial molar property

Subscripts

mix = mixture

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