Analysis of Excess Free Energy Based Equations of State Models

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A comparison is made of the capabilities of various equation of state (EOS) + excess free energy (G^{ex}) models in representing the activity-coefficient models they incorporate. Such EOS models need to reproduce the excess Gibbs free energy behavior of the activity-coefficient models as closely as possible in order to represent low-pressure vapor–liquid equilibrium behavior of complex mixtures accurately, and also to make accurate the vapor–liquid predictions at higher temperatures and pressures using only low-pressure information. It is demonstrated that the EOS models that use the excess Helmholtz free energy instead of the excess Gibbs free energy, and that combine the EOS with activity-coefficient models at the infinite pressure limit, are successful for calculations of the type just described.

Introduction

In recent years mixing rules that combine excess-free-energy (G^{ex}) and equation-of-state (EOS) models have been a subject of intense interest. Several mixing/combining rules have been proposed (Huron and Vidal, 1979; Michelsen, 1990; Dahl and Michelsen, 1990; Holderbaum and Gmehling, 1991; Wong and Sandler, 1992; Boukouvalas et al., 1994; Orbey and Sandler, 1995) and used to correlate and/or predict phase equilibrium of highly nonideal mixtures. Some recent work in this area (Kalospiros et al., 1995; Voutsas et al., 1995), however, indicates that further discussion of the nature of these models and their capabilities is needed.

One stringent test of these new EOS/G^{ex} models is their ability to reproduce the excess free energy function of the activity-coefficient model that they incorporate as indicated by several investigators (Wong et al., 1992; Kalaspiros et al., 1995). In this article we make a detailed comparison of a number of EOS/G^{ex} models in their ability to reproduce the excess free energy functions of the traditional activity-coefficient models that they use. We also show that the capabilities and shortcomings of these models in predicting vapor–liquid equilibrium (VLE) phase behavior are related to this characteristic.

Testing of this kind should clarify some of the misconceptions about EOS/G^{ex} models, help identify the better of the various models that have been proposed, and also show the shortcomings of some of the models.

Connection between the EOS Models and Activity-Coefficient Models

The activity coefficient of a species i in a mixture can be obtained from an EOS using the relation

$$\gamma_i(T,P)=\frac{\hat{\varphi}_i(T,P,x_i)}{\varphi_i(T,P)}, \tag{1}$$

where $\hat{\varphi}_i$ is the fugacity coefficient of component i in the mixture, and φ_i is the pure component fugacity both computed at the temperature T and pressure P of the mixture with an equation of state. The molar excess Gibbs free energy can then be obtained from

$$\frac{G^{ex}}{RT}=\sum_i x_i \ln \gamma_i, \tag{2}$$

where R is the gas constant and T is temperature. The combination of Eqs. 1 and 2 leads to

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$$\frac{G^{ex}_{EOS}(T,P,x_i)}{RT} = \ln \varphi_{mix}(T,P,x_i) - \sum_i x_i \ln \varphi_i(T,P)$$

$$= \left[Z_{mix}(T,P,x_i) - \sum_i x_i Z_i(T,P)\right]$$

$$- \left[\ln Z_{mix}(T,P,x_i) - \sum_i x_i \ln Z_i(T,P)\right]$$

$$- \left[\int_{\infty}^{V_{mix}(T,P,x_i)} \frac{Z_{mix}-1}{V_{mix}} dV - \sum_i x_i \int_{\infty}^{V_i(T,P)} \frac{Z_i - 1}{V_i}\, dV\right] \quad (3)$$

for the excess Gibbs free energy. Equivalently for the excess Helmholtz free energy of mixing we have

$$\frac{A^{ex}_{EOS}(T,P,x_i)}{RT} = -\left[\sum_i x_i \ln \frac{Z_{mix}(T,P,x_i)}{Z_i(T,P)}\right]$$

$$- \left[\int_{\infty}^{V_{mix}(T,P,x_i)} \frac{Z_{mix}-1}{V_{mix}}\, dV - \sum_i x_i \int_{\infty}^{V(T,P_i)} \frac{Z_i - 1}{V_i}\, dV\right]. \quad (4)$$

In the preceding equations φ_{mix} is the fugacity of the mixture, Z is the compressibility factor, P is pressure, x_i is the mole fraction of species i, and V is the molar volume. In the EOS/G^{ex} models, these relations are used to obtain the a parameter of the cubic EOS for a mixture in terms of the activity coefficient model parameters and the van der Waals hard core term b.

For a van der Waals type of two-parameter cubic equations, the preceding relations can be written as

$$\frac{G^{ex}_{EOS}}{RT} = Z_{mix} - \sum_i x_i Z_i - \sum_i x_i \ln\left(\frac{Z_{mix}}{Z_i}\right)$$

$$- \sum_i x_i \ln\left[\frac{1 - \dfrac{b_{mix}}{V_{mix}}}{1 - \dfrac{b_i}{V_i}}\right] + \left(\frac{a_{mix}}{b_{mix}RT}\right) C(V_{mix})$$

$$- \sum_i x_i \left(\frac{a_i}{b_i RT}\right) C(V_i) \quad (5)$$

and

$$\frac{A^{ex}_{EOS}}{RT} = - \sum_i x_i \ln\left(\frac{Z_{mix}}{Z_i}\right) - \sum_i x_i \ln\left[\frac{1 - \dfrac{b_{mix}}{V_{mix}}}{1 - \dfrac{b_i}{V_i}}\right]$$

$$+ \left(\frac{a_{mix}}{b_{mix}RT}\right) C(V_{mix}) - \sum_i x_i \left(\frac{a_i}{b_i RT}\right) C(V_i). \quad (6)$$

Here $C(V)$ is a molar-volume-dependent function specific to the EOS chosen. For example, for the Peng–Robinson equation used here is

$$C(V) = \frac{1}{2\sqrt{2}} \ln\left\{\frac{V + (1-\sqrt{2})b}{V + (1+\sqrt{2})b}\right\}.$$

We note that in the limit of infinite pressure, $V_i \rightarrow b_i$ and $V_{mix} \rightarrow b_{mix}$ [so that $C(V_{mix} = b_{mix}) = C(V_i = b_i) = C^*$; for the Peng–Robinson equation, $C^* = \ln\, (\sqrt{2} - 1)]/\sqrt{2} = -0.62323$ and Eqs. 5 and 6 become

$$\frac{A^{ex}_{EOS}(T,P \rightarrow \infty, x_i)}{C^* RT} = \frac{1}{RT}\left[\frac{a_{mix}}{b_{mix}} - \sum_i x_i \frac{a_i}{b_i}\right] \quad (7)$$

$$\frac{G^{ex}_{EOS}(T,P \rightarrow \infty, x_i)}{C^* RT} = \frac{1}{RT}\left[\frac{a_{mix}}{b_{mix}} - \sum_i x_i \frac{a_i}{b_i}\right]$$

$$+ \frac{P}{RT} \sum_i x_i (b_{mix} - b_i). \quad (8)$$

Equations 7 and 8 are the mathematically rigorous solutions to Eqs. 5 and 6, and relate the excess free energy functions from an EOS and from an activity-coefficient model at infinite pressure.

For future reference, note that the second term in Eq. 8 vanishes when the following mixing rule for the hard core parameter is used

$$b_{mix} = \sum_i x_i b_i. \quad (9)$$

Equation 9 is used in all the models tested in this work, except for the WS model for which b is given as

$$b_{mix} = \frac{RT \sum_i \sum_j x_i x_j \left(b_{ij} - \dfrac{a_{ij}}{RT}\right)}{RT - \left[\sum_i x_i \dfrac{a_i}{b_i} + \dfrac{A^{ex}_{\gamma}(T,P^*,x_i)}{C^*}\right]}, \quad (10)$$

with

$$\left(b_{ij} - \frac{a_{ij}}{RT}\right) = \frac{1}{2}\left[\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)\right](1 - k_{ij}), \quad (11)$$

where k_{ij} is a binary interaction parameter, and A^{ex}_{γ} is the molar excess Helmholtz free energy term for which an expression from any of the existing liquid models, such as van Laar or Wilson, can be used.

From the conventional definition of an excess property change on mixing, it is necessary that the pure components and the mixture be in the same state of aggregation to use equations such as Eqs. 3 and 4. It is clear from these equations that the excess Gibbs and Helmholtz free energies of mixing computed from an equation of state is a function of pressure, whereas activity-coefficient models are independent of pressure or density. Therefore, the equality between G^{ex} (or A^{ex}) from an equation-of-state and from an activity-coefficient model can be made at only a single pressure. Some models make this link at infinite pressure (Huron and Vidal, 1979; Wong and Sandler, 1992) and use the expressions of Eqs. 7 or 8, while others make this connection at low or zero pressure (Michelsen, 1990; Dahl and Michelsen, 1990; Holderbaum and Gmehling, 1991). As has been indicated repeatedly by users of this latter class of equations, in the zero-pressure limit there is no mathematically rigorous solution that is applicable to all phase equilibrium problems. This is because above some temperature a cubic EOS will not have the necessary real liquid root at zero pressure. Consequently, an approximation must be introduced in such cases.

However, a mathematically rigorous connection between an EOS and an activity coefficient model can always be made at infinite pressure. This was done by Huron and Vidal (1979) using the excess Gibbs free energy (Eq. 8). The problem with their approach is that the Gibbs free energy calculated from an EOS at low pressures is much different from the Gibbs free energy at infinite (or very high) pressures. Thus, as will be seen again below, this EOS/G^{ex} model cannot reproduce the excess functions of the traditional activity-coefficient models at low pressure. Consequently, their model did not allow the direct use of the parameters obtained with an activity-coefficient model in an equation of state; rather all data had to be recorrelated.

Wong and Sandler (1992) used Helmholtz free energy (Eq. 7), rather than Gibbs free energy at infinite pressure. The Helmholtz excess free energy of mixing of a liquid is much less a function of pressure, indeed it is almost pressure independent, compared to the excess Gibbs free energy of mixing. Therefore, to a reasonable approximation we have that

$$A_\gamma^{ex}(T,P=\infty,x_i) \approx A_\gamma^{ex}(T,P^*,x_i) = G_\gamma^{ex}(T,P^*,x_i) - P^* V^{ex}(T,P^*,x_i) \approx G_\gamma^{ex}(T,P^*,x_i). \quad (12)$$

Here P^* is any (low) pressure at which experimental data are available; the last equality is valid if this pressure is low. Sandler and coworkers (Wong et al., 1992; Orbey et al., 1993) have selected the binary interaction parameter k_{ij} in Eq. 11 so that A_{EOS}^{ex} is essentially independent of pressure, or equivalently that the experimental G_γ^{ex} curve is reproduced at the pressure of the measurements. Consequently, the parameter k_{ij} contains no further information other than that already included in G_γ^{ex}.

If mathematical rigor in establishing the tie between excess free energy models and EOS is to be sacrificed, then several successful approximate models can be developed in the limit of infinite pressure. One such model was introduced by Orbey and Sandler (1995) and will also be tested here. In this model it is assumed that there is a universal linear algebraic function that relates the liquid molar volumes to their hard core volumes as $V = ub$, where u is a positive constant larger than unity. Using the Helmholtz free energy function for the reasons explained earlier and assuming that at infinite pressure, both for mixtures and for pure components, u approaches a unique value close to unity, they obtained

$$\frac{A_{EOS}^{ex}}{RT} = -\sum_i x_i \ln\left(\frac{b_{mix}}{b_i}\right) + C^*\left(\frac{a_{mix}}{b_{mix}RT} - \sum_i x_i \frac{a_i}{b_i RT}\right). \quad (13)$$

In this modification of the Huron–Vidal approach, which we refer to as the HVOS model, Eqs. 9 and 13 are used to obtain the EOS parameters a and b. This model is an approximate one (but in agreement with the spirit of the van der Waals hard core concept), and it is algebraically very similar to several currently used zero-pressure models. Yet it does not contain any arbitrary constant or function, it is as simple as the zero-pressure models, and as will be shown below, it is generally more successful than them also.

Among the zero-pressure models, the modified Huron–Vidal mixing rule of Michelsen (1990) is the closest to being "exact," that is, a mathematically rigorous model. The idea behind this mixing rule is to use Eq. 5 at $P = 0$ to obtain

$$\frac{G_{EOS}^{ex}(P=0)}{RT} = -\sum_i x_i \ln\left(\frac{V_{mix}^0 - b_{mix}}{V_i^0 - b_i}\right) - \sum_i x_i \ln\left(\frac{b_{mix}}{b_i}\right) + \left(\frac{a_{mix}}{b_{mix}RT}\right)C(V_{mix}^0) - \sum_i x_i\left(\frac{a_i}{b_i RT}\right)C(V_i^o), \quad (14)$$

where the superscript zero indicates a property at zero pressure. To look more like the form presented by Michelsen Eq. 14 can be rewritten as

$$q\left(\frac{a_{mix}}{b_{mix}RT}\right) = \sum_i x_i q\left(\frac{a_i}{b_i RT}\right) + \frac{G_\gamma^{ex}(T,P=0,x_i)}{RT} + \sum_i x_i \ln\left(\frac{b_{mix}}{b_i}\right), \quad (15)$$

where

$$q\left(\alpha = \frac{a}{bRT}\right) = -\ln\left(\frac{V(T,P=0)}{b} - 1\right) + \frac{a}{bRT}C(V^0). \quad (16)$$

To avoid the problem of lack of a liquid root for the terms on the right-hand side of Eq. 16 at certain temperatures, Michelsen chose an approximate linear extrapolation

$$q(\alpha) = q_0 + q_1\alpha \quad (17)$$

that is used for all values of α resulting in the relation

$$\frac{G_{EOS}^{ex}}{RT} = -\sum_i x_i \ln\left(\frac{b_{mix}}{b_i}\right) + q_1\left(\frac{a_{mix}}{b_{mix}RT} - \sum_i x_i \frac{a_i}{b_i}\right). \quad (18)$$

This equation is algebraically very similar to Eq. 13, and the combination of this relation with Eq. 9 is the MHV1 model that is tested here. Later, for better accuracy, a quadratic expression was proposed for $q(\alpha)$

$$q(\alpha) = q_0 + q_1\alpha + q_2\alpha^2, \quad (19)$$

with parameters chosen to ensure continuity of q and its derivatives. The relation between the excess Gibbs free energy from an EOS and from an activity coefficient model takes the following quadratic form in this approach

$$q_1\left(\alpha_{mix} - \sum_i x_i \alpha_i\right) + q_2\left(\alpha_{mix}^2 - \sum_i x_i \alpha_i^2\right) = \frac{G_\gamma^{ex}(T,P=0,x_i)}{RT} + \sum_i x_i \ln\left(\frac{b_{mix}}{b_i}\right). \quad (20)$$

This equation, together with Eq. 9, is known as MHV2 model (Dahl and Michelsen, 1990) and is also tested here.

Boukouvalas et al. (1994) related the excess free energy functions of EOS and activity coefficient models by forming the following linear combination of the Huron–Vidal and MHV1 models, referred to as the LCVM model,

$$\frac{a_{\text{mix}}}{b_{\text{mix}}RT} = \left(\frac{\lambda}{C^*} - \frac{1-\lambda}{q_1}\right)\frac{G_\gamma^{\text{ex}}}{RT} + \frac{1-\lambda}{q_1}\sum_i x_i \ln\left(\frac{b_{\text{mix}}}{b_i}\right) + \sum_i x_i \frac{a_i}{b_i RT}, \quad (21)$$

where λ is an arbitrarily selected constant. These authors ignore the pressure dependence of the excess Gibbs free energy of mixing and assume that G_γ^{ex} of the Huron–Vidal model, which is evaluated at infinite pressure, and G_γ^{ex} of the MHV1 model, which is evaluated at zero pressure, are identical. This model is also tested here.

Method of Comparison

Here we compare the performance of all the mixing rules discussed earlier. Specifically, we consider the following mixing rules developed in the infinite pressure limit: the original Huron–Vidal model (HVO), the Wong–Sandler model (WS), and the approximate model introduced by Orbey and Sandler (1995) as a modification of the Huron and Vidal model (HVOS). Among the zero-pressure models, the following were tested: the MHV1 model of Michelsen (1990), the MHV2 model of Dahl and Michelsen (1990), and the linear combination of HVO and MHV1 models by Boukovalas et al. (1994) (LCVM). In all cases we used the Peng–Robinson EOS as modified by Stryjek and Vera (1986). [For the MHV2 model the parameters q_1 and q_2 to be used with the PRSV equation were optimized in this work as -0.41754 and -0.00461, respectively; these are slightly different from the values -0.4347 and -0.003654 reported by Huang and Sandler (1993)]. Since the choice of EOS has little effect on the results, the conclusions reached here should be valid for any two-parameter cubic EOS. For this test we used the original UNIFAC equation as the excess free energy model. It needs to be emphasized that the main part of this test is not an attempt to reproduce experimental data, but rather to test the ability of the EOS/G^{ex} model to reproduce the activity-coefficient model that it incorporates. However, in all cases we have chosen systems for which experimental data were available so comparisons could be made, especially for extrapolations with temperature. In one case we have also used the UNIQUAC equation as a correlative model so that direct comparison with experimental data could be made.

We considered binary systems ranging from nearly ideal mixtures [hexane + hexadecane (Weiguo et al., 1990), acetone + benzene (DECHEMA, 1977)], to azeotrope-forming more nonideal mixtures [methanol + benzene (Butcher and Medani, 1968), acetone + water (DECHEMA, 1977), and 2-propanol + water (Barr-David and Dodge, 1959)]. For brevity here we present the results for the acetone + water and 2-propanol + water binary mixtures only, though the conclusions reached apply to all the systems investigated. We also studied infinite dilution activity coefficients of some alkane mixtures (Kniaz, 1991).

In each case we calculated the low-pressure excess Gibbs free energy function of the UNIFAC activity-coefficient model and also from each of the EOS/G^{ex} (in this case EOS/UNIFAC) models and observed how well they match. Then we predicted the VLE with the EOS models at low pressures to ascertain how the quality of the match in the excess free energy is reflected on the accuracy of the VLE predictions. Finally, we checked the predictive capability of these models by extrapolating phase equilibrium information to higher temperatures and pressures.

Results

In Figure 1, the excess Gibbs free energy of the various EOS/G^{ex} models considered here is shown for the acetone + water system at 25°C. The filled dots are the predictions of the UNIFAC excess free energy model, and the lines are G^{ex} obtained by using various EOS/UNIFAC models. Among the models used, the UNIFAC model behavior is most closely matched by the WS model using $k_{ij} = 0.2458$. This value was selected by matching the excess Gibbs free energy obtained from the UNIFAC model with that of the UNIFAC/WS/EOS model; no VLE data were used. As a result of its binary parameter k_{ij}, only the WS model among the models considered here has an extra degree of flexibility that allows better fitting of the G^{ex} function. For this case the MHV2, HVOS, and LCVM models cluster together, all slightly underpredicting the Gibbs free energy. The largest deviations are for the HVO and MHV1 models, and interestingly the satisfactory performance of the LCVM model, which is a linear combina-

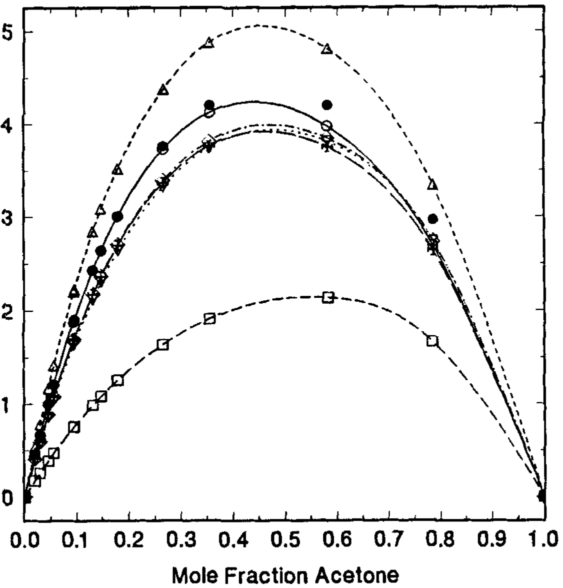

Figure 1. Excess Gibbs free energy predictions for the acetone+water system at 25°C.

Filled circles are the UNIFAC predictions; the solid line (-⊖-) represents the results of the WS model; the large (✻), medium (-□-), and short (--Δ--) dashed lines are from the HVOS, HVO, and MHV1 models, respectively; the dotted line (··∇··) is from the MHV2 model; and the dot-dash line (–·–) results from the LCVM model.

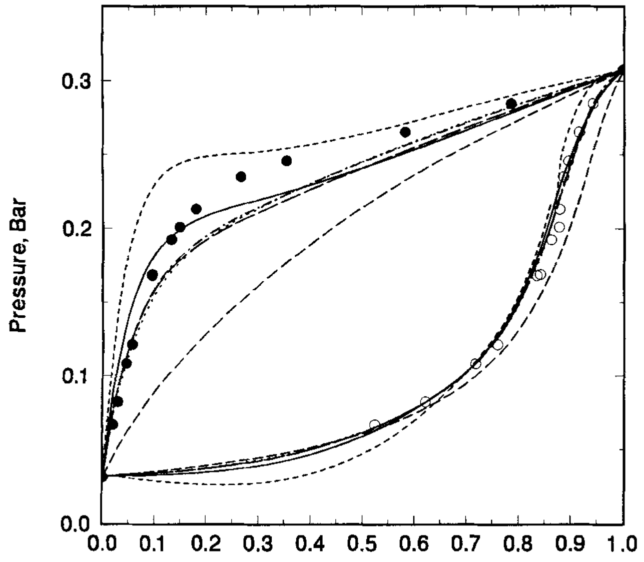

Figure 2. Vapor–liquid equilibrium for the acetone + water system at 25°C.

Filled circles are the experimental data, and the lines are as in Figure 1.

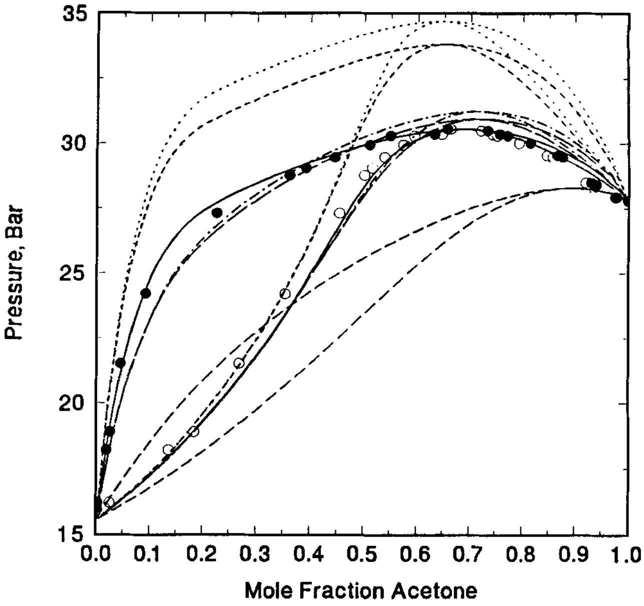

Figure 3. Predictions for the vapor liquid equilibria for the acetone + water system at 200°C using the parameters obtained at 25°C.

Filled circles are the experimental data, and the lines are as in Figure 1.

tion of the HVO and MHV1 models, is the result of a cancellation of errors between these two models. The VLE predictions of the various models are shown in Figure 2 at 25°C, and the same trends found in predicting the excess Gibbs free energy are exhibited in the VLE predictions. Since the UNIFAC predictions are not perfect for this system, even the models that best reproduce the UNIFAC excess Gibbs free energy are not in complete agreement with the experimental data.

The VLE predictions for the acetone + water system at 200°C in Figure 3 using the 25°C parameters is revealing. The most accurate results are obtained with the WS mixing rule. The extrapolations using the HVOS and LCVM models are also reasonably good, though less accurate at dilute concentrations. The MHV2 model that produced similar predictions to the HVOS and LCVM models at 25°C, now shows the largest overprediction of the saturation pressure. The MHV1 model also overpredicts the saturation pressure, while the HVO model fails in representing the azeotrope and by underpredicting the saturation pressure over the whole concentration range. As before, the LCVM model is a combination of the two worst models for extrapolating VLE information. For the hexane + hexadecane, acetone + benzene, and for methanol + benzene binary systems similar results were obtained, but they are not presented here for brevity.

The other example we consider is the 2-propanol + water system, which we selected to show how inaccuracies of the activity coefficient model used affects the performance of the EOS/G^{ex} model. In Figure 4, the excess free energy predictions for this system at 25°C are shown. By setting k_{ij} of the WS model to 0.3834, we can represent the UNIFAC G^{ex} behavior very closely, though not exactly. All of the other EOS/G^{ex} models deviate from the UNIFAC G^{ex} behavior to varying extents, especially in the midconcentration range. Examining the VLE behavior of this mixture at 25°C in Figure 5, we see that none of the EOS/G^{ex} models are satisfactory. For comparison, we also show as crosses in the figure the VLE prediction resulting from the direct activity coefficient method. Since the UNIFAC model does not provide an accurate description of this system, even giving a false liquid–liquid split in the water-rich region, an EOS/UNIFAC model like WS that can reproduce the UNIFAC excess free energy behavior closely also inherits its problems, show-

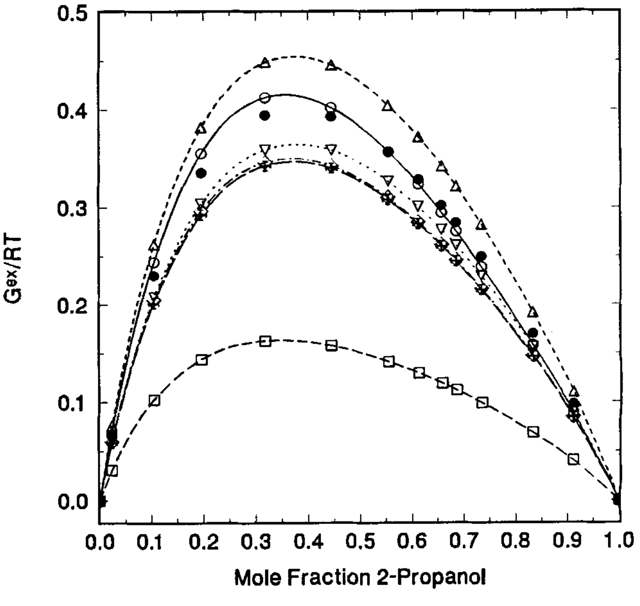

Figure 4. Excess Gibbs free energy predictions for the 2-propanol + water system at 25°C (legend as in Figure 1).

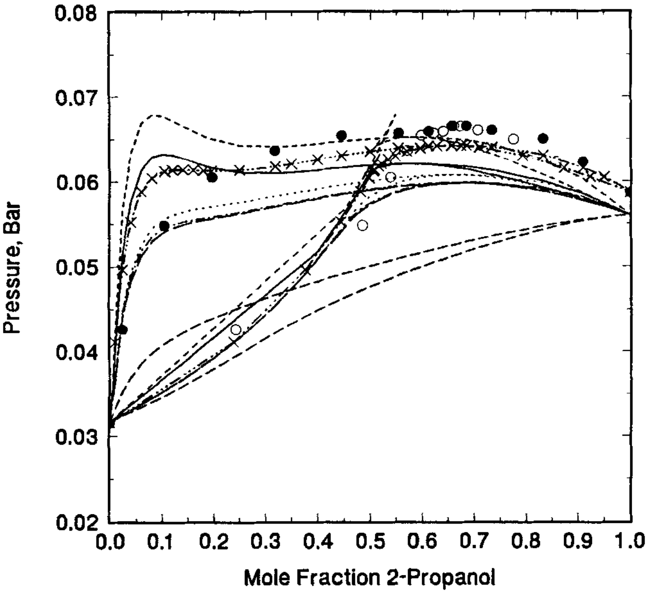

Figure 5. Vapor–liquid equilibrium for the 2-propanol + water system at 25°C.

Filled circles are the experimental data, and the lines are as in Figure 1, except for dash-cross-dash (– × – × –) line that represent UNIFAC predictions.

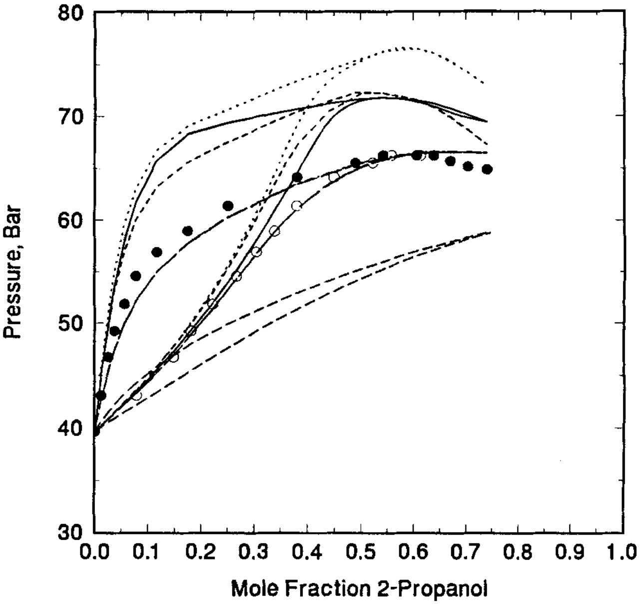

Figure 6. Predictions for the vapor–liquid equilibria for the 2-propanol + water system at 250°C using the parameters obtained at 25°C.

Filled circles are the experimental data, and the lines are as in Figure 1.

ing the same erroneous phase split. This also causes a more severe problem when the EOS/UNIFAC models are used to predict phase behavior at elevated temperatures and pressures as seen in Figure 6 for 2-propanol + water binary system at 250°C. The MHV2 model gives the largest overprediction of pressure, followed by the MHV1 and WS models. The HVO model underpredicts the pressure. The best results are obtained by the HVOS and LCVM models, which behave almost identically. However, those two models underpredicted the experimental saturation pressures at 25°C so the agreement here must be viewed as fortuitous.

We consider the 2-propanol + water system again now using the correlative UNIQUAC model to examine the effect on high-temperature predictions of accurately fitting low-temperature data. Since UNIQUAC is a correlative model, it is possible to fit the parameters of each EOS/UNIQUAC model to VLE data at 25°C; the fitted parameters are given in Table 1. The VLE correlations at 25°C and the predictions at 250°C are shown in Figures 7 and 8, respectively. All models can very accurately fit the low-pressure data, as shown in Figure 7. However, when the same parameters are used to predict the VLE behavior of this system at 250°C, the performance of various models differ as shown in Figure 8. The WS model gives the best fit, followed by the HVOS and then the LCVM models, both of which somewhat underpredict the saturation pressure. The HVO model underpredicts the pressure significantly, and both the MHV1 and MHV2 models overpredict the pressure, with the MHV2 model being more seriously in error.

Recently, Kalospiros et al. (1995) compared the capabilities of several EOS/G^{ex} models in predicting infinite dilution activity coefficients. Following Kalospiros et al., we used the models tested here to predict infinite dilution activity coefficients of some heavy alkanes in *n*-hexane. The results are presented in Figure 9. The dots are data of Kniaz (1991), and the lines are predictions of the various EOS/UNIFAC models. With the WS model a value of k_{ij} can be selected for each binary to represent one infinite dilution activity coefficient exactly, so the results for the WS model are not shown in the figure, as they are coincident with the experimental data. For comparison, we do show as a triangle the infinite dilution activity coefficient of hexadecane in *n*-hexane obtained from the WS model with $k_{ij} = 0.3795$ found by matching the UNIFAC excess Gibbs function with the WS model. Instead choosing $k_{ij} = 0.43$ in this model results in exact agreement with the experimental infinite dilution activity coefficient of hexadecane in *n*-hexane, as shown by the square in the figure. For this relatively ideal binary mixture, fitting k_{ij} to the infinite dilution activity-coefficient data also improved the VLE predictions by the WS model as shown in Figure 10.

Table 1. UNIQUAC Model Parameters for 2-Propanol + Water Binary System* at 25°C for Various Mixing Rules

	HVO	MHV1	MHV2	LCVM	HVOS	WS†
Δu_{12} (cal/mol)	646.29	745.57	706.23	666.57	724.34	837.65
Δu_{21} (cal/mol)	214.79	–240.76	–128.26	–93.44	–108.02	–28.38

*UNIQUAC pure component parameters are $r = 2.78$, $q = q' = 2.51$ for 2-propanol, and $r = 0.92$, $q = q' = 1.4$ for water.
†$k_{ij} = 0.15$.

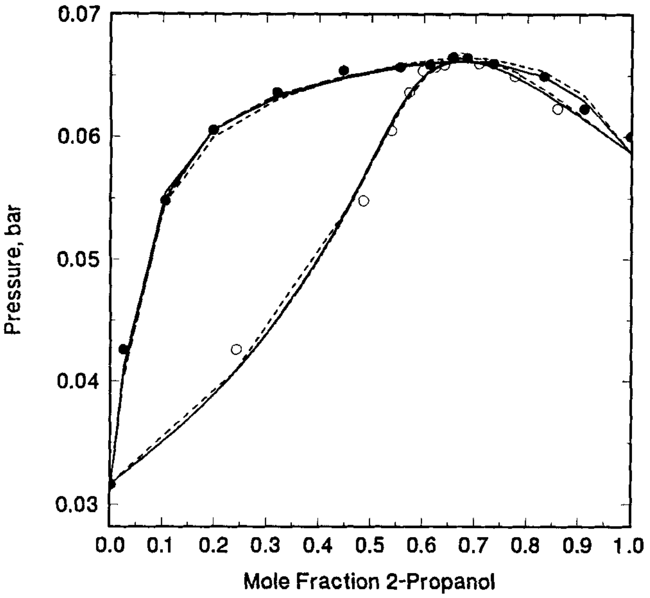

Figure 7. Correlations of the vapor–liquid equilibria for the 2-propanol + water system at 25°C using the UNIQUAC correlation method with the EOS/G^{ex} models.

Filled circles are the experimental data, and the lines are as in Figure 1.

All of the other models show various degrees of deviations from the experimental infinite dilution data. Among them the best predictions are obtained with the HVOS model (long dashed line in Figure 9). Only the MHV1 model (short dashed line) generates positive deviations from Raoult's law (activity coefficients larger than unity); all the other models, including the direct use of the UNIFAC model (solid line), give negative deviations from ideality. The HVOS model slightly overpredicts the infinite dilution activity coefficients; the remain-

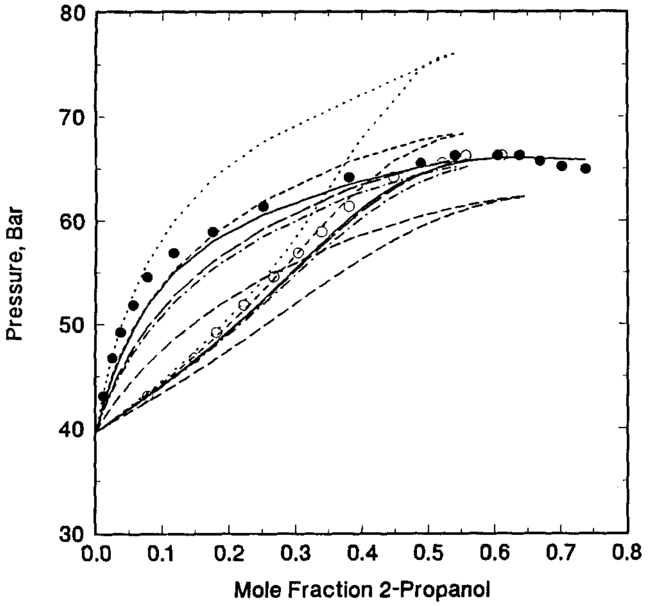

Figure 8. Predictions for the vapor–liquid equilibria for the 2-propanol + water system at 250°C using the UNIQUAC model with parameters obtained at 25°C.

Filled circles are the experimental data, and the lines are as in Figure 1.

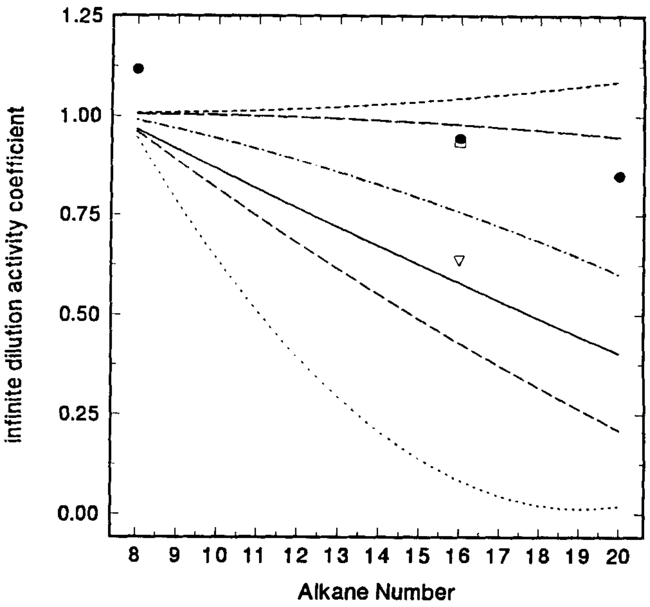

Figure 9. Infinite dilution activity coefficients of *n*-alkanes in *n*-hexane.

Filled dots are the experimental data; the solid line is the UNIFAC predictions; the large, medium and short dashed lines are from the HVOS, HVO, and MHV1 models, respectively; the dotted line is from the MHV2 model, and the dot-dash line results from the LCVM model. The inverted triangle results from the WS model with the binary parameter fit to the complete G^{ex} curve, and the square is from the WS model fit to the infinite dilution activity coefficient.

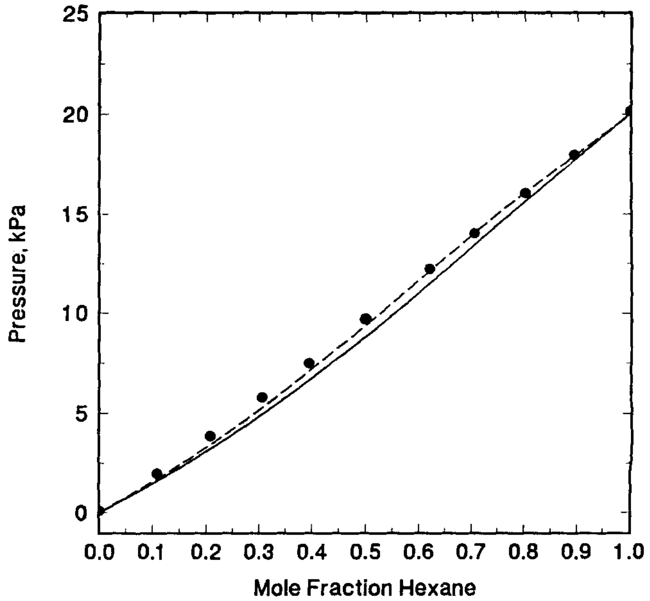

Figure 10. Vapor–liquid equilibria for the hexane + hexadecane system at 25°C.

The points are the experimental data; the solid line results from fitting the UNIFAC G^{ex} curve ($k_{ij} = 0.3794$); and the dashed line represents setting k_{ij} to 0.43 to match the infinite dilution activity coefficient of hexadecane in hexane.

ing EOS/G^{ex} models underpredict the experimental values, with the largest error coming from the MHV2 model (dotted line). The LCVM (dot-dash line) model, which is a linear combination of the HVO (medium dashed line) and MHV1 models, due to a cancellation of errors, again gives better results than both these other models.

Conclusions

The conclusions from this study that we want to emphasize are as follows:

1. A mathematically rigorous combination of excess free energy models with equations of state at all temperatures can only be made at the infinite pressure limit where the excess free energy function from an EOS at liquid densities can be defined without approximation. This connection can either be done using the excess Gibbs free energy, as demonstrated by Huron and Vidal (1979), or more successfully by using the excess Helmholtz free energy, as shown by Wong and Sandler (1992).

2. The excess Gibbs free energy as computed from an EOS is strongly pressure dependent, while the pressure dependence of the excess Helmholtz free energy is much less. Consequently, in order to use a single set of parameters in such EOS models for both low and high pressures, it is necessary to use the excess Helmholtz free energy.

3. In the zero-pressure limit (or at low pressures), the excess Helmholtz free energy and excess Gibbs free energy calculated from an EOS are virtually indistinguishable and can be used interchangeably. With this in mind, for successful VLE predictions by such models there are two conditions to be satisfied:

> a. the excess free energy function obtained from the conventional free energy model used in the EOS should be in agreement with the experimental excess Gibbs free energy at low pressure;
> b. The excess free energy computed from the EOS/G^{ex} model should match the conventional excess free energy model as closely as possible.

If either of these conditions is not satisfied, then the combined EOS/G^{ex} model may fail to represent low-pressure phase equilibria, or lead to inaccurate extrapolations to high pressures and temperatures with the parameters obtained at low pressures, or both.

4. Among the models studied here the WS model can be made to match the excess free energy from a conventional activity-coefficient model closely by varying the model parameter k_{ij}. This flexibility can also be used to incorporate infinite dilution activity-coefficient information into this model.

5. If a less rigorous EOS/G^{ex} model is to be used, the results presented here and earlier (Orbey and Sandler, 1995) suggest that the simple HVOS model obtained at the infinite pressure limit performs as well as, and sometimes better than, the approximate zero-pressure models.

Acknowledgment

This research was supported, in part, by grant no. DOE-FG02-85ER13436 from the U.S. Department of Energy and grant no. CTS-9123434 from the U.S. National Science Foundation, both to the University of Delaware.

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Manuscript received Aug. 9, 1995, and revision received Dec. 11, 1995.