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PHASE BEHAVIOR OF LIGHT GASES IN HYDROCARBON AND AQUEOUS SOLVENTS

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PHASE BEHAVIOR OF LIGHT GASES IN HYDROCARBON AND AQUEOUS SOLVENTS

ABSTRACT

Under previous support from the Department of Energy, an experimental facility has been established and operated to measure valuable vapor-liquid equilibrium data for systems of interest in the production and processing of coal fluids. To facilitate the development and testing of models for prediction of the phase behavior for such systems, we have acquired substantial amounts of data on the equilibrium phase compositions for binary mixtures of heavy hydrocarbon solvents with a variety of supercritical solutes, including hydrogen, methane, ethane, carbon monoxide, and carbon dioxide.

The present project focuses on measuring the phase behavior of light gases and water in Fischer-Tropsch (F-T) type solvents at conditions encountered in indirect liquefaction processes and evaluating and developing theoretically-based correlating frameworks to predict the phase behavior of such systems. Specific goals of the proposed work include (a) developing a state-of-the-art experimental facility to permit highly accurate measurements of equilibrium phase compositions (solubilities) of challenging F-T systems, (b) measuring these properties for systematically-selected *binary, ternary and molten F-T wax* mixtures to provide critically needed input data for correlation development, (c) developing and testing models suitable for describing the phase behavior of such mixtures, and (d) presenting the modeling results in generalized, practical formats suitable for use in process engineering calculations.

During the present reporting period, our solubility apparatus was refurbished and restored to full service. To test the experimental apparatus and procedures used, measurements were obtained for the solubility of CO_2 in benzene at 160 °F. Having confirmed the accuracy of the newly acquired data in comparison with our previous measurements and data reported in the literature for this test system, we have begun to measure the solubility of hydrogen in hexane. The measurements for this system will cover the temperature range from 160 to 280 °F at pressures to 2,500 psia.

As part of our model evaluation efforts, we examined the predictive abilities of an alternative approach we have proposed for calculating the phase behavior properties of highly non-ideal systems. Using this approach, the liquid phase fugacities generated from an equation of state (EOS) are augmented by a fugacity deviation function correction. The correlative abilities of this approach are compared with those of an EOS equipped with the recently introduced Wong-Sandler (MWS) mixing rules. These two approaches are compared with the current methods for vapor-liquid equilibrium (VLE) calculations, i.e., the EOS (ϕ/ϕ) approach with the van der Waals mixing rules and the split (γ/ϕ) approach. The evaluations were conducted on a database comprised of non-ideal low pressure binary systems as well as asymmetric high pressure binary systems. These systems are of interest in the coal liquefaction and utilization processes. The Peng-Robinson EOS was selected for the purposes of this evaluation.

The proposed method, called the (θ/ϕ) approach, can successfully correlate the binary VLE of highly non-ideal low pressure systems as well as asymmetric high pressure systems. Bubble point pressures were correlated within 2% for low pressure systems and within 1% for high pressure systems. The (θ/ϕ) approach shows accuracy comparable to the MWS mixing rules for correlating the binary VLE of the systems considered here. Thus, the use of either approach extends the applicability of equations of state to highly non-ideal systems. However, the proposed amendment to the VLE framework offers a direct means for handling various types of systems and the potential for more useful generalizations and simpler implementation.

A manuscript we have prepared for publication is attached in lieu of detailed technical information.

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EXECUTIVE SUMMARY

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An Amended Framework for Vapor-Liquid Equilibrium Calculations

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ABSTRACT

Complex mixing rules have been proposed to improve the predictive abilities of equations of state (EOS) for highly non-ideal systems. However, some of these mixing rules are not theoretically sound and are not very widely used. An alternative approach is proposed in this study, wherein the liquid phase fugacities generated from an EOS are augmented by a fugacity deviation function correction. The correlative abilities of this approach are compared with those of an EOS equipped with the recently introduced Wong-Sandler (MWS) mixing rules. These two approaches are compared with the current methods for vapor-liquid equilibrium (VLE) calculations, i.e., the EOS (ϕ/ϕ) approach with the van der Waals mixing rules and the split (γ/ϕ) approach. The evaluations were conducted on a database comprised of non-ideal low pressure binary systems as well as asymmetric high pressure binary systems. The Peng-Robinson EOS was selected for the purposes of this evaluation.

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INTRODUCTION

The accurate prediction of thermodynamic properties of mixtures is essential in nearly every area of chemical engineering for process design and optimization calculations. The most convenient tool for the description of equilibrium phase behavior has long been recognized to be analytic equations of state (Prausnitz, 1977). Historically, the most commonly used equations of state (EOS) are the cubic van der Waals type equations such as the Peng-Robinson (Peng and Robinson, 1976) and the Soave-Redlich-Kwong (Soave, 1972) EOS. Perhaps, the greatest utility of cubic EOS is for phase equilibrium calculations involving mixtures (see, e.g., Prausnitz et al., 1986; Walas, 1985; Anderko, 1990). The assumption inherent in such calculations is that the same EOS can be used both for pure fluids and mixtures, once a satisfactory procedure for obtaining the mixture parameters from pure fluid parameters is identified. This is accomplished using mixing rules, the most common being the van der Waals one-fluid mixing rules equipped with combining rules containing adjustable parameters. However, the van der Waals mixing rules generally cannot describe the behavior of highly non-ideal mixtures containing polar or associating molecules. For such mixtures, the alternative approach has been the use of activity coefficient models for the condensed phase and an EOS for the vapor phase (Prausnitz, 1977). However, this approach, the spli (γ/ϕ) approach also has its drawbacks, the most prominent of which is the need for the use of hypothetical standard states.

To avoid the use of activity coefficient models and to improve the predictive abilities of the conventional EOS, various complex mixing rules have been proposed. However, most of these mixing rules also have fundamental drawbacks and are not very widely used (Sandler et al., 1994). Recently, a new set of mixing rules, which are theoretically sound were introduced by

Wong and Sandler (1992). Orbey and Sandler (1995) proposed a reformulation of these mixing rules. The predictive abilities of these modified Wong-Sandler (MWS) mixing rules are not very well known, and the need exists for evaluating their ability to describe the behavior of complex mixtures.

An alternative approach has been suggested to address some of the limitations of the current VLE framework (Gasem, 1989). The basic premise of this new method is to use a fugacity deviation function to augment the fugacity calculated from an EOS. As mentioned previously, an EOS with the conventional mixing rules cannot represent the behavior of highly non-ideal solutions. The hypothesis is that a systematic correction to the fugacities calculated from the EOS may alleviate this problem without altering the EOS mixing rules.

The main goal of this work is to assess the efficacy of this new VLE framework. The specific objectives of this study are to

1. Evaluate the effect of a fugacity deviation function correction on the phase behavior predictive abilities of an EOS.
2. Evaluate the comparable phase behavior predictive abilities of the EOS using the MWS mixing rules.
3. Compare the above with the conventional methods for calculating phase equilibrium properties, i.e., the EOS (ϕ/ϕ) approach with the van der Waals mixing rules and the split (γ/ϕ) approach.

PROPOSED METHOD

The EOS (ϕ/ϕ) approach has inherent limitations in that it cannot model phase equilibrium for systems which exhibit appreciable solution non-ideality (see, e.g., Prausnitz, 1977; Sandler et al., 1994). The main problem with this approach is the accurate representation of liquid phase behavior. An attempt was made to alleviate this drawback by correcting the EOS liquid phase fugacities by using a deviation function (Gasem, 1989). The fugacity deviation function, say $\hat{\theta}_i$, can be defined by

$$\hat{\theta}_i = \frac{\hat{f}_i}{\hat{f}_i^{eos}} \tag{1}$$

where, $\hat{f}_i$ is the actual fugacity of the component and $\hat{f}_i^{eos}$ is the fugacity calculated by the EOS used to model the solution behavior. There are two important limits at which the value of $\hat{\theta}_i$ needs to be defined. These are

$$\begin{aligned} &\hat{\theta}_i \to 1 \quad \text{as} \quad z_i \to 1 \\ &\hat{\theta}_i \to 1 \quad \text{as} \quad p \to 0 \end{aligned} \tag{2}$$

The first limit makes the fugacities calculated by the EOS applicable at the pure limits. The second limit ensures that the fugacity of a component approaches the partial pressure at the limit of zero pressure. Other limiting conditions, however, may be used to define the pure component limits; for example, a volume translation could be implemented to improve the pure fluid property predictions.

Accordingly, the chemical potential of a component in a phase can be expressed by

$$\mu_i = \mu_i^o + RT\ln \hat{\theta}_i \hat{f}_i^{eos} \tag{3}$$

where μ_i^o is the pure component chemical potential at the system temperature and unit fugacity. The total Gibbs free energy of a phase is defined by (Denbigh, 1981)

$$G = \sum n_i \mu_i \tag{4}$$

Substituting the value of the chemical potential from Equation (3)

$$G = \sum n_i \mu_i^o + RT\sum n_i \ln \hat{f}_i^{eos} + RT\sum n_i \ln \hat{\theta}_i \tag{5}$$

If the solution behavior is modeled solely by the EOS, the last term would be zero. Therefore, the excess free energy (with reference to the particular EOS) is

$$G_{eos}^E = RT\sum n_i \ln \hat{\theta}_i \tag{6}$$

If we differentiate the above expression at constant temperature and pressure

$$dG_{eos}^E = RT\sum n_i d\ln \hat{\theta}_i + RT\sum \ln \hat{\theta}_i d\, n_i \tag{7}$$

The Gibbs-Duhem equation for a given phase is (Denbigh, 1981)

$$-SdT + Vdp - \sum n_i d\mu_i = 0 \tag{8}$$

At a constant temperature and pressure, substituting for the chemical potential from Equation (3), the above equation can be written as

$$\sum n_i d\ln \hat{\theta}_i + \sum n_i d\ln \hat{f}_i^{eos} = 0 \tag{9}$$

The second term on the left hand side of the above equation has to be equal to zero to satisfy the Gibbs-Duhem equation for the conventional EOS approach. Thus, the first term is also equal to zero. It follows from the preceding discussion, that at a constant temperature, pressure and mole numbers of the other components of the mixture (n_j), Equation (7) leads to

$$\left(\frac{\partial G_{eos}^E}{\partial n_i}\right)_{T,P,n_j} = RT\ln \hat{\theta}_i \tag{10}$$

Thus, if an expression can be obtained for the excess Gibbs energy, G_{eos}^E, the coefficients $\hat{\theta}_i$ for the individual species can be determined by differentiating G_{eos}^E with respect to n_i. The fugacity deviation function $\hat{\theta}_i$ can also be calculated from experimental partial molar volume data by the following equation

$$\ln\hat{\theta}_i = \frac{1}{RT}\int_0^p \left(\tilde{v}_i - \tilde{v}_i^{eos}\right) dp \tag{11}$$

where $\tilde{v}_i$ is the actual partial molar volume and $\tilde{v}_i^{eos}$ is the partial molar volume calculated by the EOS. For convenience, the fugacity deviation function θ can also be correlated empirically by any of the conventional activity coefficient models (or any correlation that obeys the Gibbs-Duhem relation). However, such a strategy is not optimum for deriving the full benefit of this approach.

This approach may be called the (θ/ϕ) approach to distinguish it from the (ϕ/ϕ) approach. In terms of deviation functions, this method essentially involves selecting an EOS as the reference model for evaluating mixture properties. Figure 1 compares the deviation functions θ (deviation from an EOS) and γ (deviation from an ideal solution) obtained for the acetone + water system at 373.2 K. This figure is shown for illustrative purposes only and no inference regarding the relative magnitudes of the deviation functions can be drawn from it. However, one should normally expect the deviation function θ to be smaller than γ, since an EOS is generally a better reference model than an ideal solution. Also, θ may at times show maxima or minima, when plotted as a function of composition, and a model for θ should be able to handle such behavior.

MODEL EVALUATIONS

Four different methods were evaluated in this study for correlating binary vapor-liquid equilibrium (VLE) of the systems considered. The four VLE methods are listed in Table 1 as specific case studies. In Case 1, the Peng-Robinson EOS is used with the traditional van der Waals mixing rules for the vapor phase (with no interaction parameters) and the NRTL model (Renon and Prausnitz, 1965) for the liquid phase. The Peng-Robinson EOS (Peng and Robinson, 1976) is given as follows

$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{12}$$

where

$$a(T) = a_c \alpha(T) \tag{13}$$

$$b = 0.07780 RT_c / p_c \tag{14}$$

and

$$a_c = 0.45724 R^2 T_c^2 / p_c \tag{15}$$

$$\alpha(T)^{1/2} = 1 + K(1 - T_r^{1/2}) \tag{16}$$

$$K = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{17}$$

The equations for the van der Waals mixing rules are shown below

$$a = \sum\sum z_i z_j a_{ij} \tag{18}$$

$$b = \sum\sum z_i z_j b_{ij} \tag{19}$$

In addition, combining rules are needed for the parameters a_{ij} and b_{ij}. The usual combining rules are

$$a_{ij} = \sqrt{a_{ii} a_{jj}}(1 - C_{ij}) \tag{20}$$

$$b_{ij} = \frac{1}{2}(b_{ii} + b_{jj})(1 + D_{ij}) \tag{21}$$

where C_{ij} and D_{ij} are empirical “binary interaction parameters” obtained by fitting EOS predictions to experimental data.

The NRTL model can be written as

$$\frac{\overline{G}^E}{RT} = \sum_i z_i \left[\frac{\sum_j z_j G_{ji} \tau_{ji}}{\sum_k z_k G_{ki}} \right] \tag{22}$$

$$G_{ji} = \exp(-\alpha_{ij}\tau_{ji}) \tag{23}$$

where $\overline{G}^{E}$ is the molar excess Gibbs free energy. The expression for the activity coefficient is

$$\ln\gamma_i = \frac{\sum_j z_j \tau_{ji} G_{ji}}{\sum_k z_k G_{ki}} + \sum_j \frac{z_j G_{ij}}{\sum_k z_k G_{kj}} \left(\tau_{ij} - \frac{\sum_l z_l \tau_{lj} G_{lj}}{\sum_k z_k G_{kj}} \right) \tag{24}$$

In this case, the parameters to be regressed are the model parameters τ_{12}, τ_{21} and α_{12}. This is the split (γ/ϕ) approach. Case 1 has been used for non-ideal low pressure systems only, as excess free energy models are well suited for such systems.

In Case 2, the Peng-Robinson EOS, equipped with the van der Waals mixing rules employing two interaction parameters (C_{ij} and D_{ij}), is used. The parameters to be regressed are the interaction parameters C_{ij} and D_{ij}. Case 2 has been used for high pressure systems only, as equations of state with the van der Waals mixing rules generally cannot handle the behavior of highly non-ideal systems (Sandler et al., 1994).

In Case 3, the Peng-Robinson EOS equipped with the MWS mixing rules is used. The equations for the MWS mixing rules are shown below

$$b = \frac{\sum\sum z_i z_j \left(b - \frac{a}{RT} \right)_{ij}}{1 - \frac{\overline{A}^{E}}{\sigma RT} - \sum z_i \frac{a_i}{RTb_i}} \tag{25}$$

$$\frac{a}{b} = \sum z_i \frac{a_i}{b_i} + \frac{\overline{A}^{E}}{\sigma} \tag{26}$$

In Equations (25) and (26), $\overline{A}^{E}$ is the molar excess Helmholtz free energy and σ is a numerical constant, which depends on the EOS being used (e.g., $\sigma = -0.62323$ for the Peng-Robinson EOS). The combining rule for the cross second virial coefficient in Equation (25) is

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j}}{RT}\left(1 - C_{ij}\right) \tag{27}$$

The Gibbs excess model used with these mixing rules was a modified NRTL model (Huron and Vidal, 1979). The equations for the modified NRTL model are the same as Equations (22) and (24). Only Equation (23) is changed to

$$G_{ji} = b_j \exp(-\alpha_{ij}\tau_{ji}) \tag{28}$$

where b_j is the EOS covolume parameter (Equation 12). In this case, the parameters to be regressed are the interaction parameter C_{ij} and the excess model parameters τ_{12}, τ_{21} and α_{12}. Cases 2 and 3 both represent variations of the (ϕ/ϕ) approach. However, in this study, a reference to the (ϕ/ϕ) approach, without any mention of the mixing rules used, should be understood as a reference to Case 2, as it is the more commonly used approach.

In Case 4, the Peng-Robinson EOS is used with the van der Waals mixing rules employing one interaction parameter (C_{ij}), and a fugacity deviation function correction is applied to the calculated liquid fugacity. The fugacity deviation function used for this case was the Redlich-Kister model (Walas, 1985)

$$\ln\hat{\theta}_1 = z_2^2\left[B + C(3z_1 - z_2) + D(z_1 - z_2)(5z_1 - z_2)\right] \tag{29}$$

$$\ln\hat{\theta}_2 = z_1^2\left[B + C(z_1 - 3z_2) + D(z_1 - z_2)(z_1 - 5z_2)\right] \tag{30}$$

The excess Gibbs free energy model from which these equations are derived is

$$\frac{\overline{G}^E}{RT} = z_1 z_2\left[B + C(z_1 - z_2) + D(z_1 - z_2)^2\right] \tag{31}$$

In this case, the parameters to be regressed are the interaction parameter C_{ij} and the model parameters B, C and D. This is the proposed (θ/ϕ) approach. The Redlich-Kister model was selected, in preference to some other models, after some preliminary trials. However, it was not selected for theoretical reasons but as a flexible model to explore the merits of this method. Eventually, one should seek a more precise excess model to account for deviations in phase behavior beyond the reference EOS.

The model evaluations were performed using the GEOS (Generalized EOS)software developed at Oklahoma State University (Gasem, 1988-1996). Model parameters were regressed to minimize deviations in bubble point pressure predictions only. The objective function used for minimization was

$$SS = \sum_{i=1}^{npts} \left(\frac{p_i^{exp} - p_i^{cal}}{p_i^{exp}} \right)^2 \tag{32}$$

where, the superscripts exp and cal refer to experimental and calculated values, respectively. The summation is over the total number of points (npts) in the data set. The quality of fit was assessed by calculating the root-mean-squared error (RMSE), percentage average absolute deviation (%AAD) and bias (BIAS) for each data set. Definitions of these statistics are given in the Nomenclature.

DATABASE USED

The four methods discussed in the previous section were evaluated using a database comprised of non-ideal systems at low pressures as well as systems at high pressures. Only binary VLE data were used in this study. At low pressures, a majority of the systems considered involved water with different compounds. The compounds were chosen to represent several classes of chemicals (alcohols, acids, aldehydes, ethers, ketones, etc.). Some other systems exhibiting near-ideal behavior were also considered. The data for most low pressure systems were taken from the DECHEMA Chemistry Data Series (DECHEMA, 1977). At high pressures, the database consisted of binary mixtures of different hydrocarbons with ethane, carbon dioxide, nitrogen and hydrogen. The hydrocarbons were chosen to represent several classes of compounds (n-alkanes, naphthenes and aromatics). The data for these systems were taken from an extensive database previously compiled at Oklahoma State University (Raghunathan, 1996). The sources and range of data used are shown in Tables 2-6. Table 7 lists the physical constants (T_c, p_c and ω) used in the evaluation and their sources. Physical constants and the vapor pressure model for compounds involved in the systems at low pressure have been taken from Aspen Plus™ (AspenTech, 1995).

RESULTS

The overall results for the different types of systems studied here are summarized in Table 8. For low pressure systems, Case 1 shows the best results of the three cases studied (RMSE = 0.007 bar, %AAD = 1.02). As mentioned previously, Case 2 was not studied for non-ideal low pressure systems, as EOS with the van der Waals mixing rules often cannot handle the behavior of these systems. The overall results for these systems are essentially similar for Case 3 (RMSE = 0.009 bar, %AAD = 1.84) and Case 4 (RMSE = 0.009 bar, %AAD = 1.58) for bubble point pressure predictions. VLE plots for a few sample systems, comparing the different methods, are also shown in Figures 2-4. For all the figures, the continuous lines represent model predictions and the symbols represent experimental data, with the filled symbols representing the liquid phase. The figures indicate that good representation of the phase behavior is obtained in Cases 3 and 4. In addition, dramatic improvement in the quality of the fit near the pure limits (comparable to Case 1) is realized when the pure component vapor pressures are accurately reproduced, as shown by Figures 2 and 4.

As mentioned previously, Case 1 was not studied for high pressure systems as activity coefficient models are not well suited for such systems. The results for the binary ethane + hydrocarbon systems indicate that all three models show similar results. Case 2 (RMSE = 0.43 bar, %AAD = 1.17) and Case 3 (RMSE = 0.42 bar, %AAD = 0.88) do slightly worse than Case 4 (RMSE = 0.19 bar, %AAD = 0.51). The results for the binary carbon dioxide + hydrocarbon systems show the same trend. Case 4 (RMSE = 0.28 bar, %AAD = 0.58) does marginally better than Case 2 (RMSE = 0.78 bar, %AAD = 0.96) and Case 3 (RMSE = 0.36 bar, %AAD = 0.78). The results for the binary nitrogen + hydrocarbon systems indicate that Case 2 (RMSE = 2.24 bar, %AAD = 1.91), Case 3 (RMSE = 2.27 bar, %AAD = 1.57) and Case 4 (RMSE = 2.08 bar, %AAD = 1.54) show essentially the same results, albeit, on a relative (%AAD) basis, Case 2 does slightly worse than Cases 3 and 4. However, the model parameters for Case 3 are not stable for some systems, and difficulties in convergence were experienced.

Typically, systems for which convergence was difficult resulted in large values for the parameter τ_{12}. The nitrogen + n-decane system offers an example of the convergence problem. In this case, one data point at 410.9 K did not converge. Thus, the parameters were optimized after discarding that particular point, and the isotherm was not included in the overall analysis. The results for the binary hydrogen + hydrocarbon systems indicate that Case 2 (RMSE = 1.81 bar, %AAD = 1.02) and Case 3 (RMSE = 2.08 bar, %AAD = 1.13) show essentially similar results. Case 4 (RMSE = 0.85 bar, %AAD = 0.56) does marginally better than Cases 2 and 3. However, Case 3 again showed convergence problems. The hydrogen + n-hexadecane system at 622.9 K and the hydrogen + benzene system at 423.2 K each had one non-convergent point. Again, the parameters were optimized after discarding the non-convergent points and the particular isotherms were not included in the overall analysis.

The results for the non-ideal low pressure systems show that the (γ/ϕ) approach (Case 1) does better than Cases 3 and 4. However, this should be expected since the (γ/ϕ) approach uses a vapor pressure model to obtain accurate pure component vapor pressures. The calculations using the MWS mixing rules (Case 3) and the (θ/ϕ) approach (Case 4) were performed without any tuning of pure fluid parameters to obtain accurate pure component vapor pressures. Accurate representation of pure component vapor pressures is one of the important factors affecting phase equilibrium predictions. Figures 2(B) and 4(B), representing VLE for the 2-propanol + water system and the acetonitrile + tert-butanol system respectively, are excellent examples which illustrate this assertion. In these figures, the acentric factors of the individual components were tuned to generate accurate pure component vapor pressures for Cases 3 and 4. A comparison of Figures 2(B) and 4(B) with Figures 2(A) and 4(A) respectively, shows improved accuracy for Cases 3 and 4, which may be ascribed to good pure component parameters.

The overall results for the asymmetric high pressure systems considered here indicate that both Cases 3 and 4 show better results than Case 2. However, this should be expected of four-parameter models like the ones used in this study compared to an equation of state with only two interaction parameters. However, the point in question is not the correlative ability of models for specific systems, but developing a framework which can be used for a wider variety of systems than is currently possible. To this extent, both the MWS mixing rules and the (θ/ϕ) approach proved successful. The use of either approach also eliminates the need for reference states for calculating fugacities, which is a major drawback of the (γ/ϕ) method.

The (θ/ϕ) Approach Model Parameter Temperature Dependence

The analysis for the systems studied here was done on an isotherm-by-isotherm basis, i.e., model parameters were regressed for individual isotherms of each system. This represents the ultimate ability of any model to correlate phase behavior. However, in practice, a single set of parameters is generally used to represent the phase behavior of a system over a range of temperature. For this purpose, the temperature dependence of the model parameters for the (θ/ϕ) approach was investigated for certain sample systems.

The temperature dependence was investigated using five systems. The systems chosen were acetone + water, ethane + n-octacosane, carbon dioxide + n-decane, nitrogen + n-hexadecane and hydrogen + toluene. The temperature dependence was investigated for three different cases. Case 4, as discussed in the previous section, is the correlation of the vapor-liquid equilibrium of the system with individual parameters for each temperature. Case 4a is the prediction of vapor-liquid equilibrium of the system at all temperatures using parameters based on a single (lowest) temperature. Case 4b is the correlation of vapor-liquid equilibrium of the system at all temperatures using a set of regressed parameters determined to fit the entire data set. The results for the representation of bubble point pressures for the three cases are shown in Table 9.

Sample VLE curves are also shown in Figures 5-8.

The results for the acetone + water system are shown on two separate figures (Figures 5 and 6) due to a different scale being required for the highest temperature. Case 4, as expected, shows the best results for all the systems considered here. Case 4a is in good agreement with the experimental data at 323.2 K, but at 373.2 K, it predicts slightly different bubble point pressures. The same observation applies to results for Case 4b, which shows a qualitatively better fit than Case 4a. Both cases predict vapor compositions for acetone which are slightly high. The results for the ethane + n-octacosane system indicate that all three cases yield very similar results. For the carbon dioxide + n-decane system, Case 4a predicts slightly higher bubble point pressures for the 410.9 K and 510.9 K isotherms. Case 4b, however shows excellent agreement with the data for all isotherms. The results for the nitrogen + hexadecane system, shown in Figure 7, indicate excellent results for both Case 4a and 4b. The results for the hydrogen + toluene system are shown in Figure 8. In this case, the results for Cases 4a and 4b are the same, i.e., the parameters for the lowest isotherm (461.9 K) gave a fit comparable to that using parameters regressed for the complete data set. Thus, only a single curve has been drawn for both cases. There is good qualitative agreement with the data for both isotherms, but at higher pressures, the predicted bubble point pressures are slightly lower.

In general, the results for Case 4a indicate that the model parameters, though not temperature independent, show good qualitative fits for temperatures higher than the temperature at which they were obtained. Case 4b shows slightly better results, which indicates that a single set of parameters could be used over a range of temperature to give reasonably accurate predictions. Table 10 compares the results for Case 4b with the results obtained using the conventional approaches (Cases 1 and 2 described in the previous section) on a system-by-system basis, i.e., one set of parameters for a system. The comparison shows that the (θ/ϕ) approach does marginally better than the (ϕ/ϕ) approach (Case 1) for systems at high pressures and does marginally worse than the (γ/ϕ) approach (Case 2) for the acetone + water system. The overall results indicate that Case 4 is required for high accuracies using the (θ/ϕ) approach.

DISCUSSION

Parity in the correlative abilities of the proposed (θ/ϕ) approach and the MWS mixing rules is a positive and significant outcome. The results indicate that amending the VLE framework offers good correlative capabilities without resorting to complexity in the EOS mixing rules. Moreover, the present study demonstrates the efficacy of perturbation of auxiliary equilibrium functions (such as fugacity), as opposed to potential energy functions (e.g., Helmholtz energy) or a partition function at the molecular level.

The current excess energy mixing rules are limited to use with cubic equations of state only, whereas the (θ/ϕ) approach can be used with any equation of state. Also, as stated previously, these excess mixing rules (such as MWS) are limited to certain excess energy models and parameter values if they are to be used with the van der Waals mixing rules in multicomponent systems. However, there is no such limitation on the (θ/ϕ) approach, as its function is to model deviations from any equation of state with any set of mixing rules. The (θ/ϕ) approach, being an amendment to the VLE framework, offers a direct means of extending the applicability of equations of state to highly non-ideal systems, has potential for more useful generalizations, and reduces the need for developing complex mixing rules like the MWS rules. Moreover, the (θ/ϕ) approach is very easy to implement within *existing* computational algorithms for any equation of state.

This preliminary study indicates that the proposed (θ/ϕ) approach addresses some of the limitations of the current VLE framework and offers a unified method for handling diversity in phase behavior. Nevertheless, further studies are required to address several outstanding issues. As was stated earlier, the Redlich-Kister excess Gibbs energy model was selected, after some preliminary trials, as the fugacity deviation function model. The selection was based mostly on empirical consideration and for the purpose of demonstrating the viability of the proposed method. To fully benefit from the (θ/ϕ) approach, efforts should be directed toward developing a more rational excess model to account for deviations in phase behavior beyond the reference EOS.

In addition to rigorous derivation of the fugacity deviation function θ, the choice of reference EOS will also have a significant influence on the equality of the equilibrium predictions. In this study, we have used the Peng-Robinson EOS with a binary interaction parameter. Ideally, one should use theoretically-based EOS founded on clearly stated molecular attributes; thus, the observed phase behavior is correlated with the structure of the molecules involved. In such a case, the deviation function θ would be an amendment reflective of the molecular complexity. For example, one could use an EOS capable of representing normal fluids as a reference model and the deviation function θ to account for polarity or molecular size disparity.

The model evaluations in this study were limited to binary systems only. However, the (θ/ϕ) approach may be extended to systems containing three or more components. For extension to multicomponent systems (ternary or higher), excess free energy models structurally akin to the NRTL or Wilson model are recommended for θ. These models can be applied to multicomponent systems with binary parameters, whereas models like the Redlich-Kister model need ternary or higher parameters for such systems.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. The proposed method, called the (θ/ϕ) approach, can successfully correlate the binary VLE of highly non-ideal low pressure systems as well as asymmetric high pressure systems. Bubble point pressures were correlated within 2% for low pressure systems and within 1% for high pressure systems.
2. The (θ/ϕ) approach shows accuracy comparable to the MWS mixing rules for correlating the binary VLE of the systems considered here. Thus, the use of either approach extends the applicability of equations of state to highly non-ideal systems. However, the proposed amendment to the VLE framework offers a direct means for handling various types of systems and the potential for more useful generalizations and simpler implementation.
3. The temperature dependence of the model parameters for the (θ/ϕ) approach was investigated using a number of sample systems. The results show that good qualitative fits are obtained using a single set of parameters over a range of temperature. However, a set of parameters for each temperature is recommended for high precision.

Recommendations

1. The model used in this work for the fugacity deviation function was selected, based on limited preliminary trials. Effective modeling of both the reference EOS and the fugacity deviation function, using the current advancements in molecular thermodynamics, should be attempted to develop a theoretically sound model. This, in turn, might lead to generalizability of model parameters, if not reasonable *a priori* prediction of phase behavior for systems for which experimental data are not available.

2. The applicability of the (θ/ϕ) approach to multicomponent systems (ternary or higher) should be investigated.
3. The generalizability of the deviation function model parameters should be addressed.

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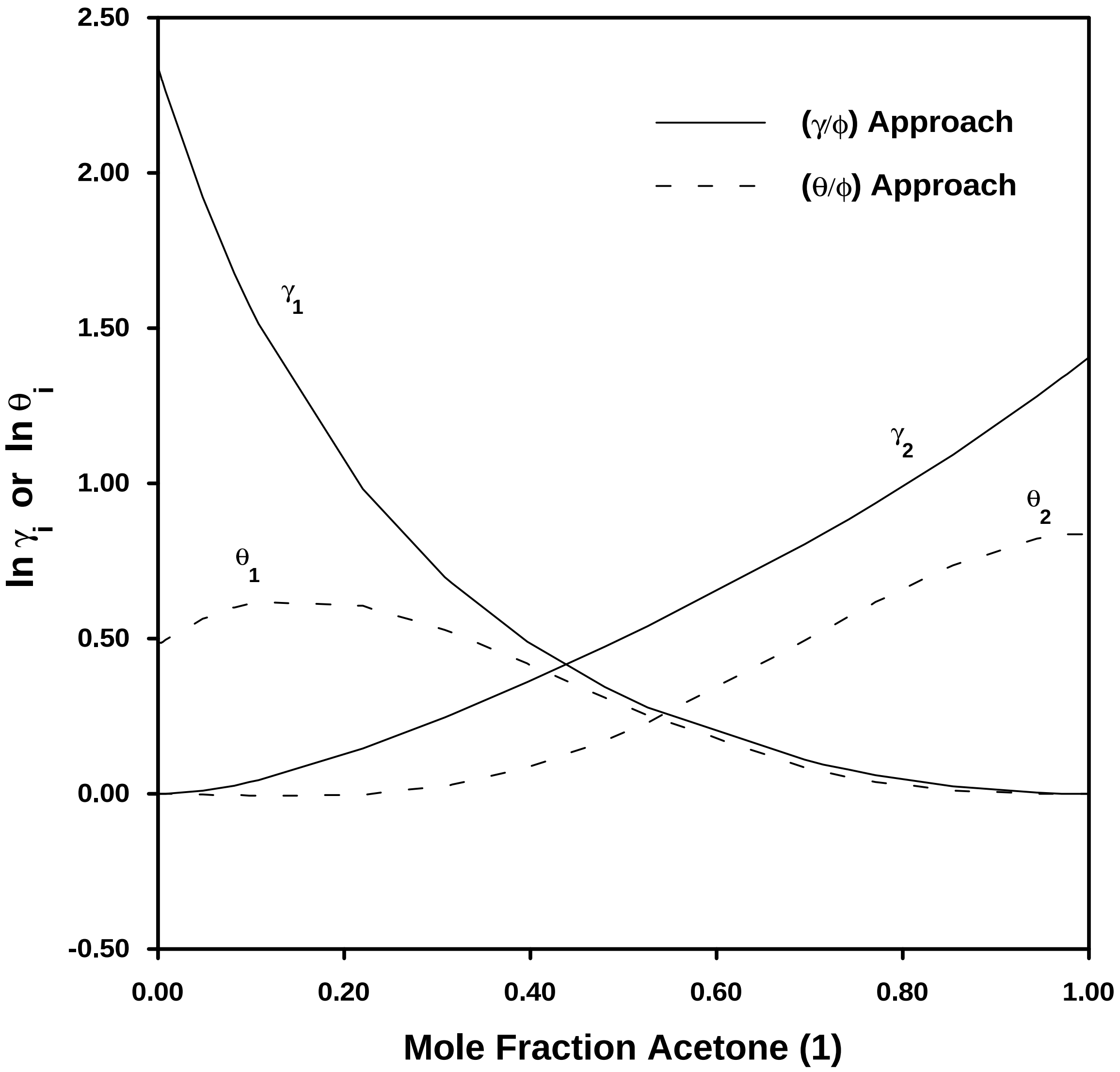

Figure 1. Comparison of Deviation Functions Generated from the (γ/ϕ) Approach and the (θ/ϕ) Approach for the Acetone (1) + Water (2) System at 373.2 K

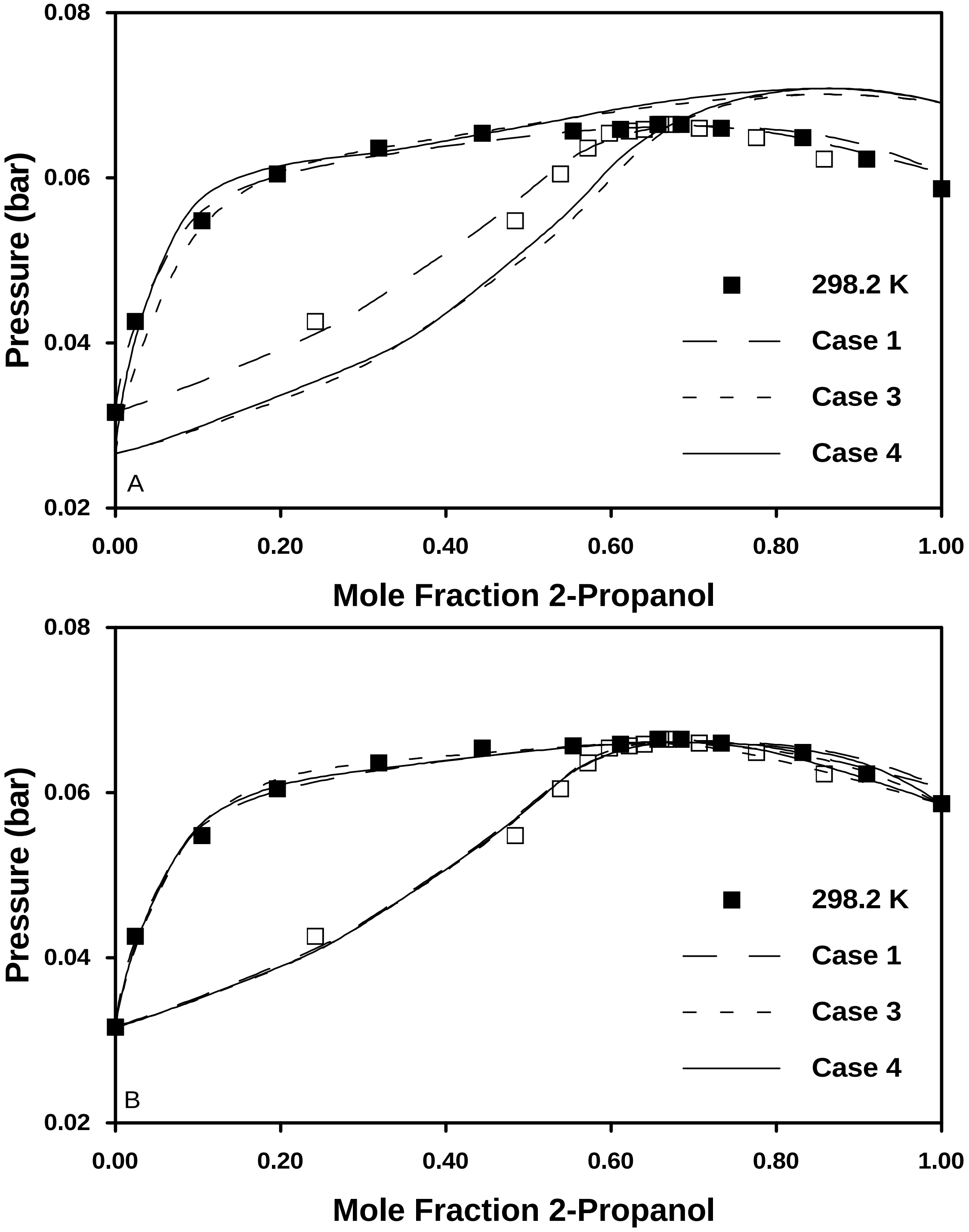

Figure 2. Representation of Vapor-Liquid Equilibrium of the 2-Propanol + Water System at 298.2 K for the Cases Studied. Experimental Data are from Sazonov (1986)

Figure 2(A): No Tuning of Pure Component EOS Parameters for Case 3 and Case 4

Figure 2(B): Tuned Pure Component EOS Parameters for Case 3 and Case 4

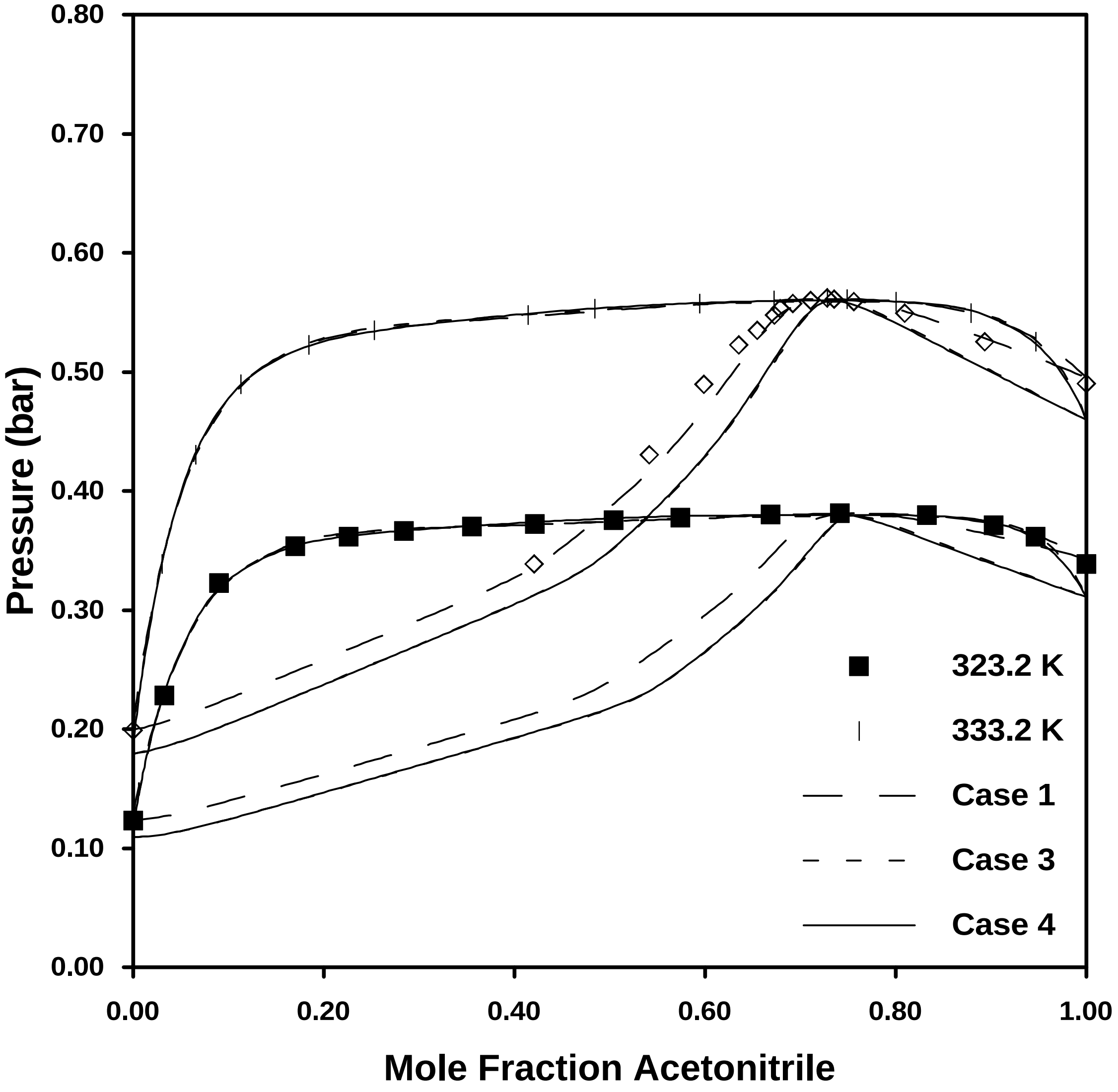

Figure 3. Representation of Vapor-Liquid Equilibrium of the Acetonitrile + Water System for the Cases Studied. Experimental Data at 323.2 K are from Wilson et al. (1979) and at 333.2 K are from Sugi and Katayama (1983).

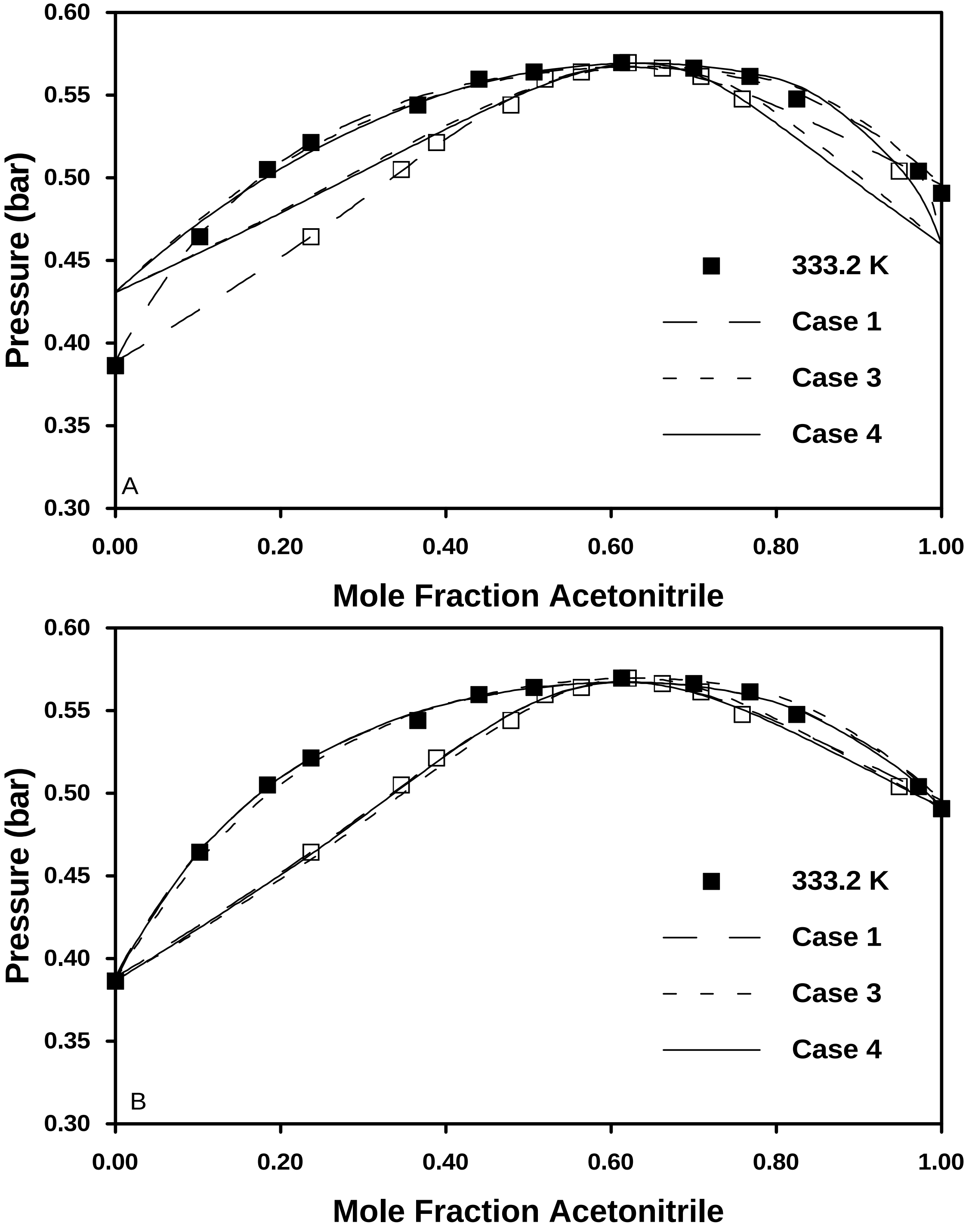

Figure 4. Representation of Vapor-Liquid Equilibrium of the Acetonitrile + Tert-Butanol System for the Cases Studied. Experimental Data are from Nagata (1989)

Figure 5(A): No Tuning of Pure Component EOS Parameters for Case 3 and Case 4

Figure 5(B): Tuned Pure Component EOS Parameters for Case 3 and Case 4

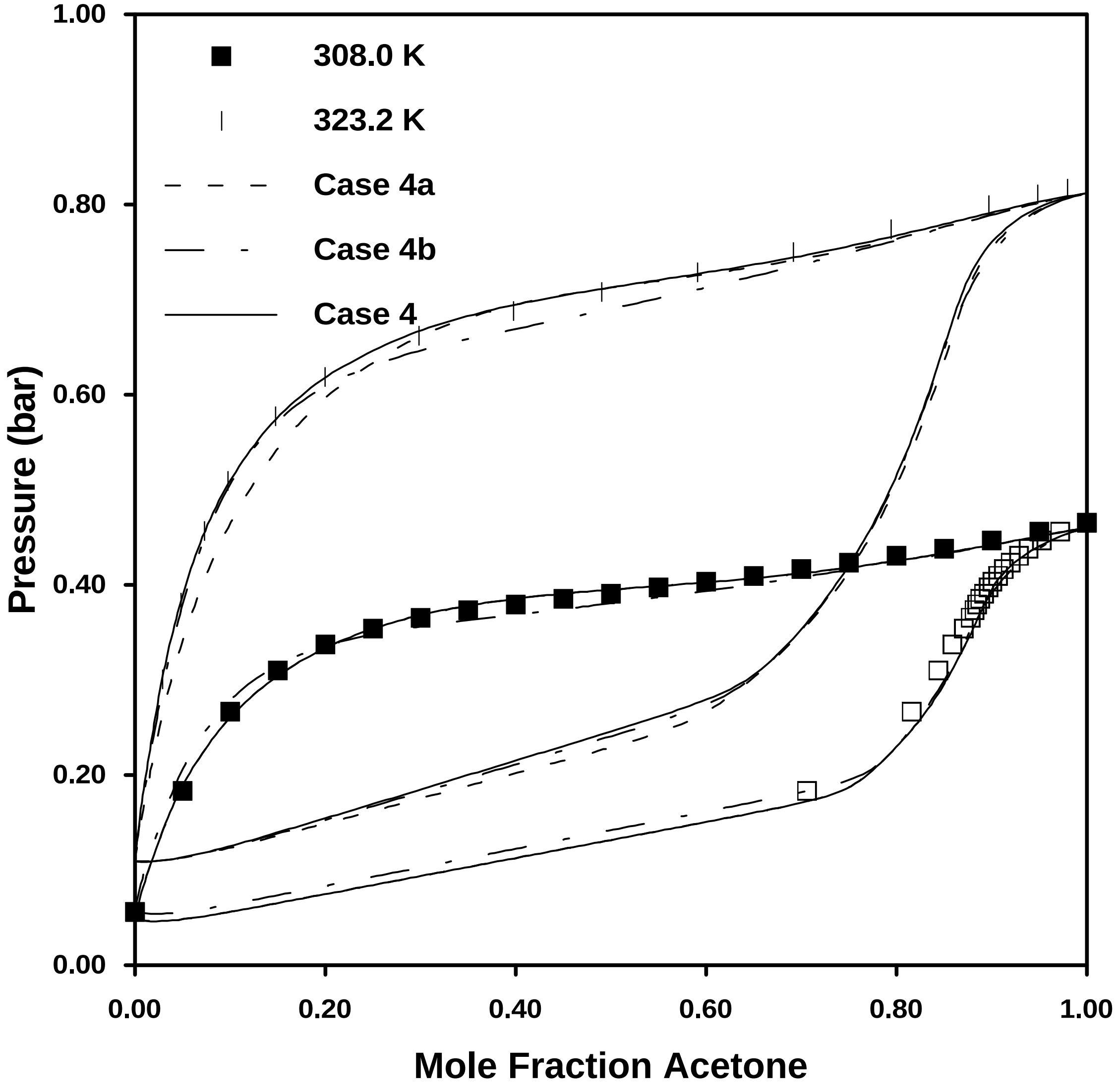

Figure 5. Representation of Vapor-liquid Equilibrium of the Acetone + Water System at 308.2 K and 323.2 K Using the (θ/ϕ) Approach. Experimental Data at 308.2 K are from Lieberwerth and Schuberth (1979) and at 323.2 K are from Chaudhary et al. (1980)

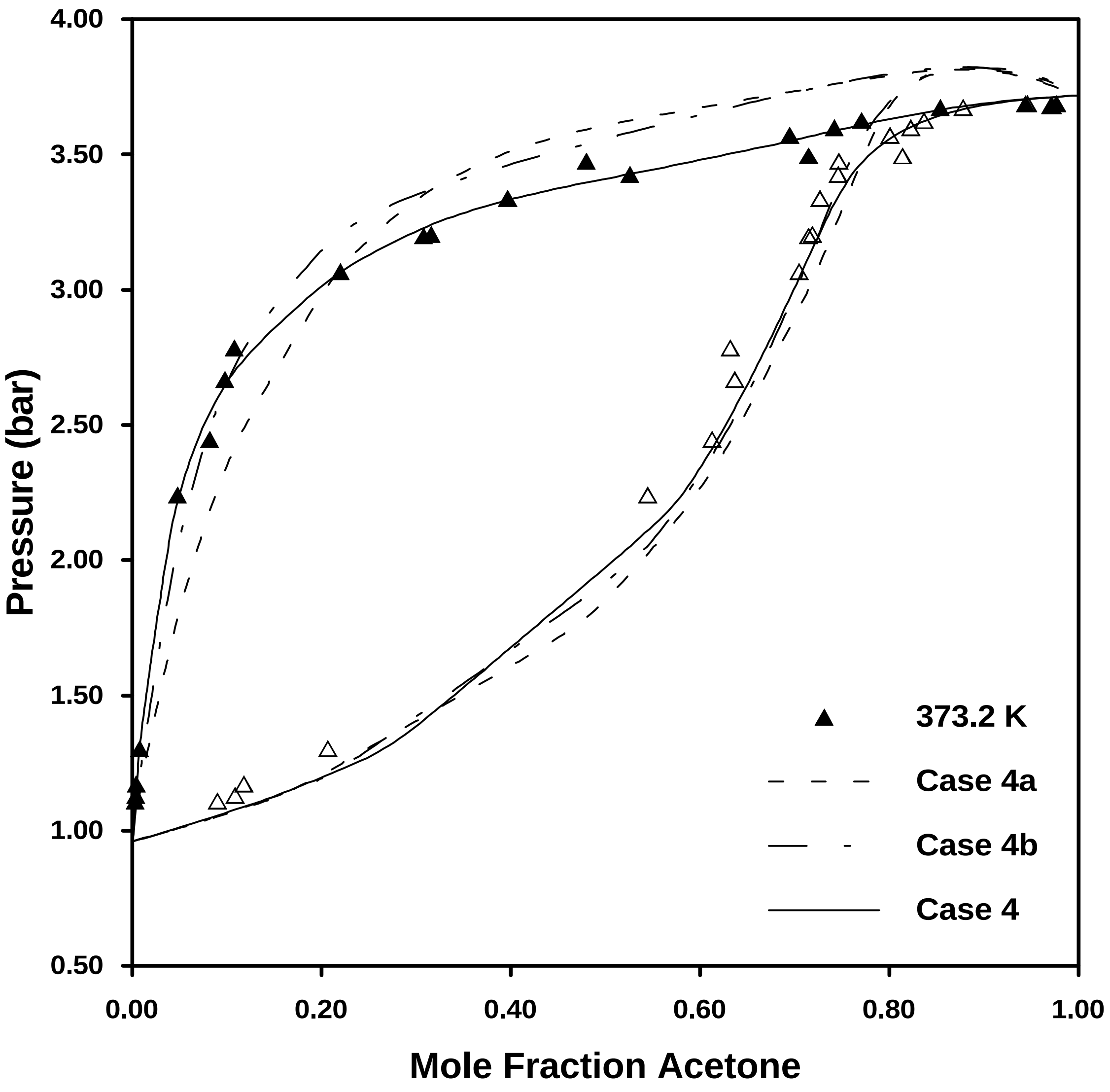

Figure 6. Representation of Vapor-liquid Equilibrium of the Acetone + Water System at 373.2 K Using the (θ/ϕ) Approach. Experimental Data are from Griswold and Wong (1952)

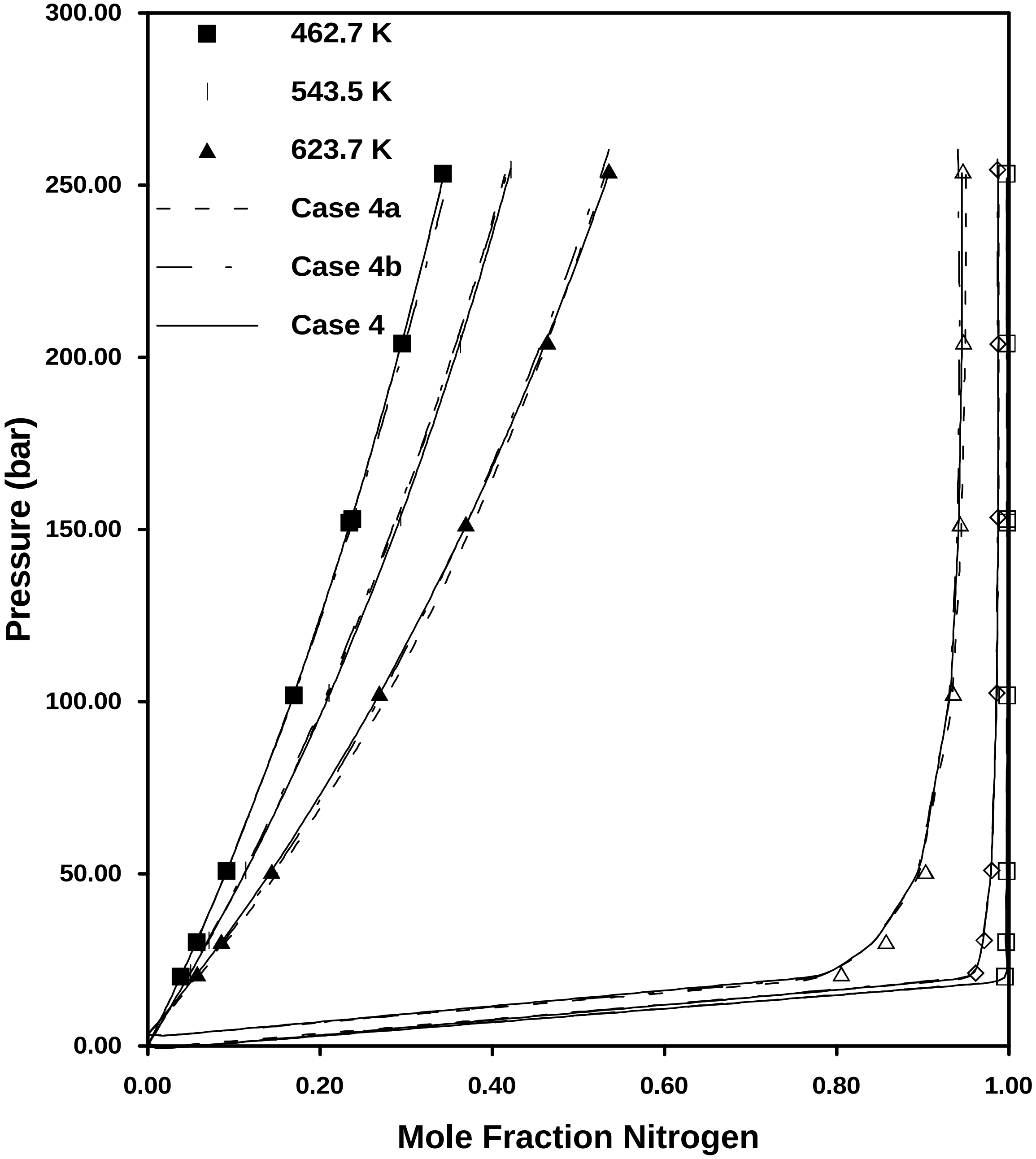

Figure 7. Representation of Vapor-Liquid Equilibrium of the Nitrogen + n-Hexadecane System Using the (θ/ϕ) Approach. Experimental Data are from Lin et al. (1981)

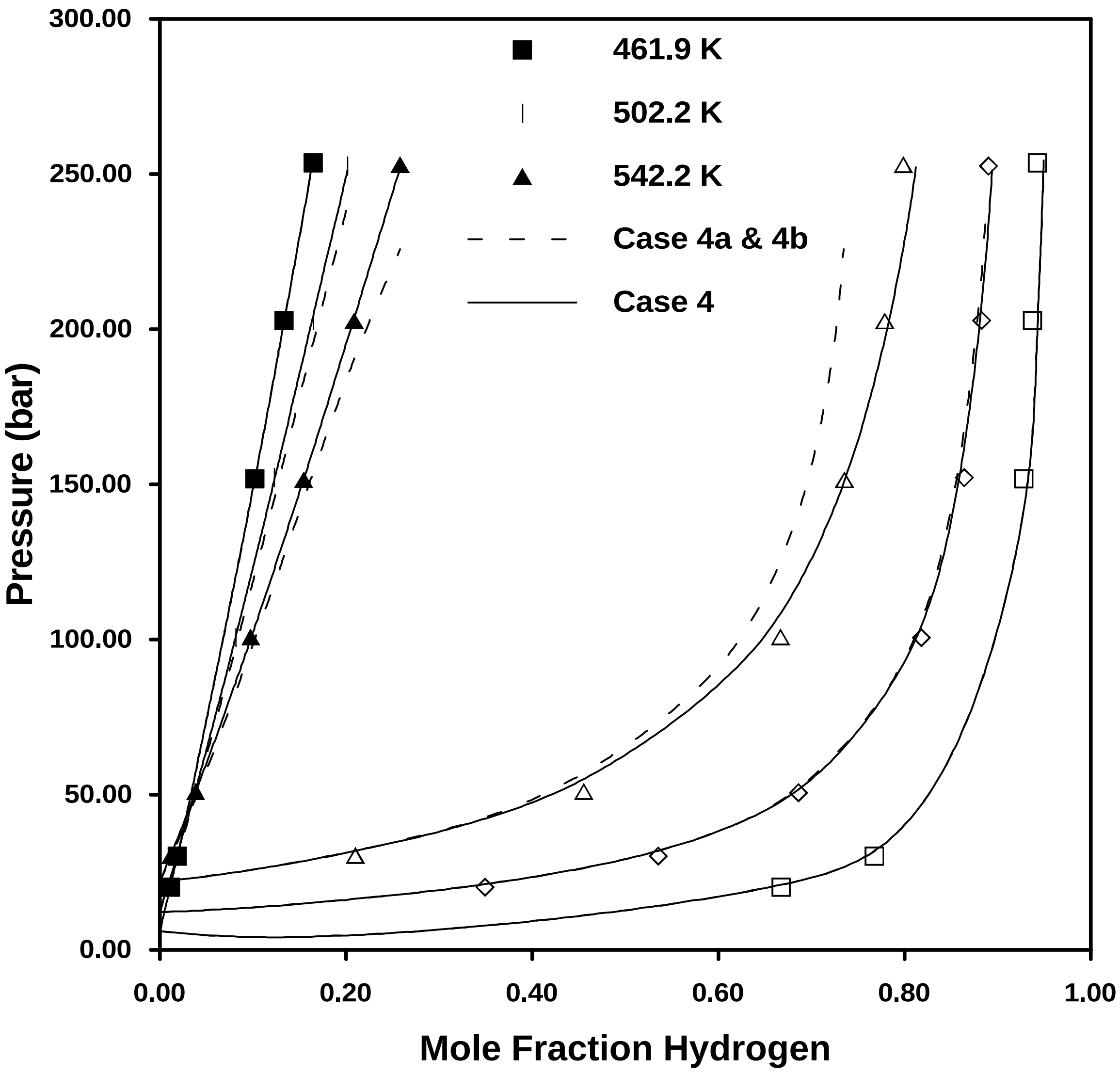

Figure 8. Representation of Vapor-Liquid Equilibrium of the Hydrogen + Toluene System Using the (θ/ϕ) Approach. Experimental Data are from Simnick et al. (1978)

Table 1

Cases studied in model evaluations

Case	Description
1	The Split (γ/ϕ) Approach Peng-Robinson equation of state with the van der Waals mixing rules (with no interaction parameter) for the vapor phase and the NRTL model for the liquid phase. This case is used for highly nonideal low pressure systems only.
2	The (ϕ/ϕ) Approach with the van der Waals Mixing Rules Peng-Robinson equation of state using the van der Waals mixing rules with two interaction parameters (C_{ij} and D_{ij}). This case is used for systems at high pressure only.
3	The (ϕ/ϕ) Approach with the MWS Mixing Rules Peng-Robinson equation of state with the MWS mixing rules. Excess model used with the mixing rules is the modified NRTL model.
4	The New (θ/ϕ) Approach Peng-Robinson equation of state using the van der Waals mixing rules with one interaction parameter (C_{ij}), and a fugacity deviation function correction applied to the calculated liquid fugacity. The Redlich-Kister model is used for the fugacity deviation function.

Table 2

Low pressure binary VLE data used in model calculations

System	Temperature Range (K)	Pressure Range (Bar)	First Component Liquid Mole Fraction Range	First Component Vapor Mole Fraction Range	Reference
Methanol + Water	298.2	0.0420 - 0.1615	0.0444 - 0.9361	0.2777 - 0.9817	Kooner et al. (1980)
	313.1	0.1404 - 0.3134	0.1499 - 0.8607	0.6279 - 0.9572	Wresky (1913)
	318.2	0.1813 - 0.4077	0.1220 - 0.8390		Zharov and Pervukhin (1972)
Ethanol + Water	298.2	0.0442 - 0.0774	0.0523 - 0.7810	0.3164 - 0.8161	Dobson (1925)
	303.2 - 308.2	0.0720 - 0.1326	0.1000 - 0.9000		D'Avila and Cotrim (1973)
2-Propanol + Water	298.2	0.0426 - 0.0665	0.0240 - 0.9097	0.2420 - 0.8580	Sazonov (1986)
	328.2	0.2337 - 0.3353	0.0320 - 0.7300	0.4190 - 0.7230	Tunik and Zharov (1980)
Water + 1-Butanol	323.2 - 403.2	0.0707 - 3.3160	0.0776 - 0.9951	0.2970 - 0.9247	Kharin et al. (1969)
Water + 2-Pentanol	343.2 - 363.2	0.1485 - 0.9250	0.0160 - 0.9990		Zou and Prausnitz (1987)
Water + 1-Hexanol	294.2 - 313.2	0.0080 - 0.0759	0.0540 - 0.9990	0.8370 - 0.9860	Filippov et al. (1977)

Table 2 (Continued)

System	Temperature Range (K)	Pressure Range (Bar)	First Component Liquid Mole Fraction Range	First Component Vapor Mole Fraction Range	Reference
Allyl Alcohol + Water	294.2 - 313.2	0.0377 - 0.1128	0.1740 - 0.7880		Ewert (1936)
Water + 2-Butoxyethanol	278.2 - 358.2	0.0019 - 0.5944	0.0703 - 0.8986	0.7193 - 0.9880	Scatchard and Wilson (1964)
Water + Cyclohexanol	363.2	0.1397 - 0.7451	0.0180 - 0.9980	0.4350 - 0.9770	Gorodetsky and Olevsky (1960)
Water + Acetic Acid	372.8 - 412.6	0.6205 - 3.5922	0.0313 - 0.9937	0.0582 - 0.9953	Freeman and Wilson (1985)
Water + Propionic Acid	333.2 - 373.2	0.0491 - 1.0296	0.0080 - 0.9850	0.0419 - 0.9850	Rafflenbeul and Hartmann (1978)
Acetone + Water	308.2	0.1833 - 0.4561	0.0500 - 0.9500	0.7060 - 0.9720	Lieberwirth and Schuberth (1979)
	323.2	0.3005 - 0.8170	0.0290 - 0.9796		Chaudhary et al. (1980)
	373.2	1.1101 - 3.6887	0.0033 - 0.9770	0.0902 - 0.9780	Griswold and Wong (1952)
2-Butanone + Water	333.2	0.3718 - 0.6146	0.0134 - 0.9250		Zou and Prausnitz (1987)

Table 2 (Continued)

System	Temperature Range (K)	Pressure Range (Bar)	First Component Liquid Mole Fraction Range	First Component Vapor Mole Fraction Range	Reference
Di-Ethyl Ether +	298.2	0.1727 - 0.7189	0.0020 - 0.9900		Signer et al. (1969)
Water	308.2	0.1876 - 1.0466	0.0014 - 0.9901		Villamanan et al. (1984)
Acetonitrile +	323.2	0.2283 - 0.3815	0.0328 - 0.9472		Wilson et al. (1979)
Water	333.2	0.4305 - 0.5622	0.0300 - 0.9471	0.4209 - 0.8939	Sugi and Katayama (1978)
Water + Ethanolamine	333.2 - 364.9	0.0131 - 0.6910	0.0690 - 0.9440		Nath and Bender (1983)
Tetrahydrofuran + Water	298.2	0.1547 - 0.2223	0.0500 - 0.9500		Signer et al. (1969)
Acetaldehyde +	283.2 - 303.2	0.2398 - 1.3350	0.1000 - 0.9000		D'Avila and Silva (1970)
Water	373.2	1.7732 - 4.8636	0.0100 - 0.1500	0.4800 - 0.7950	Byk et al. (1963)
Water +	294.2 - 313.2	0.0367 - 0.1667	0.0340 - 0.9940	0.2560 - 0.8270	Filippov et al. (1977)
Nitromethane	323.2	0.1713 - 0.2623	0.0330 - 0.9970	0.1090 - 0.9650	Schuberth (1964)
Water + 2-Methylpyridine	298.2 - 318.2	0.0217 - 0.1079	0.1270 - 0.9531		Abe et al. (1978)

Table 2 (Continued)

System	Temperature Range (K)	Pressure Range (Bar)	First Component Liquid Mole Fraction Range	First Component Vapor Mole Fraction Range	Reference
Ethyl Acetate + Water	323.2 - 353.2	0.1707 - 1.3506	0.0021 - 0.9439	0.2207 - 0.8565	Kharin et al. (1968)
Acetonitrile + tert-Butanol	333.2	0.4645 - 0.5700	0.1020 - 0.9720	0.2370 - 0.9490	Nagata (1989)
1,3-Butadiene + Acetonitrile	305.0 - 329.9	0.7260 - 6.3950	0.0560 - 0.9130		Laird and Howat (1990)
Methyl tert-Butyl Ether + Acetonitrile	313.2	0.2565 - 0.6102	0.0122 - 0.9902	0.1237 - 0.9868	Mato and Berro (1991)
Methanol + tert-Butanol	298.2 313.2	0.0612 - 0.1626 0.1395 - 0.3457	0.0773 - 0.9523 0.0155 - 0.9658	0.1535 - 0.9880	Polak et al. (1970) Oracz (1989)
tr-1,3-Pentadiene + Acetonitrile	303.2 - 313.2	0.3560 - 0.9466	0.1000 - 0.9000		Gromov et al. (1969)
Dimethyl Sulfide + Methanol	263.2 - 288.2	0.0845 - 0.4501	0.1042 - 0.9642		Jackowski (1980)

Table 2 (Continued)

System	Temperature Range (K)	Pressure Range (Bar)	First Component Liquid Mole Fraction Range	First Component Vapor Mole Fraction Range	Reference
Methyl Mercaptan + Methanol	269.2 - 288.2	0.2846 - 1.3884	0.1078 - 0.9399		Kim and Rousseau (1985)
Methyl Mercaptan + Dimethyl Sulfide	263.2 - 288.2	0.1720 - 1.3315	0.0819 - 0.9022		Jackowski (1980)
1-Butene + 1,3-Butadiene	310.9 - 338.7	4.1640 - 8.6850	0.1000 - 0.9000	0.1051 - 0.9009	Lawrence and Swift (1974)
Methanol + Dimethyl DiSulfide	310.9 - 335.9	0.2417 - 0.9619	0.1221 - 0.9802	0.7031 - 0.9734	Zudkevitch et al. (1990)

Table 3

Binary VLE data for ethane + hydrocarbons used in model evaluations

Solvent	Temperature Range (K)	Pressure Range (Bar)	Ethane Liquid Mole Fraction Range	Ethane Vapor Mole Fraction Range	Reference
n-Butane	303.2 - 363.4	4.41 - 53.26	0.0440 - 0.8370	0.1690 - 0.9510	Lhotak and Wichterle (1981)
n-Decane	311.1 - 411.1	4.23 - 82.36	0.1050 - 0.6380		Bufkin (1986)
n-Hexadecane	285.0 - 325.0	12.44 - 49.93	0.1990 - 0.8750		DeGoede et al. (1989)
n-Docosane	320.0 - 360.0	7.25 - 71.43	0.0541 - 0.8530		Peters et al. (1988)
n-Octacosane	348.2 - 423.2	5.63 - 43.94	0.1020 - 0.5200		Robinson and Gasem (1987)
n-Hexatriacontane	373.2 - 423.2	3.68 - 47.60	0.0870 - 0.5310		Robinson and Gasem (1987)
n-Tetratetracontane	373.2 - 423.2	3.87 - 31.70	0.0990 - 0.5160		Robinson and Gasem (1987)
Benzene	323.2 - 423.2	4.78 - 84.59	0.0490 - 0.6000		Bufkin (1986)
	298.2	7.76 - 38.01	0.1200 - 0.9300		Ohgaki et al. (1976)
Toluene	313.1 - 473.2	6.30 - 114.80	0.0270 - 0.9050	0.3410 - 1.0000	Richon et al. (1991)
Naphthalene	373.2 - 423.2	21.45 - 104.28	0.0850 - 0.4930		Bufkin (1986)
Cyclohexane	323.2 - 423.2	3.26 - 77.71	0.0490 - 0.6010		Bufkin (1986)
Phenanthrene	383.2 - 423.2	22.64 - 116.53	0.0810 - 0.3130		Bufkin (1986)
Pyrene	433.2	28.57 - 99.18	0.0720 - 0.2090		Bufkin (1986)

Table 4

Binary VLE data for carbon dioxide + hydrocarbons used in model evaluations

Solvent	Temperature Range (K)	Pressure Range (Bar)	CO_2 Liquid Mole Fraction Range	CO_2 Vapor Mole Fraction Range	Reference
n-Butane	277.9 - 387.6	3.45 - 62.12	0.0390 - 0.7538	0.1789 - 0.9636	Pozo de Fernandez et al. (1989)
n-Decane	310.9 - 510.9	6.89 - 86.18	0.0450 - 0.8640		Reamer and Sage (1963).
n-Hexadecane	463.1 - 623.6	20.06 - 50.87	0.0912 - 0.2350	0.7860 - 0.9955	Sebastian et al. (1980)
n-Docosane	323.2 - 373.2	9.62 - 71.78	0.0830 - 0.5930		Fall and Luks (1984)
n-Octacosane	348.2 - 423.2	8.07 - 96.04	0.0700 - 0.6170		Gasem (1986)
n-Hexatriacontane	373.2 - 423.2	5.24 - 86.53	0.0620 - 0.5020		Gasem (1986)
n-Tetratetracontane	373.2 - 423.2	5.79 - 70.81	0.0800 - 0.5020		Gasem (1986)
Benzene	298.2	8.94 - 57.73	0.1060 - 0.9130	0.9815 - 0.9959	Ohgaki et al. (1976)
	344.3	68.95 - 109.20	0.4530 - 0.8460	0.9320 - 0.9410	Nagarajan and Robinson (1987)
	413.6	38.70 - 153.90	0.1430 - 0.7010	0.8660 - 0.9080	Inomata et al. (1987)
Toluene	353.4 - 393.2	5.20 - 64.50	0.0190 - 0.3610	0.7540 - 0.9800	Kim et al. (1986)
Naphthalene	373.2 - 423.2	13.90 - 104.50	0.0470 - 0.3360		Barrick et al. (1987)
Cyclohexane	348.2 - 423.2	19.80 - 104.30	0.1030 - 0.5770		Anderson et al. (1988)
Phenanthrene	383.2 - 423.2	18.80 - 106.20	0.0470 - 0.2290		Barrick et al. (1987)
Pyrene	433.2	7.30 - 105.70	0.0140 - 0.1720		Barrick et al. (1987)

Table 5

Binary VLE data for nitrogen + hydrocarbons used in model evaluations

Solvent	Temperature Range (K)	Pressure Range (Bar)	N_2 Liquid Mole Fraction Range	N_2 Vapor Mole Fraction Range	Reference
n-Butane	250.0 - 344.4	4.83 - 157.85	0.0040 - 0.2680	0.1830 - 0.9840	Brown et al. (1989)
n-Decane	310.9 - 410.9	17.24 - 344.74	0.0385 - 0.3980	0.9270 - 1.0000	Azarnoosh and McKetta (1963)
n-Hexadecane	462.7 - 623.7	20.12 - 254.60	0.0380 - 0.5360	0.8060 - 0.9980	Lin et al. (1981)
n-Eicosane	323.2 - 423.2	38.25 - 172.29	0.0610 - 0.2120		Tong (1994)
n-Octacosane	348.2 - 423.2	42.99 - 164.71	0.0730 - 0.2580		Tong (1994)
n-Hexatriacontane	373.2 - 423.2	52.80 - 179.85	0.1050 - 0.2970		Tong (1994)
Benzene	348.2 - 398.2	62.11 - 307.12	0.0345 - 0.2044	0.9168 - 1.0000	Lin et al. (1981)
Toluene	323.2 - 348.2	36.40 - 353.50	0.0180 - 0.1590		Llave and Chung (1988)
Cyclohexane	366.4 - 410.8	17.53 - 275.93	0.0090 - 0.2910	0.7130 - 0.9720	Shibata and Sandler (1989)

Table 6

Binary VLE data for hydrogen + hydrocarbons used in model evaluations

Solvent	Temperature Range (K)	Pressure Range (Bar)	H_2 Liquid Mole Fraction Range	H_2 Vapor Mole Fraction Range	Reference
n-Butane	327.7 - 394.3	27.93 - 168.76	0.0210 - 0.2660	0.2130 - 0.9320	Klink et al. (1975)
n-Decane	462.5 - 543.0	19.26 - 255.14	0.0251 - 0.3825	0.6025 - 0.9891	Sebastian et al. (1980)
n-Hexadecane	461.7 - 622.9	20.09 - 252.71	0.0311 - 0.4458	0.8083 - 0.9995	Lin et al. (1980)
n-Eicosane	323.2 - 423.2	22.30 - 129.10	0.0273 - 0.1289		Park (1993)
n-Octacosane	348.2 - 423.2	28.60 - 131.00	0.0452 - 0.1728		Park (1993)
n-Hexatriacontane	373.2 - 423.2	35.60 - 167.50	0.0677 - 0.2271		Park (1993)
Benzene	323.2 - 423.2	25.50 - 157.30	0.0103 - 0.0585		Park (1993)
Toluene	461.9 - 542.2	30.30 - 253.72	0.0082 - 0.2581	0.2100 - 0.9430	Simnick et al. (1978)
Naphthalene	373.2 - 423.2	42.90 - 193.90	0.0160 - 0.0570		Park (1993)
Cyclohexane	310.9 - 410.9	34.47 - 551.58	0.0125 - 0.2919	0.8582 - 0.9973	Berty et al. (1966)
Phenanthrene	398.2 - 473.2	26.13 - 252.30	0.0084 - 0.0840		Malone and Koyabashi (1990)
Pyrene	433.2	51.70 - 197.30	0.0160 - 0.0580		Park (1993)

Table 7

Physical properties used in model evaluations

Compound	T_C (K)	p_c (Bar)	ω	Source
Nitrogen	126.3	33.9	0.039	Ambrose (1978)
Hydrogen	33.2	13.0	-0.218	Reid et al. (1977)
Ethane	305.4	48.8	0.099	Reid et al. (1977)
Carbon Dioxide	304.1	73.8	0.239	Reid et al. (1977)
n-Butane	425.2	38.0	0.199	Reid et al. (1977)
n-Decane	617.7	21.2	0.489	Reid et al. (1977)
n-Hexadecane	722.0	14.1	0.742	Reid et al. (1977)
n-Eicosane	770.5	11.2	0.874	Gasem (1986)
n-Docosane	791.7	10.2	0.938	Bader (1993)
n-Octacosane	845.4	8.3	1.107	Gasem (1986)
n-Hexatriacontane	901.1	6.8	1.285	Gasem (1986)
n-Tetratetracontane	944.3	6.0	1.418	Gasem (1986)
Cyclohexane	553.5	40.7	0.212	Reid et al. (1977)
Benzene	562.2	48.9	0.212	Reid et al. (1977)
Toluene	591.8	41.0	0.263	Reid et al. (1977)
Naphthalene	748.4	40.5	0.302	Reid et al. (1977)
Pyrene	938.2	26.0	0.830	Park (1993)
Phenanthrene	873.2	33.0	0.540	API (1979)
Water	647.1	220.6	0.345	AspenTech (1995)
Methanol	512.6	81.0	0.564	AspenTech (1995)
Ethanol	513.9	61.5	0.645	AspenTech (1995)
2-Propanol	508.3	47.6	0.668	AspenTech (1995)
1-Butanol	563.1	44.2	0.593	AspenTech (1995)
tert-Butanol	506.2	39.7	0.612	AspenTech (1995)
2-Pentanol	560.4	37.1	0.563	AspenTech (1995)
1-Hexanol	611.4	35.1	0.579	AspenTech (1995)
Allyl Alcohol	545.0	56.2	0.569	AspenTech (1995)
2-Butoxyethanol	633.9	32.7	0.521	AspenTech (1995)
Cyclohexanol	650.0	42.6	0.373	AspenTech (1995)
Acetic Acid	592.0	57.9	0.467	AspenTech (1995)
Propionic Acid	600.8	46.2	0.575	AspenTech (1995)
Acetone	508.2	47.0	0.307	AspenTech (1995)
2-Butanone	535.5	41.5	0.323	AspenTech (1995)
Diethyl Ether	466.7	36.4	0.281	AspenTech (1995)
Acetonitrile	545.5	48.3	0.338	AspenTech (1995)
Ethanolamine	678.2	71.2	0.447	AspenTech (1995)
Tetrahydrofuran	540.2	51.9	0.225	AspenTech (1995)

Table 7 (Continued)

Acetaldehyde	466.0	55.5	0.291	AspenTech (1995)
Nitromethane	588.2	63.1	0.348	AspenTech (1995)
2-Methylpyridine	621.0	43.8	0.278	AspenTech (1995)
Ethyl Acetate	523.3	38.8	0.366	AspenTech (1995)
1,3-Butadiene	425.2	42.8	0.190	AspenTech (1995)
Methyl tert-butyl ether	497.1	34.3	0.266	AspenTech (1995)
trans-1,3-Pentadiene	500.0	37.4	0.116	AspenTech (1995)
Dimethyl Sulfide	503.0	55.3	0.193	AspenTech (1995)
Methyl Mercaptan	470.0	72.3	0.158	AspenTech (1995)
1-Butene	420.0	40.4	0.191	AspenTech (1995)
Dimethyl Disulfide	606.0	53.6	0.265	AspenTech (1995)

Table 8

Summary of results for the representation of bubble point pressures

	CASE 1		CASE 2		CASE 3		CASE 4		
TYPE OF SYSTEMS	RMSE (Bar)	%AAD	RMSE (Bar)	%AAD	RMSE (Bar)	%AAD	RMSE (Bar)	%AAD	NO PTS
Low Pressure Systems	0.007	1.02			0.009	1.84	0.009	1.58	797
Ethane + Hydrocarbons			0.43	1.17	0.42	0.88	0.19	0.51	266
Carbon dioxide + Hydrocarbon			0.78	0.96	0.36	0.78	0.28	0.58	264
Nitrogen + Hydrocarbons			2.24	1.91	2.28	1.57	2.08	1.54	243*
Hydrogen + Hydrocarbons			1.81	1.02	2.30	1.25	0.85	0.56	274*

* - The number of points analyzed for Case 3 for these systems was slightly less than this number due to convergence problems.

Table 9

Temperature dependence of the model parameters for the (θ/ϕ) approach

		DEVIATIONS IN PREDICTED BUBBLE POINT PRESSURES						
		CASE 4		CASE 4a		CASE 4b		
SYSTEM	TEMP RANGE (K)	RMSE (Bar)	%AAD	RMSE (Bar)	%AAD	RMSE (Bar)	%AAD	NO PTS
Acetone + Water	308.2 - 373.2	0.019	0.95	0.128	4.23	0.082	3.12	56
Ethane + n-Octacosane	348.2 - 423.2	0.11	0.49	0.26	1.09	0.21	0.94	24
Carbon dioxide + n-Decane	310.9 - 510.9	0.23	0.31	3.24	5.06	1.49	2.84	23
Nitrogen + n-Hexadecane	462.7 - 623.7	0.55	0.37	2.26	1.66	2.82	1.56	22
Hydrogen + Toluene	461.9 - 542.2	0.73	0.45	8.26	3.02	8.26	3.02	18

Table 10

Comparison of results for the representation of bubble point pressures between the (θ/ϕ) approach (Case 4b) and the conventional approaches (Case 1 or Case 2) for a system-by-system analysis

SYSTEM	TEMP RANGE (K)	CASE 4b (θ/ϕ)		CASE 1 OR 2		
		RMSE (Bar)	%AAD	RMSE (Bar)	%AAD	
Acetone + Water	308.2 - 373.2	0.082	3.12	0.066	2.81	(γ/ϕ)
Ethane + n-Octacosane	348.2 - 423.2	0.21	0.94	1.04	3.54	(ϕ/ϕ)
Carbon dioxide + n-Decane	310.9 - 510.9	1.49	2.84	1.39	2.87	(ϕ/ϕ)
Nitrogen + n-Hexadecane	462.7 - 623.7	2.82	1.56	2.68	1.98	(ϕ/ϕ)
Hydrogen + Toluene	461.9 - 542.2	8.26	3.02	8.97	4.87	(ϕ/ϕ)