A NEW FRAMEWORK FOR VAPOR-LIQUID EQUILIBRIUM CALCULATIONS

By

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NOMENCLATURE

a	Cubic equation of state cohesive energy parameter
$\overline{A}$	Molar Helmholtz free energy
b	Cubic equation of state covolume parameter
BIAS	Arithmetic average of deviations of a finite number of observations
B, C, D	Parameters for Redlich-Kister model
C_{ij}, D_{ij}	Binary interaction parameters in the van der Waals mixing rules
f	Fugacity
$\overline{G}$	Molar gibbs free energy
p	Pressure
R	Universal gas constant
RMSE	Root-mean-squared error of a finite number of observations
SS	Objective function to be minimized (Equation 4-14)
T	Temperature
v	Molar volume
z. x, y	Mole fraction
%AAD	Arithmetic average of percent absolute deviations of a finite number of observations

Greek letters

α	Temperature-dependent parameter in Equation (4-8)
ω	Acentric factor
σ	Constant in Huron-Vidal mixing rules (Equation 2-5) or Wong-Sandler mixing rules (Equation 2-10)
γ	Activity coefficient
ϕ	Fugacity coefficient
θ	Fugacity deviation function
τ_{12}, τ_{21}, α_{12}	Parameters for NRTL model

Subscripts

c	Critical state
eos	Equation of state
i, j, k, l	Component identification numbers
mix	Mixture property
r	Reduced property

Superscripts

cal	Calculated Value
E	Excess property
eos	Equation of state
exp	Experimental Value
ig	Ideal gas

is	Ideal solution
j	Phase identification number
l	Liquid phase
ref	Reference state
v	Vapor phase

CHAPTER I

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). The term "equations of state" is used in a broad sense to include mathematical description of volumetric behavior, derived properties, mixture behavior and phase equilibrium of fluids.

Historically, the most commonly used equations of state are the cubic van der Waals type equations such as the Peng-Robinson (Peng and Robinson, 1976) and the Redlich-Kwong (Redlich and Kwong, 1949) equations. While cubic equations are capable of representing the qualitative features of vapor-liquid systems, their largely empirical nature limits the interpretation that can be placed upon the equation parameters. These commonly used cubic equations also suffer from several shortcomings, including the inability to predict accurate liquid densities and an overall loss of accuracy in the critical region. In addition, cubic equations of state cannot accurately describe the behavior of mixtures containing polar or associating molecules and mixtures containing molecules with large difference in size, without elaborate tuning efforts (Gasem et al., 1993).

The greatest utility of cubic equations 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 equation of state 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 commonly used ones being the van der Waals one-fluid mixing and combining rules. The use of the van der Waals mixing rules can be justified on theoretical grounds at low densities (Sandler et al., 1994). However, a shortcoming of these mixing rules is that they are applicable only to mixtures of relatively moderate solution (in contrast to pvT) non-ideality. In fact, the limitations imposed by these mixing rules is considered one of the prime reasons for the inability of the conventional cubic equations to successfully describe the behavior of mixtures containing polar or associating molecules and mixtures containing molecules with a large difference in size. For such mixtures, the alternative approach has been the use of activity coefficient models for the condensed phase and an equation of state for the vapor phase (Prausnitz, 1977). However, as will be shown later, this approach also has it's drawbacks, which are more fundamental.

To avoid the use of activity coefficient models and to improve the predictive abilities of the conventional equations of state, various mixing rules have been proposed, which will be discussed briefly in a subsequent chapter. 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 also theoretically sound were introduced by Wong and Sandler (1992). Orbey and Sandler (1995a) 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 vapor-liquid equilibrium (VLE) framework (Gasem, 1989). The basic premise of this new method is to use a fugacity deviation function to augment the fugacity generated from an equation of state. As mentioned previously, an equation of state 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 equation of state may alleviate this problem without altering the mixing rules.

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

1. Evaluate the effect of a fugacity deviation function correction on the phase behavior predictive abilities of an equation of state.
2. Evaluate the comparable phase behavior predictive abilities of the equation of state using the modified Wong-Sandler (MWS) mixing rules.
3. Compare the above with the conventional methods for calculating phase equilibrium properties, i.e., using an equation of state for both phases or an equation of state for the vapor phase with an activity coefficient model for the liquid phase.

The Peng-Robinson equation of state was selected for the purposes of this evaluation.

Chapter II of this thesis presents a brief review of the various mixing rules used for cubic equations of state. Chapter III contains discussions involving the fugacity deviation function. Chapter IV presents the results and comparisons of the fugacity deviation function approach with the conventional approaches and the MWS mixing rules. Chapter V contains conclusions and recommendations from the current work.

CHAPTER II

LITERATURE REVIEW

A Brief Review of Mixing Rules

The most convenient form for representation of equilibrium phase behavior for process design and optimization calculations has long been recognized as that of analytic equations of state (Prausnitz, 1977). The most commonly used equations of state are the cubic van der Waals type equations such as the Peng-Robinson (Peng and Robinson, 1976) and the Redlich-Kwong (Redlich and Kwong, 1949) equations. For the application of these equations to mixtures, the mixture parameters are obtained from pure component parameters using mixing rules. The most commonly used mixing rules are the van der Waals one-fluid mixing rules (Gasem et al., 1993)

$$a = \sum \sum z_i z_j a_{ij} \tag{2-1}$$

$$b = \sum \sum z_i z_j b_{ij} \tag{2-2}$$

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

$$a_{ij} = \sqrt{a_{ii} a_{jj}}(1 - C_{ij}) \tag{2-3}$$

$$b_{ij} = \frac{1}{2}(b_{ii} + b_{jj})(1 + D_{ij}) \tag{2-4}$$

where C_{ij} and D_{ij} are empirical "binary interaction parameters" obtained by fitting equation of state predictions to experimental data.

Equating a cubic equation of state with the virial expansion, which has a sound theoretical basis at low densities, should lead to a quadratic composition dependence of the second virial coefficient (Sandler et al., 1994). This provides a justification for the van der Waals mixing rules at low densities. In fact, until recently, these were the only mixing rules in general use, and they were used at all densities. Since there are no results from statistical mechanics which are generally valid at high densities, the theoretically correct composition dependence of the mixture equation of state parameters at these conditions is unknown.

A shortcoming of the van der Waals mixing rules is that they are applicable only to mixtures of relatively moderate solution (in contrast to pvT) non-ideality. The combination of a cubic equation of state and the van der Waals mixing rules can only represent mixtures which have approximately the same degree of solution non-ideality as can be described by regular solution theory (Sandler et al., 1994). However, many mixtures of interest in the chemical industry exhibit much greater non-ideality and have been described traditionally by activity coefficient (excess Gibbs free energy) models (Prausnitz, 1977). To improve the capabilities of the cubic equations of state and thus, avoid the use of free energy models, various mixing rules have been proposed to describe highly non-ideal mixtures (see, e.g., Sandler et al., 1994).

Huron and Vidal (1979) used a combination of an equation of state and an excess Gibbs free energy model to develop the Huron-Vidal mixing rules. The mixing rule for the b parameter is the same as Equation (2-2), and the mixing rule for the a parameter is

$$a = b\left[\sum z_i\left(\frac{a_i}{b_i}\right) - \sigma\overline{G}^E\right] \tag{2-5}$$

where $\overline{G}^E$ is the molar excess Gibbs free energy, and σ is a numerical constant which depends on the equation of state being used. This mixing rule was the first to combine a free energy model with an equation of state to represent highly non-ideal solutions. Implementing this approach with the Wilson or NRTL models (Walas, 1985) has been very successful for describing some highly non-ideal systems. Nevertheless, it suffers from a number of theoretical and computational difficulties. First, the mixing rule was developed by equating the excess Gibbs free energy obtained from an equation of state to that obtained by an excess Gibbs free energy model at infinite pressure. This use of free energy models at infinite pressure is inconsistent as these models were developed for low pressures. Second, this mixing rule is not always capable of describing simple systems which have traditionally been described by the van der Waals mixing rules. Third, it does not satisfy a theoretical requirement that the second virial coefficient have a quadratic composition dependence. Fourth, the parameters obtained by the use of this mixing rule are different from the parameters obtained by the direct use of the same free energy model. Thus, one cannot use the parameter tables developed for the free energy models with this approach.

An entirely different approach has been to add an additional composition dependence to the combining rule of the a parameter in the van der Waals mixing rules, generally leaving the b parameter unchanged. Examples are the combining rules of Panagiotopoulos and Reid (1986)

$$C_{ij} = K_{ij} - \left(K_{ij} - K_{ji}\right) z_i \tag{2-6}$$

Adachie and Sugie (1986)

$$C_{ij} = K_{ij} + D_{ij}\left(z_i - z_j\right) \tag{2-7}$$

Sandoval et al. (1989)

$$C_{ij} = K_{ij} z_i + K_{ji} z_i + 0.5\left(K_{ij} + K_{ji}\right)\left(1 - z_i - z_j\right) \tag{2-8}$$

Shwartzentruber and Renon (1989a, 1989b)

$$C_{ij} = K_{ij} + D_{ij} \frac{m_{ij} z_i - m_{ji} z_j}{m_{ij} z_i + m_{ji} z_j}\left(z_i + z_j\right) \tag{2-9}$$

where in this last equation, $K_{ij} = K_{ji}, D_{ij} = -D_{ji}, m_{ji} = D_{ij} - m_{ij}, K_{ii} = D_{ii} = 0$. However, these combining rules, when used with the van der Waals mixing rules, do not satisfy the theoretical boundary condition of a quadratic composition dependence of the resulting second virial coefficient. A second problem associated with the combining rules of Equations (2-6) through (2-9) is the so-called Michelsen-Kistenmacher (1990) syndrome, in which a mixing rule is not invariant to the subdivision of a component in two or more identical components. Another problem, also pointed out by Michelsen and Kistenmacher (1990), is that the added composition-dependent term depends explicitly on mole fractions rather than on a mole ratio. Consequently, the added terms become less important as the number of components in a mixture increases. For example, the value of a_{12} will be different in binary and multicomponent mixtures with the same species 1: species 2 mole ratio.

To achieve the objective of satisfying the theoretical low density limit of a quadratic composition dependence of the second virial coefficient, there has been some research on density-dependent mixing and/or combining rules also (Michel et al., 1989; Copeman and Mathias, 1986; Sandler et al., 1986). However, a density-dependent mixing rule introduces the conceptual problem that the order of the equation of state with respect to density changes depending on the number of components, which violates the one-fluid model. For example, the volume dependence of an equation of state would change even if a pure species is mixed with one of its isomers. Moreover, the resultant higher order equation of state poses numerical difficulties in implementation and increased computation time.

Wong and Sandler (1992) developed a set of mixing rules for cubic equations of state which equates the excess Helmholtz free energy at infinite pressure from an equation of state to that from an activity coefficient model. Use of the Helmholtz free energy insures that the second virial coefficient calculated from the equation of state has a quadratic composition dependence, as required by statistical mechanics. The basic equations for the mixture parameters of a cubic equation of state, a and b are

$$b = \frac{\sum\sum z_i z_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \frac{\overline{A}^E}{\sigma RT} - \sum z_i \frac{a_i}{RTb_i}} \tag{2-10}$$

$$\frac{a}{b} = \sum z_i \frac{a_i}{b_i} + \frac{\overline{A}^E}{\sigma} \tag{2-11}$$

In the above equations, $\overline{A}^E$ is the molar excess Helmholtz free energy, and σ is a numerical constant which depends on the equation of state being used (e.g., $\sigma = -0.62323$ for the Peng-Robinson equation of state). The combining rule for the cross second virial coefficient in Equation (2-10) is

$$\left(b-\frac{a}{RT}\right)_{ij}=\frac{\left(b-\frac{a}{RT}\right)_{i}+\left(b-\frac{a}{RT}\right)_{j}}{2}\left(1-C_{ij}\right) \tag{2-12}$$

The parameter C_{ij} as used in the Wong-Sandler (WS) mixing rule is a second virial coefficient binary interaction parameter and is different from the parameter C_{ij} as used in the van der Waals mixing rule (Equation 2-3). The functionality for the excess Helmholtz free energy comes from any of the excess Gibbs free energy models currently used. The relation between the two is

$$\overline{G}^{E}=\overline{A}^{E}+pv^{E} \tag{2-13}$$

where v^E is the molar excess volume. At low pressures, the term pv^E is very small and to a good approximation, we have

$$\overline{G}^{E}(\text{low p})\approx\overline{A}^{E}(\text{low p}) \tag{2-14}$$

Also, the excess free Helmholtz energy is essentially independent of pressure (or density) and thus, the value of $\overline{A}^{E}$ obtained from Equation (2-14) can be used at infinite pressure, i.e.

$$\overline{G}^{E}(\text{low p})\approx\overline{A}^{E}(\text{low p})\approx\overline{A}^{E}(p=\infty) \tag{2-15}$$

The WS mixing rules, when used with a modified version of the Peng-Robinson equation of state (Stryjeck and Vera, 1986), have been shown to be reasonably successful in correlating the phase behavior of highly non-ideal mixtures (Wong et al., 1992; Huang and Sandler, 1993; Orbey et al., 1993; Huang et al., 1994; Eubank et al., 1995; Voutsas, et al., 1995).

Recently, Orbey and Sandler proposed a reformulation of these mixing rules (Orbey and Sandler, 1995a). The proposed reformulation ensures that the mixing rules go smoothly from activity coefficient-like behavior to the van der Waals mixing rules by variation of their parameters. This is important for the description of multicomponent mixtures in which only some of the binary pairs require mixing rules of the WS type, while other binaries can be described by the van der Waals mixing rules. Thus, multicomponent mixtures containing both types of binaries can be described in a unified framework. In the modified Wong-Sandler (MWS) mixing rules, the basic equations for b and a, Equations (2-10) and (2-11), remain the same, but the combining rule for the cross virial coefficient, Equation (2-12) is modified to

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j}}{RT}\left(1 - C_{ij}\right) \tag{2-16}$$

This ensures that the van der Waals one-fluid mixing and combining rules with the usual definition of the binary interaction parameter will be recovered. The interaction parameter C_{ij} as used in the MWS mixing rule is the same as the parameter C_{ij} used in the van der Waals mixing rule (Equation 2-3). The MWS mixing rules can be used only with certain free energy models, like the van Laar (Walas, 1985) or the modified NRTL (Huron and Vidal, 1979), if they are to be used in multicomponent systems of the type described above. The use of these models in the MWS mixing rules ensures that the van der Waals mixing rules are obtained for some model parameter values. The use of other free energy models is not incorrect, but the van der Waals mixing rule cannot be obtained if these models are used.

The suggested reformulation is a matter of convenience for the use of the relatively complex MWS mixing rules with the more commonly used and simpler van der Waals mixing rules. The choice of a free energy model ceases to be a factor if the MWS mixing rules, by themselves, are chosen to describe all the binaries of a multicomponent system. The MWS mixing rules have been shown to correlate the behavior of some systems containing alcohols and alkanols (Orbey and Sandler, 1995b). However, the range of applicability of these mixing rules and their correlative abilities, in general, are not very well known. One of the objectives of this work was to evaluate the MWS mixing rules for their ability to correlate the behavior of non-ideal mixtures.

CHAPTER III

A FUGACITY DEVIATION FUNCTION

Deviation Functions

The following discussion gives a brief overview of deviation functions and their significance (see, e.g., Abbott and Nass, 1986; Denbigh, 1981). It is rarely practical to work directly with a mixture property M. M may not be defined unambiguously, and thus, in principle, may not allow direct experimental determination. Internal energy (U) and entropy (S) are prime examples of such properties. Similarly, the Gibbs free energy (G) and the enthalpy (H) are defined in terms of U and S. Moreover, a mixture property is usually not represented by a simple sum of the pure fluid property contributions, i.e.

$$M \neq \sum_i \overline{M}_i n_i \tag{3-1}$$

where $\overline{M}_i$ is a pure fluid molar property, and n_i .represents the mole number of species i.

The partial molar property concept allows us to define a mixture property in terms of constituent contributions. Thus, we can state that

$$M = \sum_i \widetilde{M}_i n_i \tag{3-2}$$

where $\widetilde{M}_i$ is a partial molar property. The property change due to mixing can be written as

$$\Delta M_{mix} = M - \sum_i \overline{M}_i n_i \tag{3-3}$$

To overcome the problems involved in dealing with a mixture property directly, the concept of deviation functions was introduced. In this approach, mixture properties are calculated in terms of their deviations from a particular reference model under the same conditions.

$$\begin{aligned} M^{D} &= M - M^{ref} \qquad \text{or} \\ M^{D} &= \Delta M_{mix} - \Delta M_{mix}^{ref} \end{aligned} \tag{3-4}$$

Desirable attributes of the selected reference model include (Abbott and Nass, 1986)

1. The model should reflect some molecular description for the mixture at hand.
2. The model should have an analytical expression, preferably a simple one.
3. The deviation function should have unambiguous limits.

For gases, the reference model usually used is the ideal (or perfect) gas law and the deviation function is called a residual property. For liquid solutions, the reference model usually used is the ideal liquid solution and the deviation function is called an excess property. Fugacity coefficients and activity coefficients are probably the two most important quantities used in phase equilibrium calculations. These quantities are, in fact, dimensionless deviation functions and represent deviations from a perfect gas mixture and an ideal liquid solution, respectively. The fugacity coefficient for a component of a mixture, $\hat{\phi}_i$, can be defined as

$$\ln \hat{\phi}_i = \ln\left(\frac{\hat{f}_i}{p_i}\right) = \frac{\mu_i - \mu_i^{ig}}{RT} \tag{3-5}$$

where μ_i is the actual chemical potential of the component, μ_i^{ig} is the chemical potential of the component evaluated by the ideal gas model under the same conditions, and $\hat{f}_i$ and

p_i are the fugacity and partial pressure of the component, respectively. In the above equation, T is the temperature of the mixture and R is the universal gas constant. Similarly, the activity coefficient for a component of a mixture γ_i can be defined by

$$\ln \gamma_i = \ln \frac{\hat{f}_i}{\hat{f}_i^{ref}} = \frac{\mu_i - \mu_i^{is}}{RT} \tag{3-6}$$

where $\hat{f}_i^{ref} = z_i f_i$

In Equation (3-6), μ_i^{is} is the chemical potential of the component evaluated by the ideal liquid solution model under the same conditions, and f_i is the fugacity of the pure component at a selected reference state.

The criterion of equilibrium between any number of phases at a given temperature and pressure is

$$\mu_i^1 = \mu_i^2 = \mu_i^3 = \ldots = \mu_i^j \tag{3-7}$$

for $i = 1, n$

$j = 1, m$

where n and m are the number of components in the mixture and the number of phases, respectively. Thus, at equilibrium, the chemical potential of each component should be equal in all phases. Now, the fugacity of a component of a mixture is related to its chemical potential by

$$\mu_i = \mu_i^o + RT \ln \hat{f}_i \qquad \hat{f}_i / p_i \rightarrow 1 \quad \text{as} \quad p \rightarrow 0 \tag{3-8}$$

In Equation (3-8), μ_i^o is a function of temperature only. Thus, it is the chemical potential of pure i at unit fugacity. Since μ_i^o is a function of temperature only, the criterion of equilibrium for two or more phases in equilibrium at a given temperature and pressure in terms of chemical potentials can also be written as

$$\hat{f}_i^1 = \hat{f}_i^2 = \hat{f}_i^3 = \ldots = \hat{f}_i^j \qquad (3\text{-}9)$$

for $i = 1, n$

$j = 1, m$

Thus, at equilibrium, the fugacity of each component should be equal in all phases. This criterion of equilibrium is, in principle, sufficient for practical phase equilibrium calculations. The fugacity of a component in a mixture is usually calculated by means of Equation (3-5) or (3-6). Fugacity coefficients in Equation (3-5) can be calculated from an equation of state used to model the behavior of the system. This method of handling phase equilibrium problems using an equation of state for all phases is often called the (ϕ/ϕ) approach. The criterion of vapor-liquid equilibrium using the (ϕ/ϕ) approach can be written as

$$x_i p \hat{\phi}_i^l = y_i p \hat{\phi}_i^v \qquad (3\text{-}10)$$

for $i = 1, n$

In Equation (3-10), x and y represent liquid and vapor phase mole fractions and the superscripts l and v refer to the liquid and vapor phase, respectively. However, most equations of state are not highly accurate in modeling the behavior of condensed phases, especially complex mixtures. Due to this, phase equilibrium calculations using this approach have not been very successful for many systems. Figure 1 is an example of the inability of an equation of state equipped with the van der Waals mixing rules to handle the behavior of highly non-ideal systems. For all figures in this study, the continuous lines represent model predictions and the symbols represent experimental data, with the

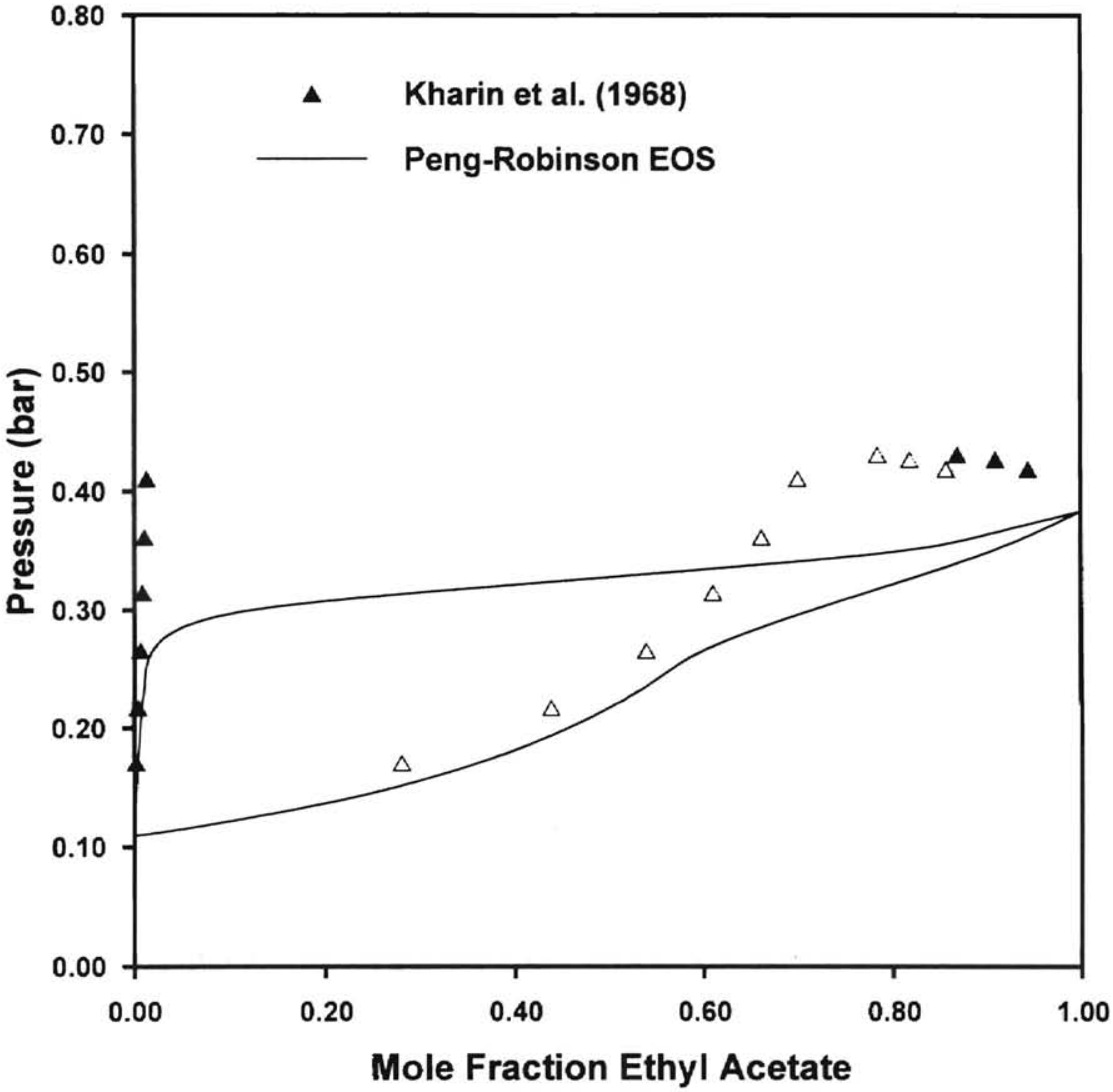

Figure 1. Representation of Vapor-liquid Equilibrium for the Ethyl Acetate + Water System at 323.2 K Using the Peng-Robinson Equation of State Equipped with the van der Waals Mixing Rules.

filled symbols representing the liquid phase.

An alternative approach has been to calculate the fugacities in the liquid phase by means of Equation (3-6) and the fugacities in the vapor phase by means of Equation (3-5). The activity coefficients are calculated by means of excess Gibbs free energy models. This method of handling phase equilibrium calculations is called the split (γ/ϕ) approach. The criterion of vapor liquid equilibrium using the (γ/ϕ) approach can be written as

$$x_i f_i^{ref} \gamma_i = y_i p \hat{\phi}_i^v \qquad (3\text{-}11)$$

for $i = 1, n$

The reference fugacity in the above equation is a pure component reference fugacity, which depends on the reference state used to define γ_i. For subcritical components, the reference state is usually the pure liquid state at the temperature and pressure of the solution. For supercritical components, a hypothetical state corresponding to extrapolation along the Henry's law gradient to a mole fraction of unity is used as a reference state. In the preceding discussion, it might be noted that, for both the methods, by same "conditions", we mean the same temperature, pressure and composition as these are the independent variables generally used in phase equilibrium calculations.

Limitations of the Split (γ/ϕ) Approach

As mentioned previously, many systems which cannot be modeled by equations of state are handled by means of activity coefficient (excess Gibbs free energy) models. These models have been reasonably successful in modeling the equilibrium behavior of many systems. However, the primary problem with these models is the need for assumption of reference states. They cannot be applied to systems where even one component does not exist as a liquid at the same temperature and pressure as that of the solution, unless hypothetical reference states are assumed (Denbigh, 1981). Further, even for systems whose components are liquids at the same temperature and pressure as that of the solution, the implications of an ideal solution, as defined by the Lewis-Randall rule, are sometimes confused with the Raoult's law model (Peng, 1990). As pointed out by the same author, for a system which follows Raoult's law, in the two-phase region, neither the vapor nor the liquid is an ideal solution in a strict sense. In addition, he showed that the use of hypothetical reference states to qualify the model fluids of Raoult's law at VLE conditions as ideal solutions may lead to confusion, if not inconsistency, in Gibbs energy analysis. Wilczek-Vera and Vera (1990) have recently reexamined and organized the common reference states used for activity coefficients. However, the need for such organization is a pointer to the ambiguities in activity coefficient models. Additional limitations of the (γ/ϕ) method include difficulties in applying it to the critical region and the need for a separate method for calculating volumetric properties (Prausnitz et al., 1986).

Proposed Method

The equation of state (ϕ/ϕ) approach has inherent limitations in that it cannot model phase equilibrium for systems which exhibit appreciable solution (in contrast to pvT) non-ideality (Sandler et al., 1994). As mentioned previously, 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 liquid phase fugacities obtained using an equation of state by a deviation function (Gasem, 1989). The fugacity deviation function, say $\hat{\theta}_i$, can be defined by

$$\hat{\theta}_i = \frac{\hat{f}_i}{\hat{f}_i^{eos}} \tag{3-12}$$

where, $\hat{f}_i$ is the actual fugacity of the component and $\hat{f}_i^{eos}$ is the fugacity calculated by the equation of state 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

$$\begin{aligned} &\hat{\theta}_i \to 1 \quad \text{as} \quad z_i \to 1 \\ &\hat{\theta}_i \to 1 \quad \text{as} \quad p \to 0 \end{aligned} \tag{3-13}$$

This makes the fugacities calculated by the equation of state applicable at the limits of the pure components. Also, this would allow the Equations (3-7) through (3-9) to be applicable to this particular approach and eliminate any ambiguities regarding limiting behavior for different systems. However, other limiting conditions may be used to define the pure component limits.

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

$$\mu_i = \mu_i^o + RT\ln\hat{\theta}_i\hat{f}_i^{eos} \tag{3-14}$$

The total Gibbs free energy of a phase is defined by (Denbigh, 1981)

$$G = \sum n_i\mu_i \tag{3-15}$$

Substituting the value of the chemical potential from Equation (3-14)

$$G = \sum n_i \mu_i^o + RT\sum n_i \ln \hat{f}_i^{eos} + RT\sum n_i \ln \hat{\theta}_i \tag{3-16}$$

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

$$G_{eos}^{E} = RT\sum n_i \ln \hat{\theta}_i \tag{3-17}$$

If we differentiate the above expression at constant temperature and pressure

$$dG_{eos}^{E} = RT\sum n_i d\ln \hat{\theta}_i + RT\sum \ln \hat{\theta}_i d n_i \tag{3-18}$$

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

$$-SdT + Vdp - \sum n_i d\mu_i = 0 \tag{3-19}$$

At a constant temperature and pressure, substituting for the chemical potential from Equation (3-14), the above equation can be written as

$$\sum n_i d\ln \hat{\theta}_i + \sum n_i d\ln \hat{f}_i^{eos} = 0 \tag{3-20}$$

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 equation of state 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 (3-18) can be written as

$$\left(\frac{\partial G_{eos}^{E}}{\partial n_i}\right)_{T,P,n_j} = RT\ln \hat{\theta}_i \tag{3-21}$$

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.

For convenience, the fugacity deviation function $\hat{\theta}_i$ can also be correlated by any of the conventional activity coefficient models (or any correlation that obeys the Gibbs-Duhem relation). However, such a strategy is not optimum in 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 equation of state as the reference model for evaluating mixture properties. Figure 2 compares the deviation functions θ (deviation from an equation of state) and γ (deviation from an ideal solution) obtained for the acetone + water system at 373.2 K. Figure 3 compares the fugacities calculated by the (θ/ϕ) approach, the (ϕ/ϕ) approach and an ideal solution for the same system. These figures are shown for illustrative purposes only and no inference regarding the relative magnitudes of the deviation functions can be drawn from them. However, one should normally expect the deviation function θ to be smaller than γ, since an equation of state is generally a better reference model than an ideal solution. Also, θ can be expected to show maxima or minima, when plotted as a function of composition, and a model for θ should be able to handle such behavior.

Calculating the Fugacity Deviation Function from Experimental Data

An equation for the calculation of $\hat{\theta}_i$ from experimental data can be derived in the same manner as the equation for the fugacity coefficient, which is derived below (Denbigh, 1981). For each component of a mixture, we have the following relation

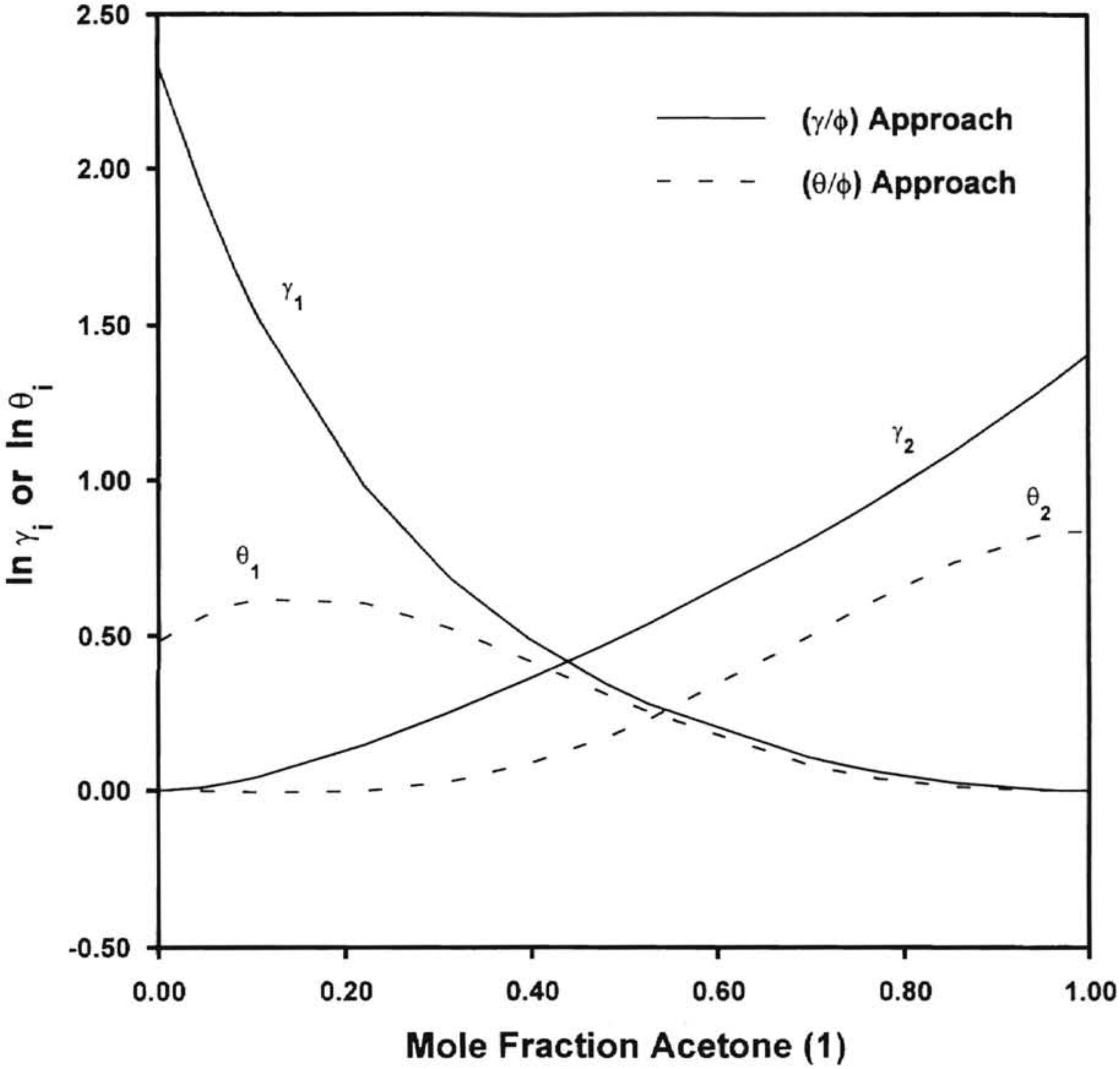

Figure 2. Comparison of Deviation Functions Generated from the (γ/ϕ) Approach and the (θ/ϕ) Approach for the Acetone (1) + Water (2) System at 373.2 K

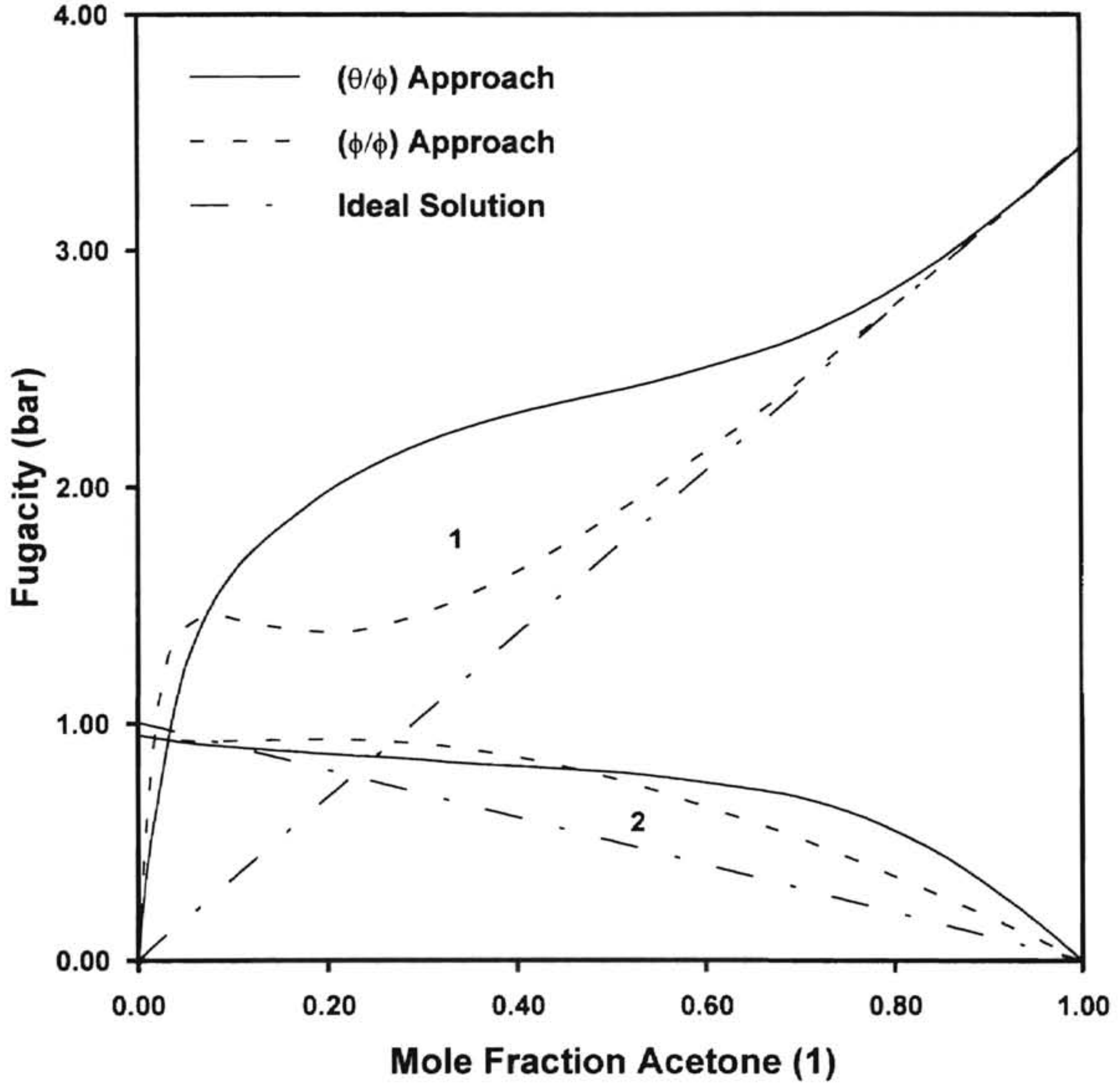

Figure 3. Comparison of Fugacities Calculated by the (θ/ϕ) Approach, the (ϕ/ϕ) Approach and the Ideal Solution Model for the Acetone (1) + Water (2) System at 373.2 K

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i,n_j} = \tilde{v}_i \tag{3-22}$$

where the differentiation is at a constant temperature and composition, and the term on the right hand side of the equation is the partial molar volume of that component. Thus, at a given temperature and composition

$$d\mu_i = \tilde{v}_i dp \tag{3-23}$$

Under the same conditions, we have

$$d\mu_i = RTd\ln\hat{f}_i \tag{3-24}$$

Thus

$$RTd\ln\hat{f}_i = \tilde{v}_i dp \tag{3-25}$$

Subtracting $RTd\ln p_i$ from both sides

$$\begin{aligned} RTd\ln\left(\hat{f}_i / p_i\right) &= \tilde{v}_i dp - RTd\ln p_i \\ &= \tilde{v}_i dp - RTd\ln p - RT\ln z_i \\ &= \left(\tilde{v}_i - \frac{RT}{p}\right) dp \end{aligned} \tag{3-26}$$

Integrating at constant temperature and composition from p = 0 to the desired system pressure p, we obtain

$$\ln\left(\hat{f}_i / p_i\right)_p = \int_0^p \left(\frac{\tilde{v}_i}{RT} - \frac{1}{p}\right) dp \tag{3-27}$$

The above result is due to the limiting condition that the fugacity of a component approaches its partial pressure as total system pressure approaches zero. For a perfect gas mixture, $\tilde{v}_i = RT/p$, and the integrand in the above equation is zero. Thus, the fugacity is equal to the partial pressure.

The derivation so far has been limited to the (ϕ/ϕ) approach. For the (θ/ϕ) approach, the derivation for the calculation of $\hat{\theta}_i$ is similar except that Equation (3-26) can now be written as

$$\begin{aligned} RTd\ln\left(\hat{\theta}_i \hat{f}_i^{eos}/p_i\right) &= \tilde{v}_i dp - RTd\ln p_i \\ &= \tilde{v}_i dp - RTd\ln p - RT\ln z_i \qquad (3\text{-}28) \\ &= \left(\tilde{v}_i - \frac{RT}{p}\right) dp \end{aligned}$$

$$RTd\ln\hat{\theta}_i + RTd\ln\left(\hat{f}_i^{eos}/p_i\right) = \left(\tilde{v}_i - \frac{RT}{p}\right) dp \qquad (3\text{-}29)$$

The second term on the left hand side of the above equation can be replaced by the right hand side of Equation (3-26)

$$RTd\ln\hat{\theta}_i + \left(\tilde{v}_i^{eos} - \frac{RT}{p}\right) dp = \left(\tilde{v}_i - \frac{RT}{p}\right) dp \qquad (3\text{-}30)$$

The superscript on the partial molar volume indicates that it is the partial molar volume calculated by the equation of state, so as to distinguish it from the actual partial molar volume. Rearranging

$$RTd\ln\hat{\theta}_i = \left(\tilde{v}_i - \tilde{v}_i^{eos}\right) dp \qquad (3\text{-}31)$$

As before, integrating at constant temperature and composition from p = 0 to the pressure p at which the value of $\hat{\theta}_i$ is to be calculated, we obtain

$$\ln\hat{\theta}_i = \frac{1}{RT}\int_0^p \left(\tilde{v}_i - \tilde{v}_i^{eos}\right) dp \qquad (3\text{-}32)$$

Again, the above result is due to the limiting condition that $\hat{\theta}_i$ approaches unity as the system pressure approaches zero. Thus, the fugacity coefficient $\hat{\phi}_i$ represents deviations from the ideal gas model, whereas $\hat{\theta}_i$ represents deviations from an equation of state.

CHAPTER IV

RESULTS AND DISCUSSION

The proposed method discussed in the previous chapter was evaluated using a database comprised of non-ideal systems at low pressures (generally handled by the split (γ/ϕ) approach) and asymmetric mixtures containing supercritical fluids with hydrocarbons at high pressures (generally handled by the equation of state (ϕ/ϕ) approach). Following are detailed descriptions of the different methods studied and the results obtained.

Model Evaluations

Desirable attributes of a thermodynamic framework for calculating phase equilibrium problems include

1. A sound theoretical basis
2. Ability to represent existing experimental data with good precision
3. Model parameters that are amenable to generalizations

As shown in the previous chapter, the proposed (θ/ϕ) approach is theoretically rigorous and can be derived from the basic equations of classical thermodynamics. The MWS mixing rules also have a sound theoretical basis. Both these methods essentially use an excess Gibbs free energy model to extend the applicability of equations of state to non-ideal systems. However, the MWS mixing rules use the excess model within the mixing rules employed by the equation of state, whereas the (θ/ϕ) approach uses the excess model to account for the deviations from an equation of state. In this study, both of these methods were compared with the conventional methods used for phase equilibrium calculations, i.e., the split (γ/ϕ) approach for low pressure systems and the equation of state (ϕ/ϕ) approach employing van der Waals mixing rules for high pressure systems.

The primary purpose of this study was to evaluate the precision of the proposed method in correlating binary vapor-liquid equilibrium of the systems considered. Therefore, model evaluations for all systems were done on an isotherm-by-isotherm basis, i.e., model parameters were regressed for individual isotherms of each system. However, for a model to be useful in practice, a single set of parameters should normally be able to represent the phase behavior of a system with reasonable accuracy. For this purpose, the temperature dependence of the model parameters for the (θ/ϕ) approach was investigated for a number of sample systems. This is discussed in brief later in this chapter.

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 I as specific case studies. In Case 1, the Peng-Robinson equation of state is used with the van der Waals mixing rules for the vapor phase (with no interaction parameters), and the NRTL model (Renon and Prausnitz, 1965) is used for the liquid phase. The Peng-Robinson equation (Peng and Robinson, 1976) is given as follows

$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \qquad (4\text{-}1)$$

where

$$a(T) = a_c\alpha(T) \tag{4-2}$$

$$b = 0.07780RT_c / p_c \tag{4-3}$$

and

$$a_c = 0.45724R^2T_c^2 / p_c \tag{4-4}$$

$$\alpha(T)^{1/2} = 1 + K(1 - T_r^{1/2}) \tag{4-5}$$

$$K = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{4-6}$$

The equations for the van der Waals mixing rules are shown in Chapter II (Equations 2-1 to 2-4). The NRTL model can be written as

$$\frac{\overline{G}^E}{RT} = \sum_i z_i \left[\frac{\sum_j z_j G_{ji} \tau_{ji}}{\sum_k z_k G_{ki}} \right] \tag{4-7}$$

$$G_{ji} = \exp(-\alpha_{ij}\tau_{ji}) \tag{4-8}$$

The expression for the activity coefficients is

$$\ln\gamma_i = \frac{\sum_j z_j \tau_{ji} G_{ji}}{\sum_k z_k G_{ki}} + \sum_j \frac{z_j G_{ij}}{\sum_k z_k G_{kj}} \left(\tau_{ij} - \frac{\sum_l z_l \tau_{lj} G_{lj}}{\sum_k z_k G_{kj}} \right) \tag{4-9}$$

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 more suited for such systems.

In Case 2, the Peng-Robinson equation of state, 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 equation of state equipped with the MWS mixing rules is used. The equations for the MWS mixing rules are shown in Chapter II (Equations 2-10, 2-11 and 2-16). The 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 (4-7) and (4-9). Only Equation (4-8) is changed to

$$G_{ji} = b_j \exp(-\alpha_{ij}\tau_{ji}) \tag{4-10}$$

where b_j is the equation of state covolume parameter (Equation 4-3). 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 equation of state 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 in this case was the Redlich-Kister model (Walas, 1985)

$$\ln\hat{\theta}_1 = z_2^2\left[B + C(3z_1 - z_2) + D(z_1 - z_2)(5z_1 - z_2)\right] \tag{4-11}$$

$$\ln\hat{\theta}_2 = z_1^2\left[B + C(z_1 - 3z_2) + D(z_1 - z_2)(z_1 - 5z_2)\right] \tag{4-12}$$

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

$$\frac{\overline{G}^{E}}{RT} = z_1 z_2\left[B + C(z_1 - z_2) + D(z_1 - z_2)^2 + ...\right] \tag{4-13}$$

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 equation of state.

TABLE I

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 parameters) for the vapor phase and the NRTL model for the liquid phase. This case is used for non-ideal 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 high pressure systems 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.

The model evaluations were performed using the GEOS software developed at Oklahoma State University (Gasem, 1988-1996). For the MWS mixing rules, some subroutines had to be added to the original source code. Validation cases studied for the modified program are presented in Appendix A. Results previously published in literature using the MWS mixing rules were replicated using the modified program, thus validating the proper implementation of the MWS mixing rules. The model parameters were regressed to minimize deviations in bubble point pressure predictions only. The objective function used for minimization was

$$SS = \sum_{i=1}^{npts} \left(\frac{p_i^{exp} - p_i^{cal}}{p_i^{exp}} \right)^2 \tag{4-14}$$

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 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 asymmetric systems at high pressures. Only binary vapor-liquid equilibrium 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 B.I - B.V of Appendix B. Table B.VI in Appendix B 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). The vapor pressure model and the constants used in the model are listed in Table B.VII in Appendix B.

Evaluation Results

Evaluation results for the four case studies outlined in Table I are presented here. The results for Cases 1-3 are presented in Appendix C. The results for the (θ/ϕ) approach (Case 4) are summarized in Tables II-VI.

Low Pressure Systems

The results for Cases 1 and 3 for the non-ideal low pressure systems are shown in Tables C.I and C.II of Appendix C. As mentioned previously, Case 2 was not studied for non-ideal low pressure systems, as equations of state with the van der Waals mixing rules often cannot handle the behavior of these systems. The results for Case 4 are shown in

Table II. Case 1 shows the best results of the three cases studied (RMSE = 0.0074 bar, %AAD = 1.02 for bubble point pressures; RMSE = 0.0160, %AAD = 2.67 for vapor compositions of the first component). The overall results for these systems are essentially similar for Case 3 (RMSE = 0.0091 bar, %AAD = 1.84) and Case 4 (RMSE = 0.0094 bar, %AAD = 1.58) for bubble point pressure predictions. The deviations in predicted vapor compositions of the first component are also fairly similar (RMSE = 0.0406, %AAD = 7.42 for Case 3 and RMSE = 0.0407, %AAD = 7.68 for Case 4). Deviations in predicted vapor compositions of the first component of each system only have been reported in this study. Deviations in predicted vapor compositions of the second component have not been reported and will be different for all systems.

Figures 4-7 show vapor-liquid equilibrium plots for a few sample systems, comparing the different methods evaluated. 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 used, as shown by Figures 4 and 7.

Asymmetric High Pressure Systems

The results for Cases 2 and 3 for the binary ethane + hydrocarbon systems are presented in Tables C.III and C.IV of Appendix C. 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 Case 4 are shown in Table III. Deviations in bubble point pressures only have been reported for systems at high pressure, since most of the available data is in the T-p-x form (no vapor phase measurements). The results for the

TABLE II

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES AND VAPOR COMPOSITIONS OF NON-IDEAL SYSTEMS AT LOW PRESSURES USING THE (θ/ϕ) APPROACH: CASE 4

						BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
Methanol +	318.2	-0.0379	-0.6072	0.5324	0.0716	0.005	-0.001	1.54				7
Water	313.1	-0.0494	-0.5151	0.4447	0.0166	0.002	0.000	0.90	0.017	-0.011	1.94	11
	298.1	-0.0909	0.3038	0.2694	0.0512	0.004	-0.002	1.84	0.039	0.024	5.49	13
Ethanol +	298.2	-0.0005	-1.8320	1.3010	-1.2480	0.001	0.000	1.93	0.062	0.053	11.54	10
Water	303.2	0.0010	-1.7590	1.3280	-1.0690	0.001	0.000	0.38				5
	308.2	0.0016	-1.7400	1.1720	-1.2020	0.002	0.000	0.91				5
2-Propanol +	298.2	-0.2700	1.8000	-0.5400	0.3300	0.004	0.002	4.70	0.073	0.070	13.57	12
Water	328.2	-0.1975	0.6851	-0.0050	-0.4394	0.002	0.000	0.69	0.014	0.011	1.99	9
Water +	323.2	0.0000	-2.2380	-2.0160	-2.2480	0.001	0.000	0.56	0.111	-0.101	16.34	6
1-Butanol	343.2	0.0023	-1.7240	-1.9370	-2.0070	0.004	-0.001	1.05	0.069	-0.063	10.34	6
	363.2	0.0031	-1.3320	-1.7850	-1.7330	0.008	0.000	1.03	0.043	-0.037	6.58	6
	403.2	-0.2110	1.4060	0.4790	0.1975	0.033	-0.002	0.77	0.023	-0.016	2.77	6
Water +	343.2	-0.2253	0.7680	-0.0236	-0.7387	0.008	0.000	2.47				17
2-Pentanol	363.2	-0.2190	0.8650	-0.0061	-0.5073	0.011	-0.002	1.02				19

TABLE II (Continued)

						BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
Water +	294.2	-0.2318	1.2670	-0.0151	-0.1594	0.003	0.000	3.35	0.047	-0.042	4.59	6
1-Hexanol	313.2	-0.2269	1.1990	-0.0155	-0.2153	0.000	0.000	1.06	0.082	-0.060	6.34	8
Allyl Alcohol +	294.2	-0.0012	-1.7430	1.6610	-1.0960	0.000	0.000	0.21				4
Water	298.2	-0.0009	-1.7530	1.5570	-0.9711	0.000	0.000	0.15				4
	303.2	-0.0003	-1.7340	1.4270	-1.1590	0.000	0.000	0.41				4
	308.2	0.0004	-1.6950	1.1990	-1.3620	0.000	0.000	0.04				4
	313.2	0.0019	-1.6700	1.2750	-0.9204	0.000	0.000	0.18				4
Water +	278.2	-0.3081	1.0600	0.2531	0.0147	0.000	0.000	2.18	0.022	-0.018	1.94	8
2-Butoxyethanol	318.2	-0.2975	1.1240	0.2335	0.0139	0.002	-0.001	1.30	0.017	-0.015	1.62	8
	358.2	-0.2862	1.2010	0.2642	-0.0225	0.002	0.000	0.33	0.010	-0.007	0.90	7
Water +	363.2	-0.1642	0.8960	-0.0820	-0.1670	0.014	-0.003	2.31	0.079	-0.074	9.54	13
Cyclohexanol												
Water +	372.8	-0.0729	-0.8137	-1.0170	0.3959	0.029	-0.006	2.57	0.038	0.012	16.31	13
Acetic Acid	412.6	-0.1987	0.7499	0.1872	0.1354	0.038	-0.009	0.72	0.020	0.002	4.61	13
Water +	333.2	-0.2043	1.4790	0.0009	0.1389	0.007	-0.003	3.71	0.039	0.006	4.37	17
Propionic Acid	373.2	-0.1862	0.9262	0.0050	0.2004	0.011	-0.001	1.28	0.047	0.024	7.59	15

TABLE II (Continued)

						BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
Acetone + Water	373.2	-0.2517	0.9625	0.1794	-0.3036	0.040	0.002	0.95	0.027	0.016	9.49	22
	323.2	-0.3190	1.7050	0.0330	0.0018	0.005	-0.002	0.67				15
	308.2	-0.3280	1.7660	0.0415	-0.0435	0.005	-0.001	1.18	0.013	0.007	1.01	19
2-Butanone + Water	333.2	-0.3437	2.3480	-0.2490	-0.0248	0.003	0.000	0.35				20
Diethyl Ether + Water	308.2	-0.0876	3.3520	4.5360	-9.0500	0.011	-0.004	1.13				13
	298.2	-0.0637	1.2710	5.4430	-7.8780	0.012	-0.001	2.16				13
Acetonitrile + Water	323.2	-0.3081	2.6010	-0.0006	0.4536	0.002	0.000	0.41				14
	333.2	-0.3002	2.3980	-0.0187	0.3545	0.001	0.000	0.18	0.040	0.020	5.62	14
Water + Ethanolamine	333.2	-0.0062	-2.9090	-0.5949	-1.0040	0.005	-0.002	4.19				12
	351.2	-0.0007	-2.6930	-0.6225	-0.8286	0.008	-0.003	4.53				12
	364.9	0.0023	-2.5030	-0.7449	-0.8433	0.010	-0.003	3.70				12
Tetrahydrofuran + Water	298.2	-0.2636	1.7040	0.2883	0.0153	0.002	0.000	0.70				19

TABLE II (Continued)

						BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
Acetaldehyde + Water	283.2	-0.3508	2.5300	0.0379	0.8854	0.030	-0.012	3.30				5
	293.2	-0.3579	2.3320	-0.0037	0.7346	0.037	-0.014	2.75				5
	303.2	-0.6103	5.9040	-2.3280	1.6490	0.041	-0.014	2.05				5
	373.2	-0.1679	1.6230	5.1890	2.9950	0.075	-0.005	2.43	0.033	0.012	4.56	5
Water + Nitromethane	323.2	-0.1542	2.7570	-0.0037	-0.1848	0.009	-0.001	3.83	0.084	-0.029	21.58	16
	313.2	-0.1550	2.8540	-0.2034	-0.1367	0.003	0.000	2.47	0.083	-0.024	17.37	7
	296.2	-0.1607	3.1240	-0.2692	-0.0693	0.002	0.000	2.60	0.092	-0.030	20.25	7
	294.2	-0.1640	3.2420	-0.2724	-0.0471	0.001	0.000	2.49	0.098	-0.026	21.54	7
Water + 2-Methylpyridine	318.2	-0.2829	0.9271	0.7078	0.0473	0.001	0.000	1.24				10
	308.2	-0.2986	1.1110	0.8202	0.3697	0.001	0.000	0.75				10
	298.2	-0.2674	0.4768	0.3739	0.0352	0.001	0.000	1.80				10
Ethyl Acetate + Water	323.2	-0.4655	3.7090	-1.6770	1.3410	0.002	0.000	0.68	0.045	0.042	8.31	9
	343.2	-0.4658	3.6050	-1.5580	1.3970	0.005	0.000	0.65	0.036	0.033	7.31	9
	353.2	-0.4766	3.7080	-1.6740	1.4300	0.006	0.000	0.52	0.031	0.029	6.77	9
Acetonitrile + tert-Butanol	333.2	0.0287	0.4595	0.3437	0.1408	0.006	0.000	0.85	0.032	-0.022	6.09	11

TABLE II (Continued)

						BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
1,3-Butadiene + Acetonitrile	305.0	0.0030	1.0420	0.1892	0.1437	0.014	-0.003	0.52				16
	329.9	0.0010	1.0250	0.1646	0.1120	0.022	-0.005	0.38				22
Methyl tert-Butyl Ether + Acetonitrile	313.2	0.0000	1.0000	-0.1120	0.1794	0.008	0.001	1.54	0.034	0.025	7.11	33
Methanol + tert-Butanol	298.2	-0.0515	-0.8073	0.9702	-0.2691	0.006	0.000	4.42	0.068	-0.042	15.18	19
	313.2	-0.0499	-0.6961	0.7419	-0.3760	0.012	0.001	4.51				13
tr-1,3-Pentadiene + Acetonitrile	303.2	-0.0002	0.8787	-0.1751	-0.0736	0.023	0.004	3.86				9
	313.2	0.0024	0.9072	-0.1737	-0.1107	0.019	0.004	1.85				9
Dimethyl Sulfide + Methanol	263.2	-0.0033	1.1110	0.4701	0.3550	0.001	0.000	0.67				8
	273.2	-0.0030	1.1470	0.4493	0.3694	0.001	0.000	0.53				8
	288.2	-0.0044	1.2060	0.4028	0.3386	0.002	0.000	0.53				8
Methyl Mercaptan + Methanol	269.2	-0.0517	2.3110	0.4755	0.4054	0.012	-0.005	1.43				7
	278.2	-0.0526	2.2520	0.4480	0.2978	0.010	-0.004	0.85				8
	288.2	-0.0501	2.1810	0.4110	0.1798	0.016	-0.005	1.19				8

TABLE II (Continued)

SYSTEM	TEMP (K)	C_{ij}	B	C	D	BUBBLE POINT PRESSURE RMSE (Bar)	BUBBLE POINT PRESSURE BIAS (Bar)	BUBBLE POINT PRESSURE %AAD	VAPOR COMPOSITION OF COMPONENT 1 RMSE	VAPOR COMPOSITION OF COMPONENT 1 BIAS	VAPOR COMPOSITION OF COMPONENT 1 %AAD	NO PTS
Methyl Mercaptan +	263.2	-0.0108	0.0564	0.0559	0.0708	0.001	0.000	0.43				5
Dimethyl Sulfide	273.2	-0.0024	-0.0540	0.0296	0.0781	0.001	0.000	0.30				5
	288.2	-0.0039	-0.0190	0.0732	0.1250	0.009	-0.003	0.56				5
1-Butene +	310.9	-0.0519	0.5330	-0.0402	0.0605	0.004	0.000	0.07	0.002	0.001	0.90	9
1,3-Butadiene	324.8	-0.0004	-0.0028	-0.0101	-0.0973	0.008	0.001	0.12	0.003	0.000	0.77	9
	338.7	-0.0674	0.5196	-0.0099	0.0017	0.002	0.000	0.02	0.000	0.000	0.06	9
Methanol +	311	0.0000	1.7670	0.0478	0.1571	0.005	-0.001	1.22	0.015	0.003	1.59	7
Dimethyl Disulfide	336	-0.0069	1.6490	0.0544	0.0983	0.001	0.000	0.09	0.006	-0.004	0.57	10

OVERALL MODEL STATISTICS

BUBBLE POINT PRESSURE

RMSE = 0.0094 Bar
BIAS = -0.0012 Bar
%AAD = 1.58
NO PTS = 797

VAPOR COMPOSITION

RMSE = 0.0407
BIAS = -0.0011
%AAD = 7.68
NO PTS = 418

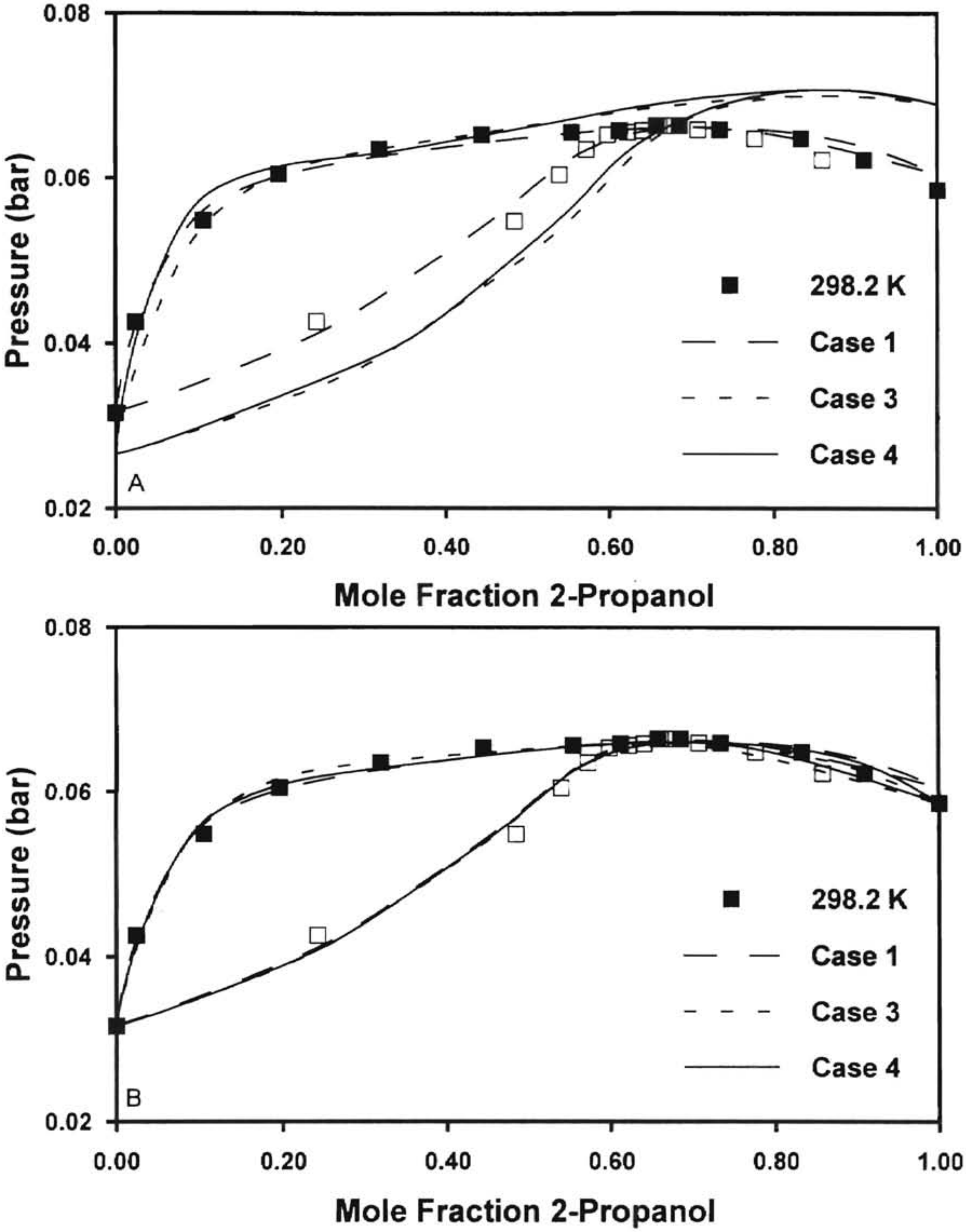

Figure 4. Representation of Vapor-Liquid Equilibrium for the 2-Propanol + Water System at 298.2 K Using the Different Cases Studied. Experimental Data Are from Sazonov (1986)

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

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

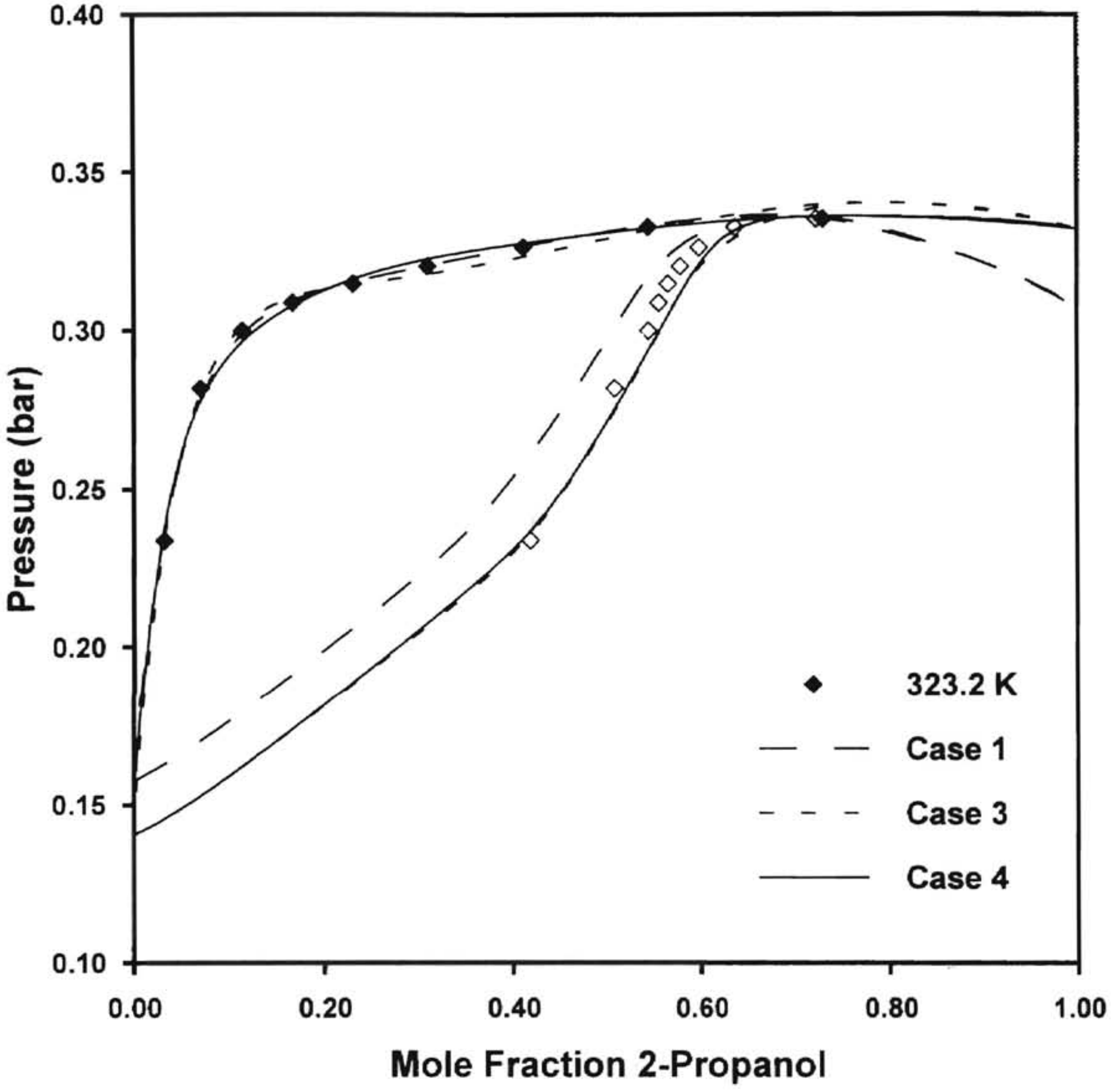

Figure 5. Representation of Vapor-Liquid Equilibrium for the 2-Propanol + Water System at 323.2 K Using the Different Cases Studied. Experimental Data Are from Tunik and Zharov (1980).

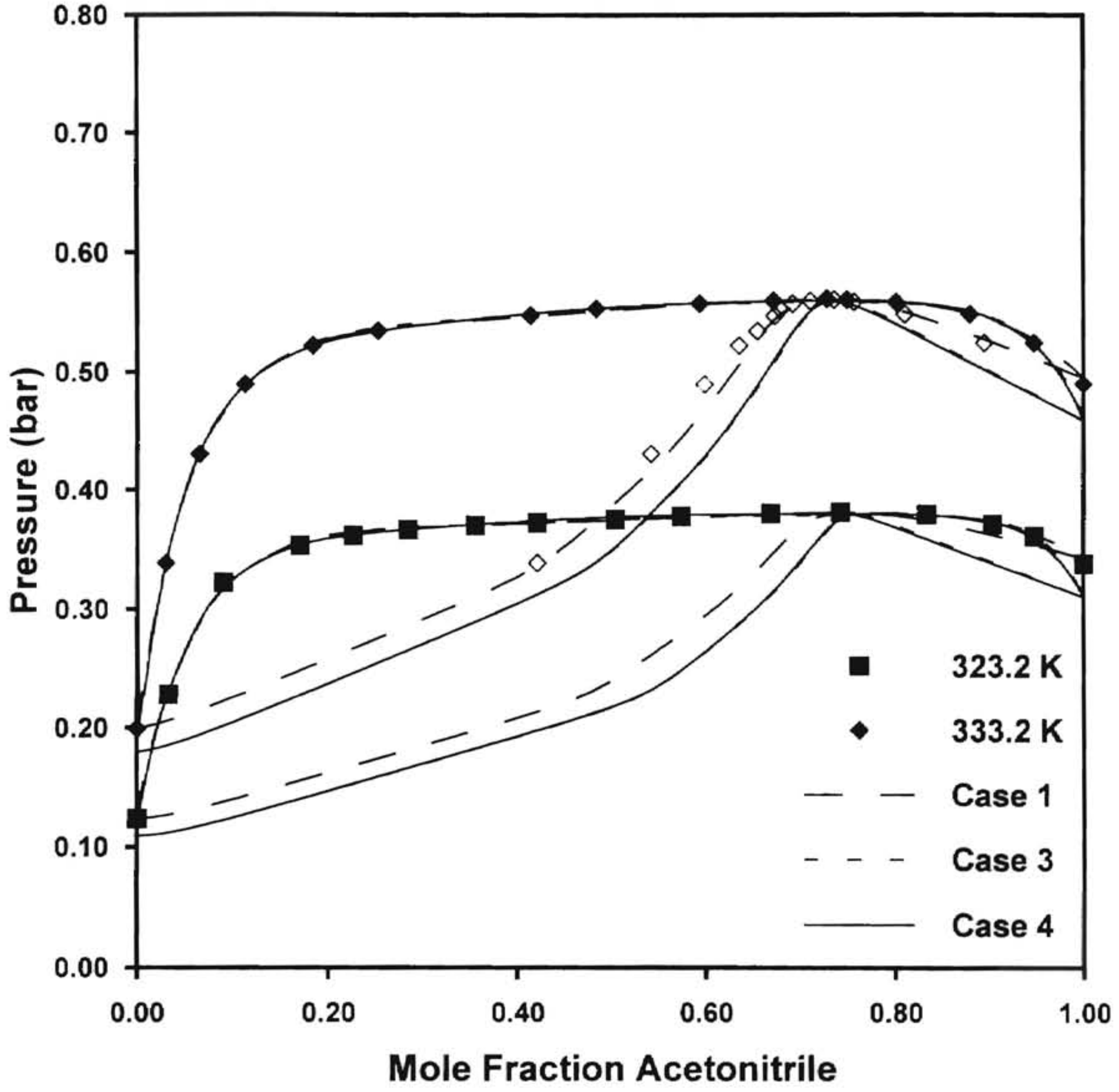

Figure 6. Representation of Vapor-Liquid Equilibrium for the Acetonitrile + Water System Using the Different Cases Studied. Experimental Data at 323.2 K Are from Wilson et al. (1979) and at 333.2 K Are from Sugi and Katayama (1983).

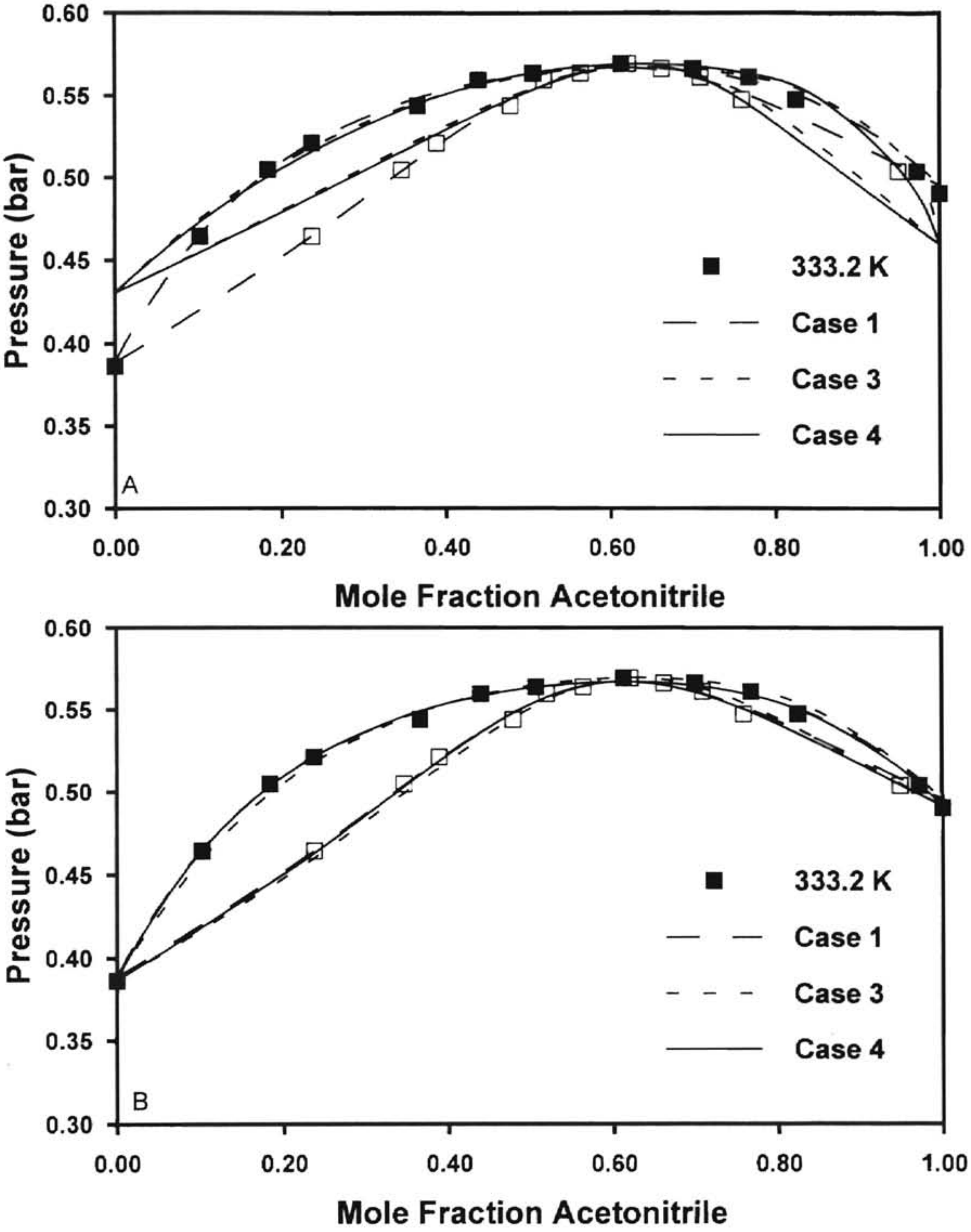

Figure 7. Representation of Vapor-Liquid Equilibrium for the Acetonitrile + Tert-Butanol System Using the Different Cases Studied. Experimental Data Are from Nagata (1989)

Figure 7(A): No Tuning of Pure Component Parameters for Case 3 and Case 4

Figure 7(B): Tuned Pure Component Parameters for Case 3 and Case 4 three cases studied indicate that all three models show essentially 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 Cases 2 and 3 for the binary carbon dioxide + hydrocarbon systems are presented in Tables C.V and C.VI of Appendix C. The results for Case 4 are shown in Table IV. The results again 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 Cases 2 and 3 for the binary nitrogen + hydrocarbon systems are presented in Tables C.VII and C.VIII of Appendix C. The results for Case 4 are shown in Table V. 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 for 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 Cases 2 and 3 for the binary hydrogen + hydrocarbon systems are presented in Tables C.IX and C.X of Appendix C. The results for Case 4 are shown in Table VI. Case 2 (RMSE = 1.81 bar, %AAD = 1.02) and Case 3 (RMSE = 2.08 bar,

TABLE III

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF ETHANE + HYDROCARBON SYSTEMS USING THE (θ/ϕ) APPROACH: CASE 4

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	303.2	0.1568	-0.9050	-0.0146	0.2373	0.130	-0.003	0.69	10
	323.2	0.0158	-0.0185	0.0330	-0.0723	0.125	0.002	0.69	10
	343.2	-0.0003	0.0209	0.0309	-0.0583	0.377	-0.001	1.42	7
	363.4	0.0189	-0.0000	0.0332	-0.0295	0.239	0.004	0.74	11
n-Decane	311.1	0.0159	-0.0923	-0.0201	0.0477	0.060	0.002	0.44	10
	344.4	0.0131	-0.0976	-0.0024	0.0279	0.144	0.014	0.57	7
	377.8	0.0139	-0.1114	0.0071	0.0252	0.075	0.000	0.14	6
	411.1	0.0052	-0.0717	0.0529	0.0515	0.053	0.002	0.11	7
n-Hexadecane	285.0	0.0502	0.0092	-0.7400	0.1736	0.197	0.019	0.56	5
	305.0	0.0261	-0.2532	-0.0217	-0.0007	0.294	-0.047	0.86	5
	325.0	-0.0120	0.0567	0.2123	0.0711	1.166	0.029	1.71	5
n-Docosane	320.0	0.0449	-0.5603	-0.1785	0.0362	0.077	-0.008	0.23	6
	340.0	0.0543	-0.6170	-0.1923	0.0048	0.282	-0.003	0.41	8
	360.0	0.0564	-0.5994	-0.1683	0.0051	0.075	-0.004	0.28	6
n-Octacosane	348.2	-0.0018	-0.4236	0.0187	0.0642	0.161	-0.001	0.84	10
	373.2	-0.0116	-0.3315	0.0310	0.1378	0.072	0.000	0.32	7

TABLE III (Continued)

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
	423.2	-0.0060	-0.4069	-0.0014	0.0677	0.058	0.004	0.17	7
n-Hexatriacontane	373.2	-0.0170	-0.4904	-0.0144	0.0486	0.072	0.005	0.34	7
	423.2	-0.0259	-0.4551	0.0243	0.2005	0.034	-0.001	0.08	6
n-Tetratetracontane	373.2	-0.0433	-0.6004	0.0689	0.1370	0.167	0.003	0.74	9
	423.2	-0.0770	-0.4294	0.0015	0.0744	0.104	0.000	0.64	7
Benzene	323.2	0.0551	-0.1236	-0.1302	-0.0394	0.062	-0.001	0.40	7
	373.2	0.0528	-0.1322	-0.0878	-0.0161	0.047	-0.002	0.14	7
	423.2	0.0388	-0.0549	-0.0116	0.0240	0.116	0.003	0.27	7
	298.2	-0.0178	0.6029	-0.0433	-0.1248	0.256	-0.022	0.63	7
Toluene	313.1	0.0449	0.0241	-0.1470	-0.0839	0.123	0.014	0.33	8
	393.1	0.0247	-0.0293	0.0267	-0.0261	0.382	0.008	0.51	9
	473.2	0.0290	-0.0123	0.0525	-0.0642	0.254	0.030	0.75	9
Naphthalene	373.2	0.0377	0.1120	-0.1217	-0.0809	0.166	0.001	0.24	10
	423.2	0.0299	0.0959	-0.0861	-0.0347	0.182	-0.005	0.31	7
Cyclohexane	323.2	0.0102	0.0080	-0.0439	-0.0042	0.105	0.018	0.36	8
	373.2	0.0054	-0.0002	-0.0208	-0.0167	0.123	-0.009	0.31	7
	423.2	0.0106	0.0000	-0.0051	-0.0016	0.058	0.001	0.12	6

TABLE III (Continued)

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
Phenanthrene	383.2	0.0411	0.2325	-0.1091	-0.0982	0.597	0.000	0.85	6
	423.2	0.0360	0.2040	-0.0830	-0.0641	0.134	-0.003	0.12	6
Pyrene	433.2	0.1037	-0.0729	0.0293	0.1333	0.629	0.010	0.81	6

OVERALL MODEL STATISTICS

RMSE = 0.1894 Bar
BIAS = 0.0021 Bar
%AAD = 0.51
NO PTS = 266

TABLE IV

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF CARBON DIOXIDE + HYDROCARBON SYSTEMS USING THE (θ/ϕ) APPROACH: CASE 4

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	277.9	0.1957	-0.4845	-0.2046	-0.0931	0.106	-0.015	0.46	8
	344.3	0.1864	-0.1696	0.0491	0.0587	0.174	0.002	0.49	8
	387.6	0.2320	0.0028	0.2948	0.1014	0.194	-0.006	0.35	7
n-Decane	310.9	0.1081	0.1189	-0.0675	-0.0867	0.305	-0.037	0.34	11
	410.9	0.0931	0.0373	0.0669	0.0149	0.053	-0.009	0.08	6
	510.9	0.1230	0.0381	0.0669	0.0901	0.254	-0.005	0.49	6
n-Hexadecane	463.1	0.0858	-0.0634	0.1438	0.2276	0.052	0.000	0.12	4
	542.9	0.0990	-0.0435	0.1357	0.0920	0.073	0.000	0.14	4
	623.6	0.1464	-0.0000	0.0846	0.0436	0.024	-0.002	0.06	4
n-Docosane	323.2	0.0848	0.0346	0.1077	0.0803	0.301	-0.012	0.70	14
	348.2	0.0698	-0.0019	0.1387	0.0842	0.409	-0.017	1.05	19
	373.2	0.0620	-0.0038	0.1056	0.0701	0.477	-0.015	1.36	11
n-Octacosane	348.2	0.0571	-0.0044	0.2491	0.1731	0.450	-0.019	0.65	8
	423.2	0.0100	-0.0109	0.2832	0.2398	0.674	-0.036	1.79	7
	573.5	-0.0010	-0.0467	0.2462	0.2730	0.100	0.003	0.30	5

TABLE IV (Continued)

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Hexatriacontane	373.2	0.0724	-0.3614	0.0000	0.0610	0.178	-0.006	0.36	10
	423.2	0.0721	-0.4458	0.0000	0.0864	0.318	-0.017	0.41	8
n-Tetratetracontane	373.2	-0.0025	-0.1796	0.2272	0.1523	0.379	-0.027	0.85	7
	423.2	-0.0114	-0.3421	0.1346	0.1478	0.219	-0.012	0.47	7
Benzene	298.2	0.0650	0.1347	-0.0255	0.0145	0.632	-0.137	0.95	8
	344.3	0.0717	0.0727	-0.0004	-0.1214	0.099	-0.002	0.08	16
	413.6	0.0762	-0.0111	-0.0378	0.0601	0.445	-0.010	0.44	9
Toluene	353.4	0.0971	0.0530	-0.0208	0.1440	0.200	-0.003	0.81	8
	373.2	0.1214	0.0016	0.2442	0.3914	0.440	0.004	1.41	7
	393.2	0.1233	-0.0042	0.1835	0.3749	0.554	-0.008	1.16	7
Naphthalene	373.2	0.1096	0.0653	-0.1852	-0.0741	0.128	-0.001	0.19	7
	423.2	0.1002	0.0309	-0.2333	-0.1408	0.107	-0.002	0.14	7
Cyclohexane	348.2	0.1027	0.2443	-0.1246	-0.1076	0.223	-0.008	0.37	6
	373.2	0.1240	0.0710	-0.1214	-0.0402	0.065	0.000	0.11	7
	423.2	0.1171	0.0518	-0.0796	-0.0227	0.063	0.002	0.07	7
Phenanthrene	383.2	0.0973	0.3249	-0.0148	-0.0000	0.386	-0.023	0.76	7
	423.2	0.0810	0.2990	0.0049	-0.0000	0.175	-0.010	0.28	7

TABLE IV (Continued)

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
Pyrene	433.2	0.1258	0.1752	-0.0129	-0.0017	0.469	-0.010	0.55	7

OVERALL MODEL STATISTICS

RMSE = 0.2812 Bar
BIAS = -0.0143 Bar
%AAD = 0.58
NO PTS = 264

TABLE V

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF NITROGEN + HYDROCARBON SYSTEMS USING THE (θ/ϕ) APPROACH: CASE 4

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	250.0	0.0363	0.2157	-0.0835	-0.0254	0.294	-0.009	0.47	9
	277.0	0.0167	0.1408	-0.3702	-0.2855	0.860	-0.040	2.60	12
	311.1	0.0078	0.1662	-0.0252	0.0372	1.419	-0.040	0.85	16
	344.4	-0.0095	0.1392	-0.0046	0.0708	0.244	-0.015	0.58	12
n-Decane	310.9	0.3298	-0.7235	-0.4038	0.0013	2.450	-0.053	1.16	22
	344.3	0.3586	-0.6668	-0.3724	0.0055	5.278	-0.338	2.58	30
	410.9	0.4456	-0.5339	-0.3727	-0.2549	4.073	-0.202	2.77	20
n-Hexadecane	462.7	0.1617	0.0238	0.0016	-0.0190	0.653	-0.074	0.44	8
	543.5	0.1372	0.0364	0.0023	0.0000	0.492	0.018	0.36	7
	623.7	0.1483	0.0719	-0.0445	-0.0365	0.504	-0.003	0.29	7
n-Eicosane	323.2	0.2479	0.1584	-0.0527	-0.0996	0.520	-0.023	0.34	8
	373.2	0.2245	0.1210	-0.0270	-0.0797	0.232	0.000	0.26	6
	423.2	0.2047	0.0908	-0.0040	-0.0503	0.232	-0.004	0.24	6
n-Octacosane	348.2	0.2410	0.3396	-0.0762	-0.2235	0.580	-0.034	0.53	7
	373.2	0.2298	0.3210	-0.0291	-0.1895	0.468	-0.046	0.48	6
	423.2	0.2061	0.2764	0.0103	-0.1107	0.657	-0.095	0.46	6

TABLE V (Continued)

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Hexatriacontane	373.2	0.4851	0.1463	-0.0744	-0.0979	0.193	-0.006	0.20	6
	423.2	0.4944	0.1346	-0.0443	-0.0729	0.228	-0.003	0.11	6
Benzene	348.2	0.0290	0.0030	-0.9985	-0.6714	1.637	-0.034	0.74	6
	373.2	0.0060	0.0126	-0.9367	-0.6706	0.944	-0.029	0.51	6
	398.2	0.1070	0.0250	-0.1219	0.0421	0.634	-0.017	0.25	7
Toluene	323.2	0.0823	0.0048	-1.2540	-0.7585	2.565	-0.067	1.46	6
	348.2	0.0631	-0.0531	-1.4510	-1.0780	3.840	-0.311	3.97	6
Cyclohexane	366.4	0.0684	0.0087	-0.2283	0.0051	7.813	-2.300	8.56	9
	410.8	0.0467	0.0213	-0.2518	-0.1813	1.337	-0.052	1.83	9

OVERALL MODEL STATISTICS

RMSE = 2.0802 Bar
BIAS = -0.1749 Bar
%AAD = 1.54
NO PTS = 243

TABLE VI

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF HYDROGEN + HYDROCARBON SYSTEMS USING THE (θ/ϕ) APPROACH: CASE 4

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	327.7	0.1641	0.0383	-0.1675	0.0458	1.402	-0.042	1.38	13
	361.0	0.2395	0.0099	-0.2441	-0.0909	1.626	-0.042	1.30	11
	394.3	0.3730	-0.0018	-0.1643	-0.0095	2.641	0.126	1.92	12
n-Decane	462.5	0.4473	0.0035	-0.0077	0.0678	0.994	0.155	0.97	7
	503.4	0.3551	0.1037	-0.0727	-0.0602	1.449	-0.025	0.82	7
	543.0	0.4486	0.1061	-0.0473	-0.0278	0.722	-0.009	0.50	7
n-Hexadecane	461.7	0.3073	0.0299	-0.0108	0.0000	0.604	0.009	0.57	7
	542.3	0.4214	0.0143	0.0058	0.0138	0.115	0.015	0.09	7
	622.9	0.4842	0.1044	-0.0001	-0.0001	0.342	0.002	0.33	7
	664.1	0.5610	0.1232	-0.0385	-0.0216	0.779	0.005	0.55	8
n-Eicosane	323.2	0.2357	0.1467	-0.0327	-0.0062	0.197	-0.003	0.17	7
	373.2	0.2231	0.1334	-0.0133	-0.0223	0.385	-0.018	0.52	9
	423.2	0.1967	0.1192	-0.0029	-0.0134	0.181	-0.002	0.26	6
n-Octacosane	348.2	0.2538	0.0665	-0.0311	-0.0209	0.195	-0.011	0.21	6
	373.2	0.2331	0.0515	-0.0184	-0.0233	0.069	0.007	0.06	5
	423.2	0.1906	0.0149	0.0006	-0.0143	0.375	0.065	0.46	9

TABLE VI (Continued)

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Hexatriacontane	373.2	0.1631	0.0335	0.0339	0.0000	0.401	-0.029	0.31	6
	423.2	0.0777	0.0054	0.0411	-0.0000	0.286	0.003	0.26	6
Benzene	323.2	0.1489	0.2062	-0.0974	0.0416	0.110	-0.001	0.10	6
	373.2	0.1498	0.1937	-0.0937	0.0241	0.180	-0.005	0.27	6
	423.2	0.1629	0.2032	-0.0746	0.0076	0.032	-0.005	0.05	6
Toluene	461.9	0.3616	-0.0001	-0.3906	-0.2272	0.526	0.011	0.47	5
	502.2	0.4069	0.0000	-0.4083	-0.2935	0.966	-0.083	0.42	7
	542.2	0.6132	-0.0012	-0.1862	-0.0468	0.610	0.004	0.46	6
Naphthalene	373.2	0.1478	0.1645	-0.1713	0.0202	0.323	-0.006	0.34	6
	423.2	0.1643	0.1590	-0.1272	0.0069	0.728	-0.024	0.54	8
Cyclohexane	310.9	0.2625	-0.0028	0.0040	0.2716	1.505	-0.105	1.00	13
	344.3	0.2475	0.0071	-0.2700	0.0112	1.234	-0.052	0.26	14
	377.6	0.2775	0.0368	-0.2419	-0.0513	1.270	-0.005	0.35	13
	410.9	0.3215	0.0800	-0.1320	-0.0678	1.647	-0.016	0.43	13
Phenanthrene	398.2	0.1930	0.2427	-0.0216	-0.0141	0.706	-0.017	0.47	7
	423.2	0.1911	0.2407	-0.0204	-0.0157	1.010	0.238	0.75	6
	448.2	0.1890	0.2389	-0.0223	-0.0166	0.120	0.014	0.13	6
	473.2	0.1826	0.2369	-0.0302	-0.0127	0.665	0.037	0.29	6

TABLE VI (Continued)

SOLVENT	TEMP (K)	C_{ij}	B	C	D	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
Pyrene	433.2	0.2292	0.1325	-0.1465	0.0127	0.303	-0.004	0.22	6

OVERALL MODEL STATISTICS

RMSE = 0.8525 Bar
BIAS = 0.0007 Bar
%AAD = 0.56
NO PTS = 274

%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 Case 2 have been taken, for the most part, from Raghunathan (1996). The parameters reported in that study were re-optimized for some systems, where it was felt that better results could be obtained.

Discussion

The overall results for the different types of systems studied here are summarized in Table VII. The results for non-ideal low pressure systems show that the (γ/ϕ) approach (Case 1) does better than both Cases 3 and 4. However, this should be expected since the (γ/ϕ) approach uses a vapor pressure model to get 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 get accurate vapor pressures. Accurate representation of pure component vapor pressures is one of the important factors affecting phase equilibrium predictions. Figures 4(B)and 7(B), representing vapor-liquid equilibrium for the 2-propanol + water system and the acetonitrile + tert-butanol system respectively, are excellent examples which illustrate the above point. In these figures, the acentric factors of the individual components were

TABLE VII

SUMMARY OF RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES FOR THE CASES STUDIED

	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			0.430	1.17	0.416	0.88	0.189	0.51	266
Carbon dioxide + Hydrocarbon			0.780	0.96	0.357	0.78	0.281	0.58	264
Nitrogen + Hydrocarbons			2.235	1.91	2.275	1.57	2.080	1.54	243*
Hydrogen + Hydrocarbons			1.809	1.02	2.297	1.25	0.853	0.56	274*

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

tuned to generate accurate pure component vapor pressures for Cases 3 and 4. A comparison of Figures 4(B) and 7(B) with Figures 4(A) and 7(A) respectively, shows improved accuracy for Cases 3 and 4, which may be ascribed to good pure component parameters. Moreover, the parameters reported in the DECHEMA Chemistry Data Series were used as initial guesses to optimize systems for Case 1. The parameters in the DECHEMA Chemistry Data Series were optimized to minimize deviations in activity coefficients for data sets which included vapor compositions. This might explain the substantial disparity in predicted vapor compositions between Case 1 and the other two cases, which were optimized to minimize deviations in bubble point pressures only.

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 have 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) approach.

Parity in the correlative abilities of the MWS mixing rules and the proposed (θ/ϕ) approach is a positive and significant outcome. The results indicate that amending the VLE framework offers the same correlative capabilities without resorting to complexity in the mixing rules.

The current MWS 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, the MWS mixing rules 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 mixing rules. Moreover, the (θ/ϕ) approach is very easy to implement with existing computational algorithms for any equation of state.

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.

The analysis for all 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 and is discussed in brief in the next section.

Temperature Dependence of the Model Parameters for the (θ/ϕ) Approach

The temperature dependence of the model parameters for the (θ/ϕ) approach 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 using 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 obtained for the lowest temperature. Case 4b is the correlation of vapor-liquid equilibrium of the system at all temperatures using one set of regressed parameters. The results for the representation of bubble point pressures for the three cases are shown in Table VIII. The model parameters obtained for Case 4b are shown in Table IX. The model parameters for Cases 4 and 4a were taken from the appropriate tables of results for Case 4 from the previous section. The predicted vapor-liquid equilibrium curves are also shown in Figures 8-13.

The results for the acetone + water system are shown on two separate figures (Figures 8 and 9) 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, but it shows a qualitatively better fit than Case 4a. Both cases predict vapor compositions on the higher side of experimental data. The results for the ethane + n-octacosane system (Figure 10) indicate that all three cases yield essentially similar results. The results for the carbon dioxide + n-decane system are shown in Figure 11. 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 12, indicate excellent results for both Case 4a and 4b. The results for the hydrogen + toluene system are shown in Figure 13. 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 the fit given by the 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 X 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 model parameters for the conventional approaches are listed in Table XI. 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 slightly worse than the (γ/ϕ) approach (Case 2) for the acetone + water system. The overall results indicate that Case 4 is required for very accurate predictions using the (θ/ϕ) approach. Also, an inspection of the results in Tables II-VI for Case 4 shows that the parameters for most systems are stable and should be amenable to generalizations in terms of temperature.

TABLE VIII

TEMPERATURE DEPENDENCE OF THE MODEL PARAMETERS FOR THE (θ/ϕ) APPROACH

SYSTEM	TEMP RANGE (K)	DEVIATIONS IN PREDICTED BUBBLE POINT PRESSURES						NO PTS
		CASE 4		CASE 4a		CASE 4b		
		RMSE (Bar)	%AAD	RMSE (Bar)	%AAD	RMSE (Bar)	%AAD	
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	0.105	0.49	0.257	1.09	0.214	0.94	24
Carbon dioxide + n-Decane	310.9 - 510.9	0.226	0.31	3.244	5.06	1.491	2.84	23
Nitrogen + n-Hexadecane	462.7 - 623.7	0.554	0.37	2.263	1.66	2.820	1.56	22
Hydrogen + Toluene	461.9 - 542.2	0.725	0.45	8.264	3.02	8.264	3.02	18

TABLE IX

MODEL PARAMETERS FOR THE (θ/ϕ) APPROACH FOR A SYSTEM-BY-SYSTEM ANALYSIS: CASE 4b

SYSTEM	TEMP RANGE (K)	C_{ij}	B	C	D
Acetone + Water	308.2 - 373.2	-0.3743	2.0240	-0.2768	0.1888
Ethane + n-Octacosane	348.2 - 423.2	-0.0014	-0.4135	0.0007	0.1042
Carbon dioxide + n-Decane	310.9 - 510.9	0.1231	-0.0285	-0.1048	-0.1187
Nitrogen + n-Hexadecane	462.7 - 623.7	0.1106	0.0778	0.0000	-0.0251
Hydrogen + Toluene	461.9 - 542.2	0.3616	-0.0001	-0.3906	-0.2272

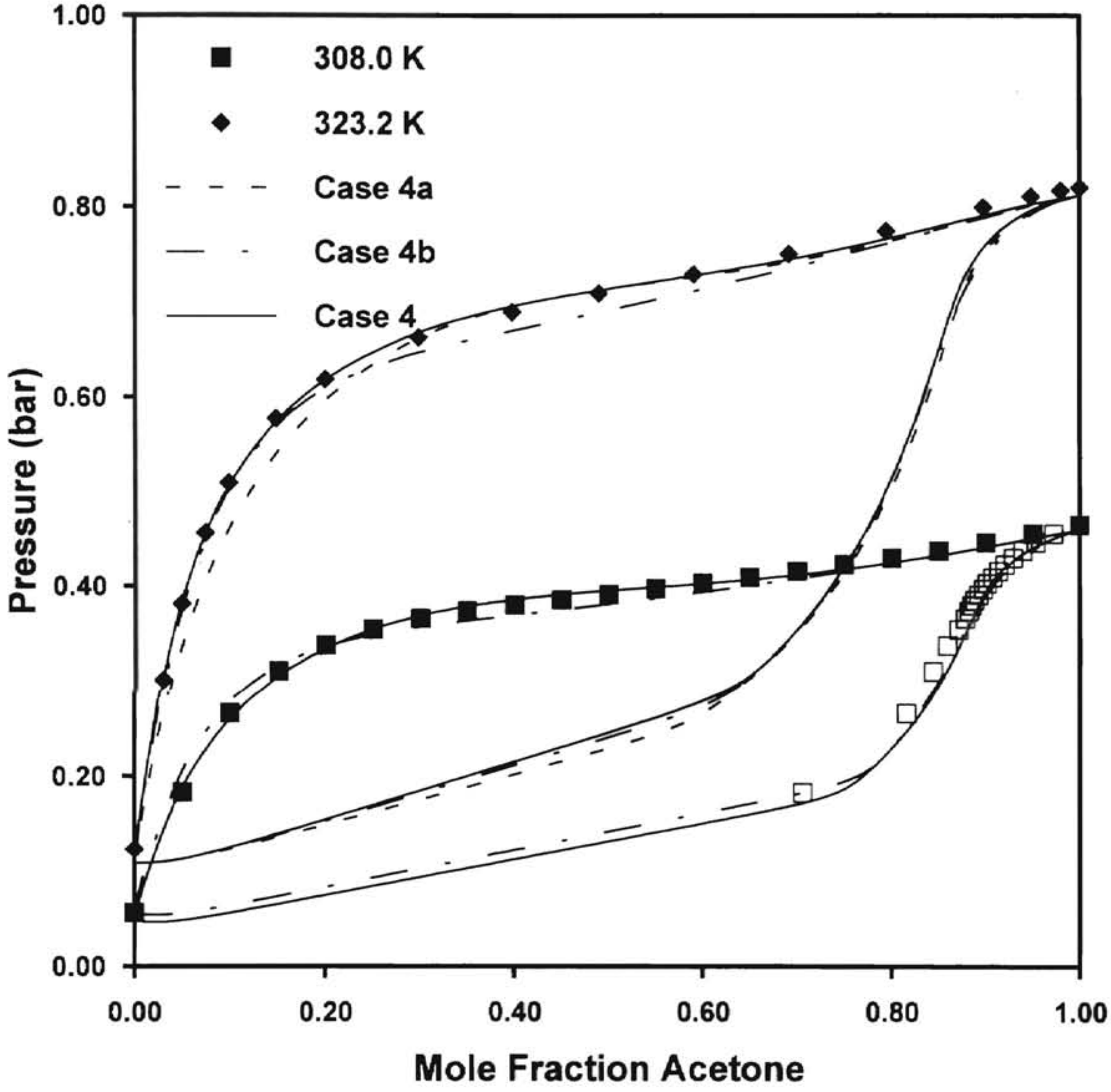

Figure 8. Representation of Vapor-liquid Equilibrium for the Acetone + Water System at 308.2 K and 323.2 K Using the (θ/ϕ) Approach. Experimental Data at 308.2 K Are from Lieberwerth and Schuberth (1979) and at 323.2 K Are from Chaudhary et al. (1980)

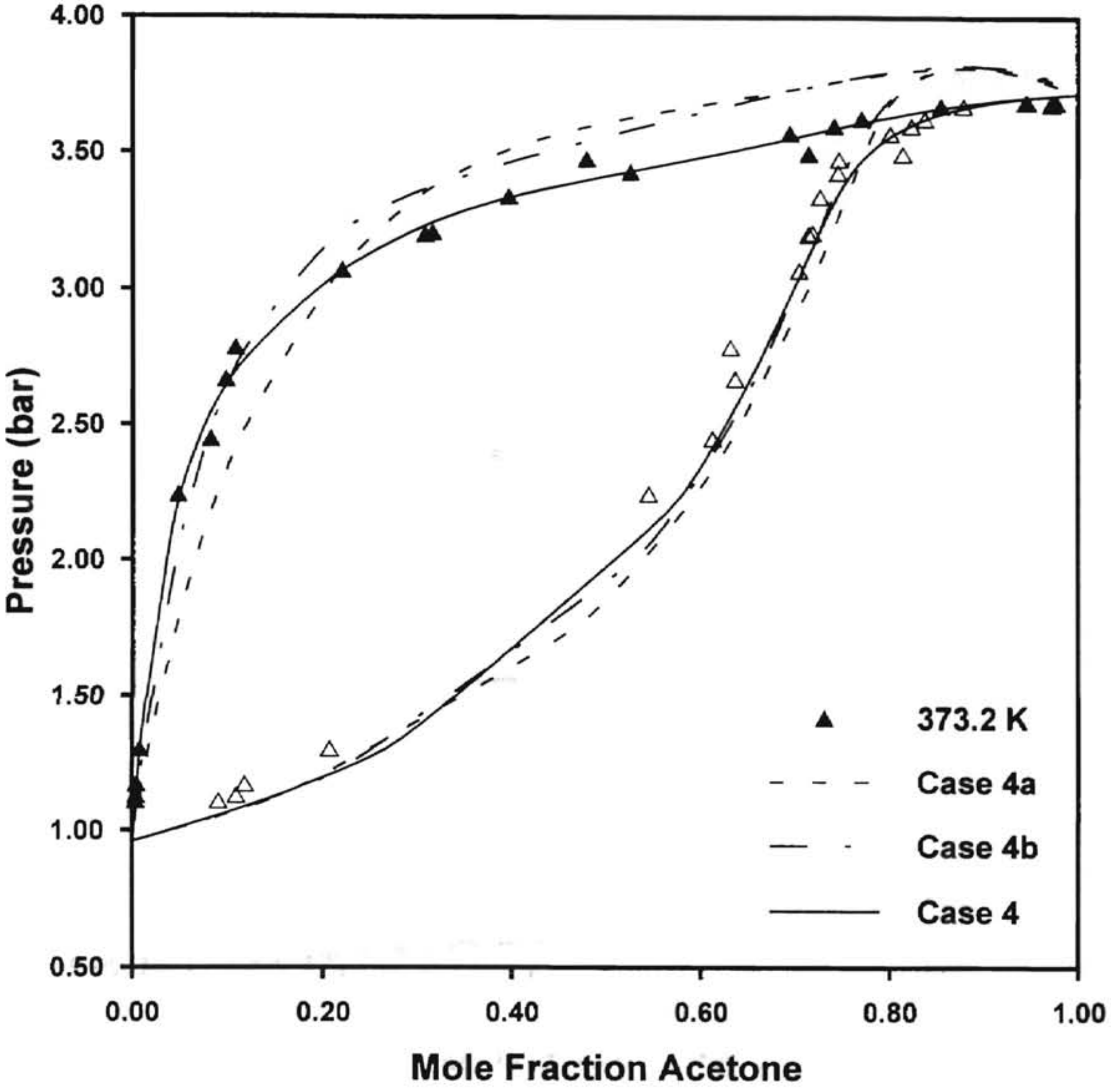

Figure 9. Representation of Vapor-liquid Equilibrium for the Acetone + Water System at 373.2 K Using the (θ/ϕ) Approach. Experimental Data Are from Griswold and Wong (1952)

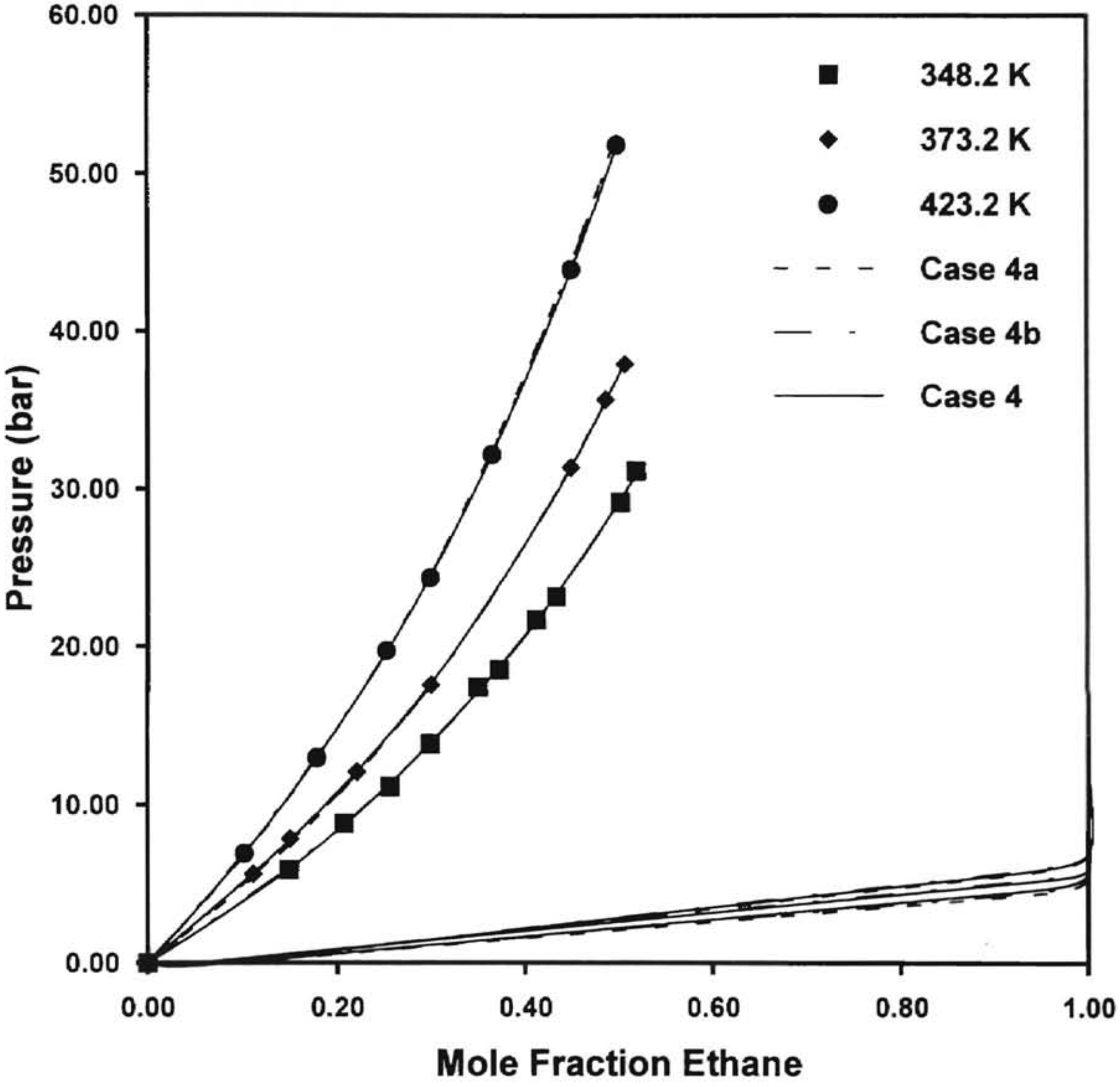

Figure 10. Representation of Vapor-liquid Equilibrium for the Ethane + n-Octacosane System Using the (θ/ϕ) Approach. Experimental Data Are from Robinson and Gasem (1987)

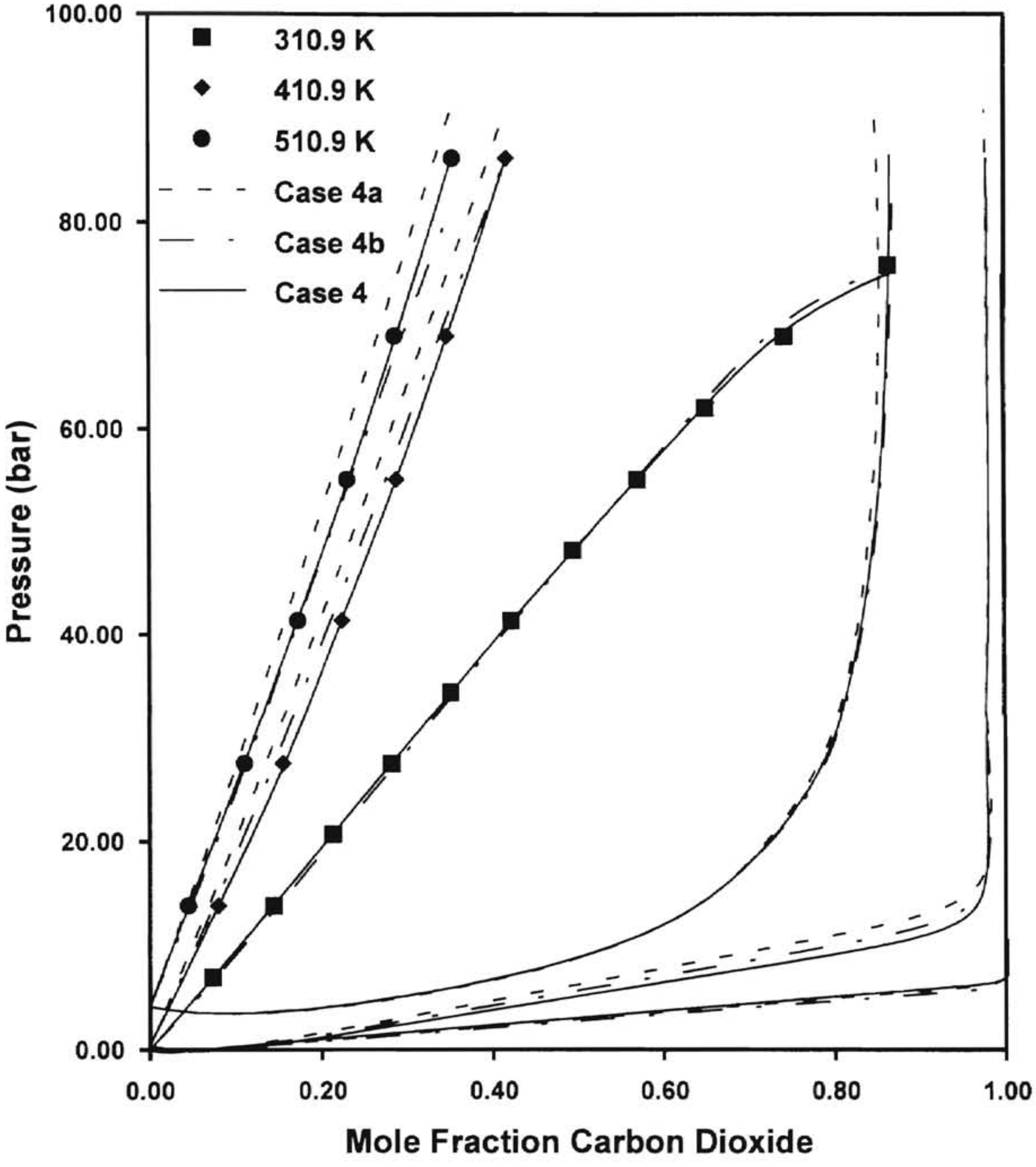

Figure 11. Representation of Vapor-liquid Equilibrium for the Carbon Dioxide + n-Decane System Using the (θ/ϕ) Approach. Experimental Data Are from Reamer and Sage (1963)

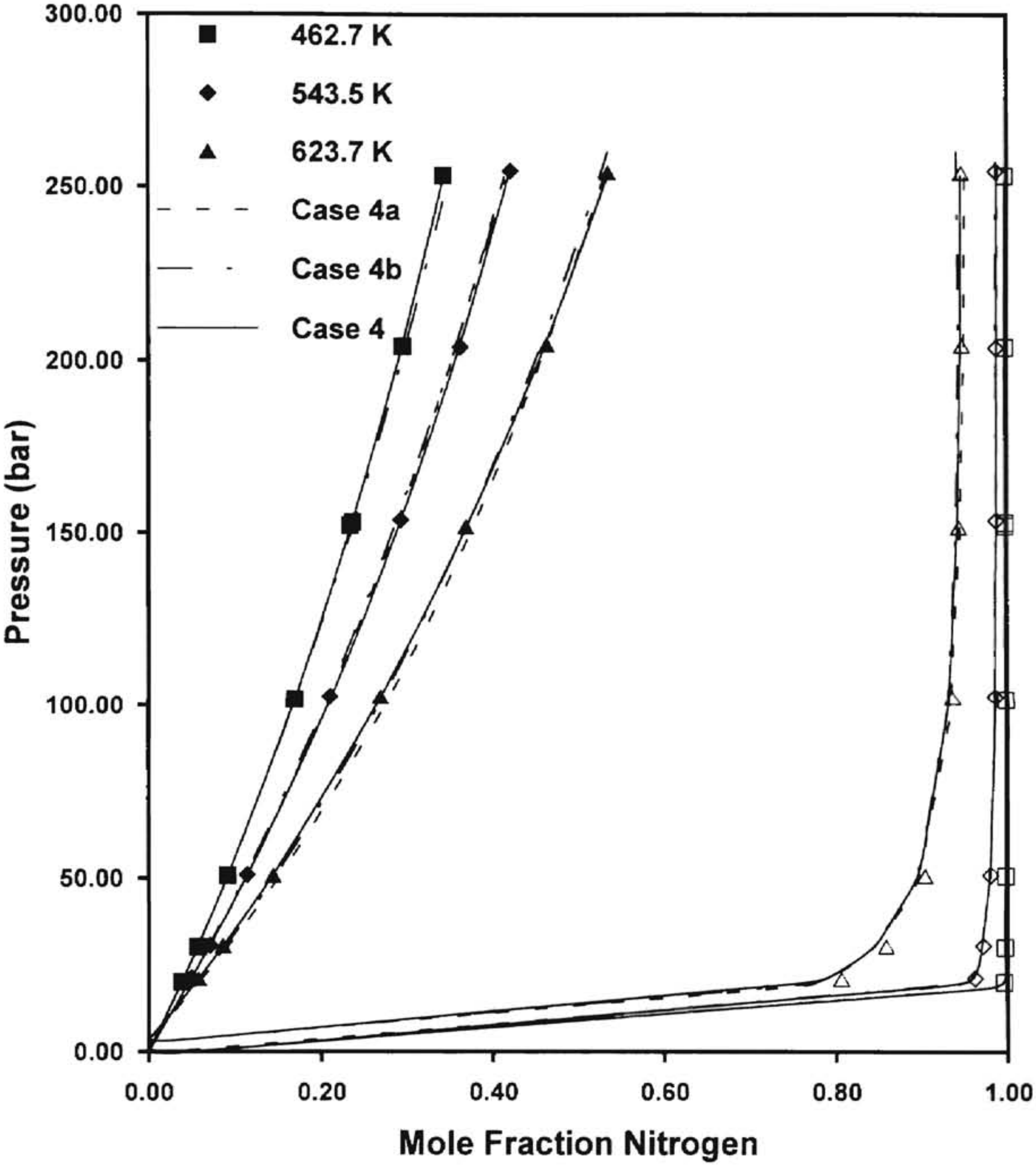

Figure 12. Representation of Vapor-Liquid Equilibrium for the Nitrogen + n-Hexadecane System Using the (θ/ϕ) Approach. Experimental Data Are from Lin et al. (1981)

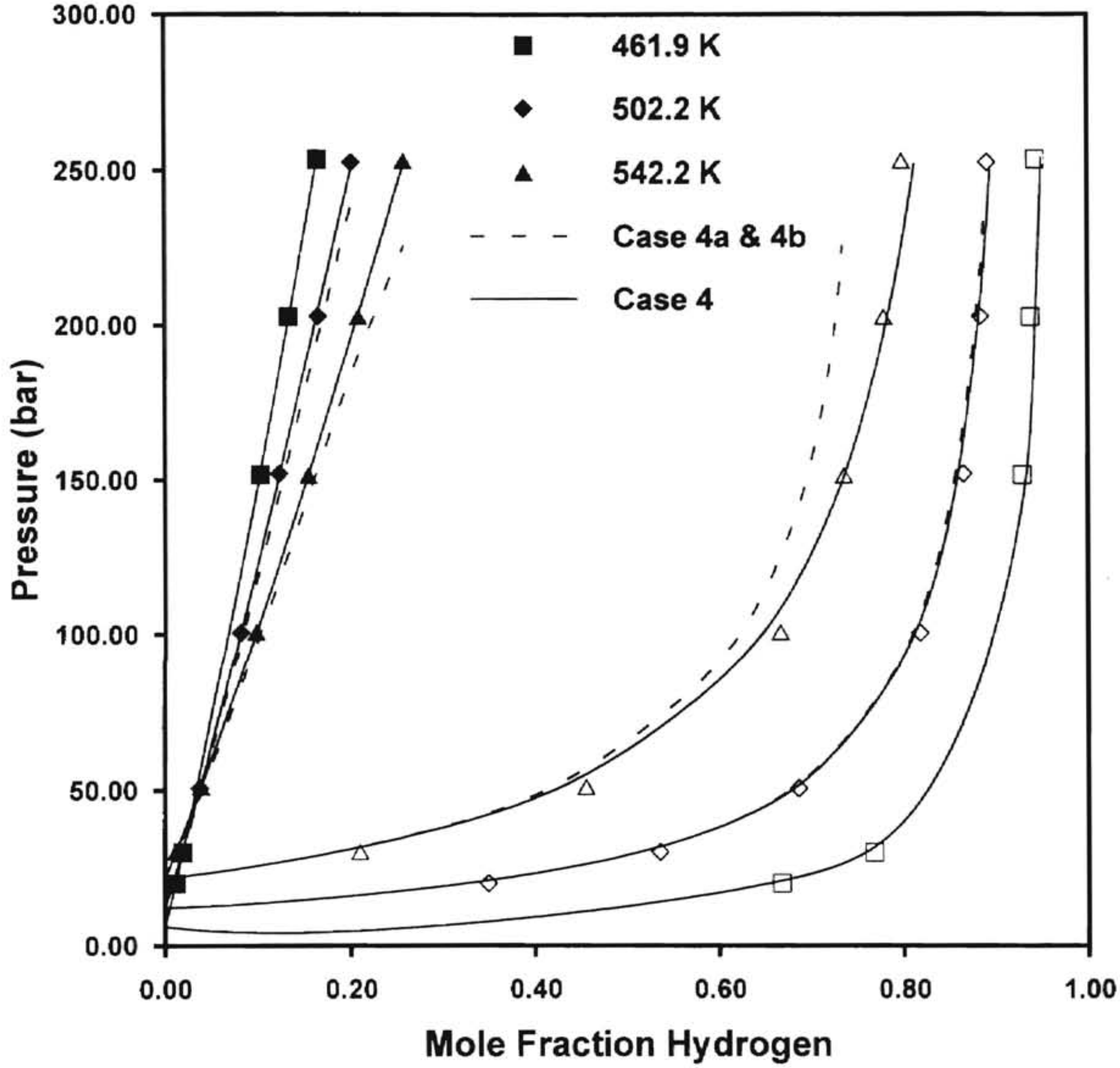

Figure 13. Representation of Vapor-Liquid Equilibrium for the Hydrogen + Toluene System Using the (θ/ϕ) Approach. Experimental Data Are from Simnick et al. (1978)

TABLE X

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	0.214	0.94	1.041	3.54	(ϕ/ϕ)
Carbon dioxide + n-Decane	310.9 - 510.9	1.491	2.84	1.389	2.87	(ϕ/ϕ)
Nitrogen + n-Hexadecane	462.7 - 623.7	2.820	1.56	2.680	1.98	(ϕ/ϕ)
Hydrogen + Toluene	461.9 - 542.2	8.264	3.02	8.973	4.87	(ϕ/ϕ)

TABLE XI

MODEL PARAMETERS OBTAINED FOR THE CONVENTIONAL APPROACHES (CASE 1 OR CASE 2) FOR A SYSTEM-BY-SYSTEM ANALYSIS

SYSTEM	TEMP RANGE (K)	C_{ij}	D_{ij}	τ_{12}	τ_{21}	α_{12}	
Acetone + Water	308.2 - 373.2			-0.0741	2.2000	0.1643	(γ/ϕ)
Ethane + n-Octacosane	348.2 - 423.2	-0.0058	-0.0200				(ϕ/ϕ)
Carbon dioxide + n-Decane	310.9 - 510.9	0.1014	0.0120				(ϕ/ϕ)
Nitrogen + n-Hexadecane	462.7 - 623.7	0.1756	0.0013				(ϕ/ϕ)
Hydrogen + Toluene	461.9 - 542.2	0.7515	-0.0343				(ϕ/ϕ)

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The primary goal of this work was to evaluate the merits of a proposed amendment to the current framework for phase equilibrium calculations. A new deviation function was introduced, wherein the fugacities generated from an equation of state are augmented by a fugacity deviation function. A secondary goal of this work was to evaluate the correlative abilities of the reformulated Wong-Sandler (MWS) mixing rules. Both of these approaches were compared with the conventional approaches for the correlation of phase equilibrium, i.e., using an equation of state with the van der Waals mixing rules and the split (γ/ϕ) approach. The evaluations were conducted using a database comprised of non-ideal binary systems at low pressures and binary asymmetric mixtures containing supercritical fluids with hydrocarbons at high pressures. Following are specific conclusions and recommendations which can be made based on this work.

Conclusions

1. The proposed method (called the (θ/ϕ) approach) can successfully correlate the binary vapor-liquid equilibrium of highly non-ideal low pressure systems as well as asymmetric high pressure systems. Bubble point pressures were correlated within 2% deviation for low pressure systems and within 1% deviation for high pressure systems.
2. The MWS mixing rules show accuracy comparable to the (θ/ϕ) approach for

correlating the binary vapor-liquid equilibrium 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 direct means for handling various types of systems, 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, 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 extension of this approach to volumetric as well as calorimetric properties should be explored through using different pure component limits for the fugacity deviation function.
3. The applicability of the (θ/ϕ) approach to multicomponent systems (ternary or

higher) should be investigated.

4. The temperature dependence and generalizability of the model parameters for the (θ/ϕ) approach should be addressed.

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APPENDIX A

VALIDATION OF PROPER IMPLEMENTATION OF THE MWS MIXING RULES

This appendix contains the validation cases for the computer program used to implement the MWS mixing rules. Two subroutines in an existing computer program, GEOS (Gasem, 1988-1996), were modified to simulate the MWS mixing rules. For validation of the modified program, two systems previously correlated by the same mixing rules by Orbey and Sandler (1995b) were used. The systems used were butane + ethanol and pentane + ethanol. The data for the butane + ethanol system were taken from Holderbaum et al. (1991) and for the pentane + ethanol system from Scott et al. (1987). For purposes of validation, a modified version of the Peng-Robinson equation of state (Stryjeck and Vera, 1986) was used. The physical properties were also the same as used by Orbey and Sandler. The model parameters reported by the same authors were used to predict the vapor-liquid equilibrium of the above systems. The predicted results are shown in Figures A.1 and A.2. The symbols represent experimental data and the continuous lines represent model predictions. The results in Figures A.1 and A.2 show the same behavior depicted by Figures 4 and 6 of Orbey and Sandler (1995b), thus validating the computer program's ability to properly implement the MWS mixing rules.

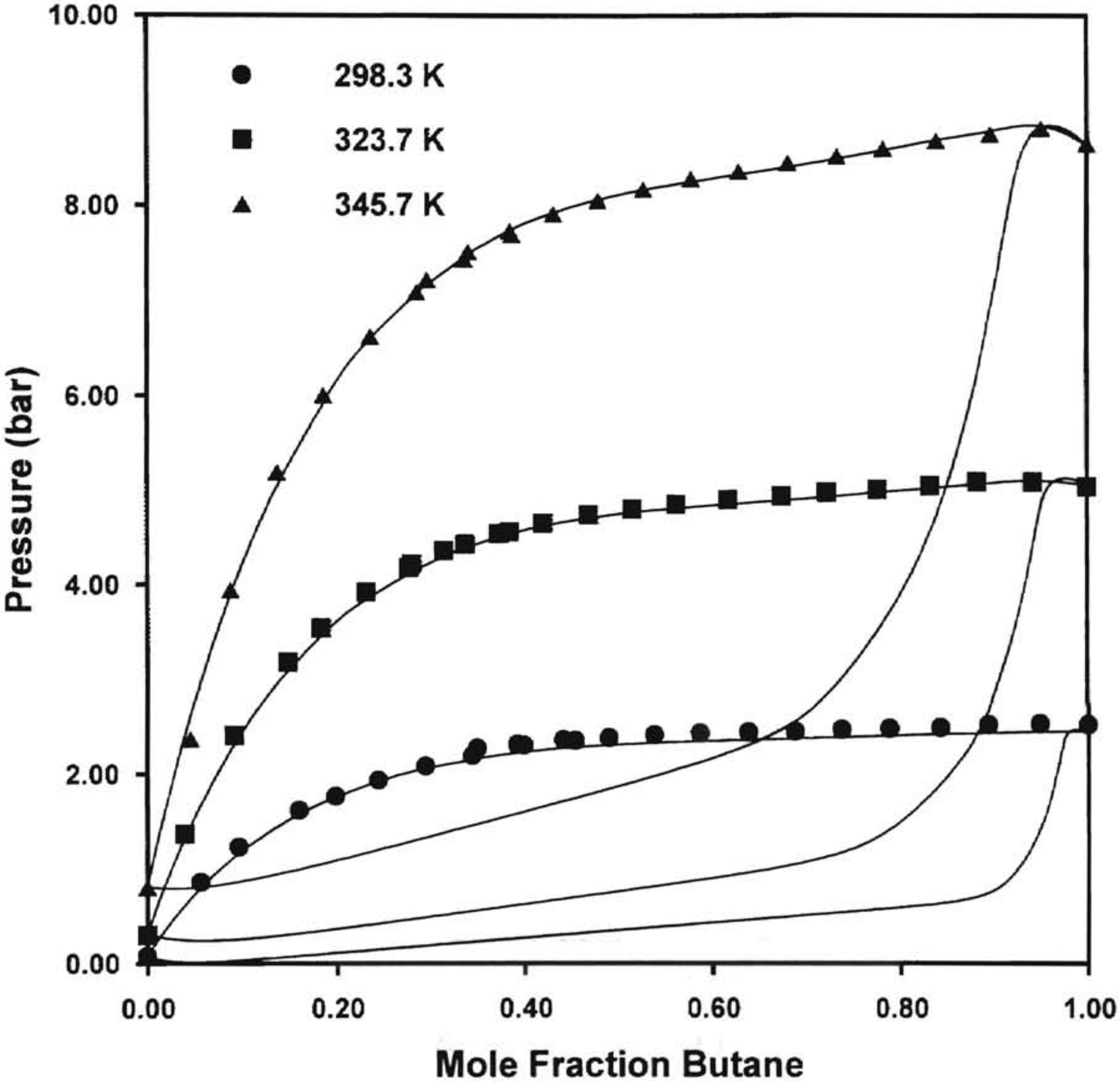

Fig. A.1. Representation of Vapor-Liquid Equilibrium for the Butane + Ethanol System Using the Reformulated Wong-Sandler Mixing Rules. Solid Lines Represent Four-Parameter Fit to 298.3 K. Experimental Data Are from Holderbaum et al. (1991)

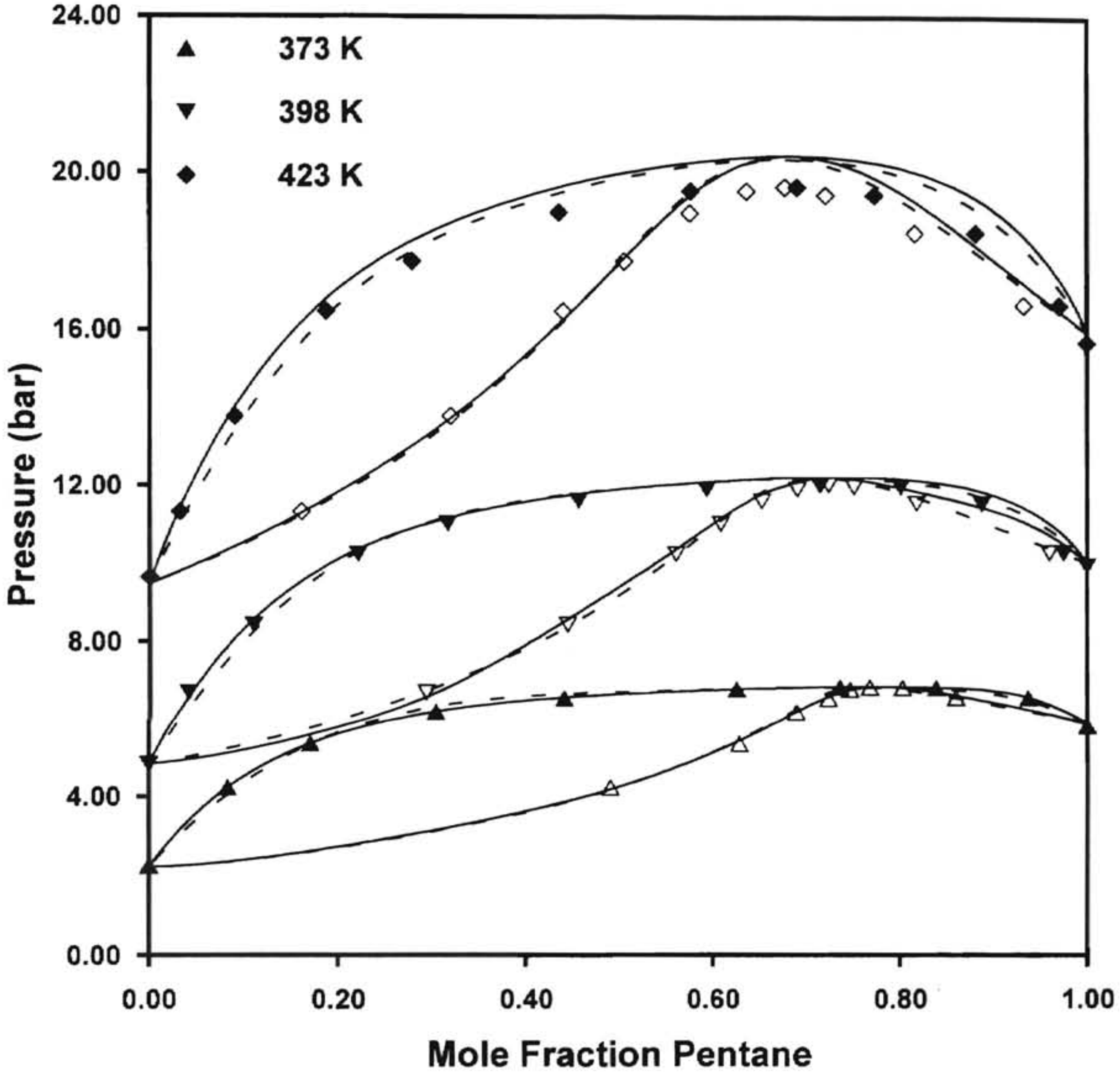

Figure A.2. Representation of Vapor-Liquid Equilibrium for the Pentane + Ethanol System Using the Reformulated Wong-Sandler Mixing Rules. Solid Lines Represent Four Parameters Fit to 373 K Data; Dashed Lines Represent Two Parameters Fit to 373 K Data. Experimental Data Are from Scott et al. (1987)

APPENDIX B

BINARY VLE DATABASE AND PURE COMPONENT PHYSICAL PROPERTIES USED

This appendix contains the sources and range of binary VLE data and pure component physical properties used in this study. The sources and range of binary VLE data used are shown in Tables B.I-B.V. Table B.VI 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). The vapor pressure model and the constants used in the model are listed in Table B.VII.

TABLE B.I

LOW PRESSURE BINARY VLE DATA USED IN MODEL EVALUATIONS

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 B.I (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 B.I (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 B.I (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	0.0612 - 0.1626	0.0773 - 0.9523	0.1535 - 0.9880	Polak et al. (1970)
	313.2	0.1395 - 0.3457	0.0155 - 0.9658		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 B.I (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 B.II

BINARY VLE DATA FOR ETHANE + HYDROCARBONS USED IN MODEL EVALUATIONS

Solvent	Temperature Range (K)	Pressure Range (Bar)	C_2H_6 Liquid Mole Fraction Range	C_2H_6 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 B.III

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 Lukes (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 B.IV

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 B.V

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 B.VI

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)

TABLE B.VI (Continued)

Compound	T_c (K)	p_c (Bar)	ω	Source
Tetrahydrofuran	540.2	51.9	0.225	AspenTech (1995)
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 B.VII

ASPEN PLUS™ VAPOR PRESSURE CONSTANTS

Compound	VP1	VP2	VP3	VP4	VP5	VP6	VP7	Tmin (K)	Tmax (K)
Water	7.3649E+02	-7.2582E+04	0.0	0.0	-7.3037E+01	4.1653E-05	2.0	273.2	647.1
Methanol	8.1768E+02	-6.8766E+04	0.0	0.0	-8.7078E+01	7.1926E-05	2.0	175.5	512.6
Ethanol	7.4475E+02	-7.1643E+04	0.0	0.0	-7.3270E+01	3.1340E-05	2.0	159.1	513.9
2-Propanol	7.6964E+02	-7.6238E+04	0.0	0.0	-7.4924E+01	5.9436E-17	6.0	185.3	508.3
1-Butanol	9.3173E+02	-9.1859E+04	0.0	0.0	-9.7464E+01	4.7796E-17	6.0	184.5	563.1
Tert-Butanol	1.7231E+03	-1.1590E+05	0.0	0.0	-2.2118E+02	1.3709E-04	2.0	299.0	506.2
2-Pentanol	1.2314E+03	-1.0534E+05	0.0	0.0	-1.4295E+02	3.9737E-05	2.0	200.0	560.4
1-Hexanol	1.1731E+03	-1.1239E+05	0.0	0.0	-1.3149E+02	9.3676E-17	6.0	228.6	611.4
Allyl Alcohol	5.9100E+02	-6.8417E+04	0.0	0.0	-4.9185E+01	-5.8895E-18	6.0	144.2	545.1
2-Butoxyethanol	1.5080E+03	-1.1728E+05	0.0	0.0	-1.8883E+02	1.1294E-04	2.0	199.2	633.9
Cyclohexanol	1.3501E+03	-1.2238E+05	0.0	0.0	-1.5702E+02	1.0349E-16	6.0	296.6	650.0
Acetic Acid	5.3270E+02	-6.3045E+04	0.0	0.0	-4.2985E+01	8.8865E-17	6.0	289.8	592.0
Propionic Acid	5.4552E+02	-7.1494E+04	0.0	0.0	-4.2769E+01	1.1843E-17	6.0	252.5	600.8
Acetone	6.9006E+02	-5.5996E+04	0.0	0.0	-7.0985E+01	6.2237E-05	2.0	178.5	508.2
2-Butanone	7.2698E+02	-6.1436E+04	0.0	0.0	-7.5779E+01	5.6476E-05	2.0	186.5	535.5
Diethyl Ether	1.3690E+03	-6.9543E+04	0.0	0.0	-1.9254E+02	2.4508E-01	1.0	156.9	466.7
Acetonitrile	5.8302E+02	-5.3856E+04	0.0	0.0	-5.4954E+01	5.3634E-05	2.0	229.3	545.6
Ethanolamine	9.2624E+02	-1.0367E+05	0.0	0.0	-9.4699E+01	1.9000E-17	6.0	283.7	678.2
Tetrahydrofuran	5.4898E+02	-5.3054E+04	0.0	0.0	-4.7627E+01	1.4291E-16	6.0	164.7	540.2
Acetaldehyde	1.9369E+03	-8.0367E+04	0.0	0.0	-2.9502E+02	4.3678E-01	1.0	150.2	466.0
Nitromethane	8.7411E+02	-7.1332E+04	0.0	0.0	-9.7786E+01	7.9061E-05	2.0	244.6	588.2

TABLE B.VII (Continued)

Compound	VP1	VP2	VP3	VP4	VP5	VP6	VP7	Tmin (K)	Tmax (K)
2-Methylpyridine	8.4039E+02	-7.5582E+04	0.0	0.0	-9.0927E+01	4.9333E-05	2.0	206.4	621.0
Ethyl Acetate	6.6824E+02	-6.2276E+04	0.0	0.0	-6.4100E+01	1.7914E-16	6.0	189.6	523.3
1,3-Butadiene	7.3522E+02	-4.5643E+04	0.0	0.0	-8.1958E+01	1.1580E-04	2.0	164.3	425.2
Methyl tert-butyl ether	5.5875E+02	-5.1316E+04	0.0	0.0	-4.9604E+01	1.9123E-16	6.0	164.6	497.1
Trans-1,3-Pentadiene	6.7926E+02	-5.1459E+04	0.0	0.0	-7.2358E+01	4.9370E-02	1.0	185.7	500.0
Dimethyl Sulfide	8.3485E+02	-5.7117E+04	0.0	0.0	-9.4999E+01	9.8449E-05	2.0	174.9	503.0
Methyl Mercaptan	5.4150E+02	-4.3377E+04	0.0	0.0	-4.8127E+01	4.5000E-16	6.0	150.2	470.0
1-Butene	6.8490E+02	-4.3502E+04	0.0	0.0	-7.4124E+01	1.0503E-04	2.0	87.8	420.0
Dimethyl Disulfide	8.8320E+02	-7.1936E+04	0.0	0.0	-9.9328E+01	7.3060E-05	2.0	188.4	606.0

Aspen Plus vapor pressure model

$$\ln(P) = VP1 + \frac{VP2}{(T + VP3)} + VP4 * T + VP5 * \ln(T) + VP6 * (T^{VP7})$$

APPENDIX C

EVALUATION RESULTS FOR CASES 1-3

This appendix contains the results obtained for Cases 1-3 in this study. The results for low pressure systems are shown in Tables C.I and C.II. As mentioned previously, Case 2 was not used for these systems. Similarly, Case 1 was not used for high pressure systems, the results for which are listed in Tables C.III - C.X.

TABLE C.I

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES AND VAPOR COMPOSITIONS OF NON-IDEAL SYSTEMS AT LOW PRESSURES USING THE SPLIT (γ/ϕ) APPROACH: CASE 1

					BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
Methanol +	318.2	-0.1022	0.8432	0.3105	0.005	-0.001	1.63				7
Water	313.1	-0.0733	0.6688	0.3869	0.003	0.001	0.85	0.046	-0.037	5.27	11
	298.1	-0.0760	0.6497	0.2914	0.001	0.000	0.67	0.005	0.001	0.65	13
Ethanol +	298.2	0.0031	1.5010	0.2790	0.001	0.000	1.15	0.007	0.001	1.16	10
Water	303.2	0.0098	1.5690	0.2780	0.001	0.000	0.95				5
	308.2	0.0165	1.5940	0.3352	0.003	0.001	1.83				5
2-Propanol +	298.2	0.5455	1.8530	0.5278	0.001	0.000	0.98	0.015	0.006	2.67	12
Water	328.2	0.4515	2.1230	0.4723	0.002	0.000	0.39	0.036	-0.031	6.06	9
Water +	323.2	4.2240	0.1507	0.3333	0.001	0.000	0.98	0.015	-0.007	2.17	6
1-Butanol	343.2	3.9190	0.2196	0.3298	0.003	0.000	0.94	0.008	0.005	1.16	6
	363.2	3.6880	0.3347	0.3572	0.011	0.001	1.38	0.014	0.008	2.14	6
	403.2	3.3990	0.2679	0.3857	0.032	0.000	0.93	0.012	-0.004	1.85	6
Water +	343.2	4.4250	0.4144	0.3231	0.003	0.000	0.56				17
2-Pentanol	363.2	4.5340	0.3743	0.3256	0.005	0.000	0.45				19

TABLE C.I (Continued)

SYSTEM	TEMP (K)	τ_{12}	τ_{21}	α_{12}	BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			NO PTS
					RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	
Water +	294.2	4.8970	0.7196	0.3005	0.000	0.000	1.53	0.020	0.016	1.76	6
1-Hexanol	313.2	3.0380	0.8016	0.3515	0.002	-0.001	2.99	0.017	0.012	1.36	8
Allyl Alcohol +	294.2	0.1594	1.9290	0.1927	0.000	0.000	0.94				4
Water	298.2	0.1268	1.9790	0.2352	0.001	0.000	1.01				4
	303.2	0.0951	2.0150	0.2918	0.001	-0.001	1.85				4
	308.2	0.0876	2.1240	0.2923	0.000	0.000	0.45				4
	313.2	0.1002	2.0130	0.2975	0.001	-0.001	0.80				4
Water +	278.2	2.7330	0.2309	0.4658	0.000	0.000	0.56	0.008	-0.006	0.68	8
2-Butoxyethanol	318.2	2.9960	0.2193	0.4423	0.001	0.000	0.79	0.011	-0.009	0.96	8
	358.2	3.2050	0.2289	0.4429	0.001	0.000	0.35	0.008	-0.006	0.77	7
Water + Cyclohexanol	363.2	4.5740	1.0660	0.4161	0.011	-0.001	1.92	0.028	0.002	2.94	13
Water +	372.8	0.6053	-0.2151	0.0722	0.023	-0.010	2.06	0.023	0.007	5.78	13
Acetic Acid	412.6	0.8418	-0.3466	0.2282	0.028	-0.001	0.69	0.021	0.005	4.73	13
Water +	333.2	1.5970	1.4690	0.7296	0.001	0.000	0.40	0.034	0.019	4.87	17
Propionic Acid	373.2	1.7450	0.7571	0.8424	0.010	0.000	1.25	0.050	0.033	7.33	15

TABLE C.I (Continued)

					BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
Acetone + Water	373.2	0.6341	1.8710	0.4727	0.052	0.008	1.44	0.008	0.004	2.50	22
	323.2	1.0600	1.6400	0.5013	0.001	0.000	0.12				15
	308.2	0.8413	1.3870	0.3654	0.002	0.000	0.39	0.008	-0.007	0.86	19
2-Butanone + Water	333.2	1.0040	2.7720	0.3665	0.003	0.000	0.32				20
Diethyl Ether + Water	308.2	1.5720	3.4790	0.2167	0.005	-0.001	0.71				13
	298.2	2.2910	3.7070	0.4220	0.012	-0.003	2.09				13
Acetonitrile + Water	323.2	1.0510	1.8970	0.4198	0.002	0.000	0.45				14
	333.2	1.0560	1.8920	0.4469	0.001	0.000	0.17	0.009	0.008	1.22	14
Water + Ethanolamine	333.2	0.6943	-1.3170	0.2837	0.003	0.001	2.32				12
	351.2	0.7682	-1.1910	0.3859	0.005	0.000	3.07				12
	364.9	0.7498	-1.1100	0.4076	0.011	0.005	3.10				12
Tetrahydrofuran + Water	298.2	1.8360	2.2200	0.4583	0.000	0.000	0.15				19

TABLE C.I (Continued)

SYSTEM	TEMP (K)	τ_{12}	τ_{21}	α_{12}	BUBBLE POINT PRESSURE RMSE (Bar)	BUBBLE POINT PRESSURE BIAS (Bar)	BUBBLE POINT PRESSURE %AAD	VAPOR COMPOSITION OF COMPONENT 1 RMSE	VAPOR COMPOSITION OF COMPONENT 1 BIAS	VAPOR COMPOSITION OF COMPONENT 1 %AAD	NO PTS
Acetaldehyde + Water	283.2	1.7570	1.2470	0.7123	0.003	-0.001	0.38				5
	293.2	1.6050	0.8963	0.7852	0.007	-0.002	0.55				5
	303.2	1.1230	0.9914	0.9000	0.022	-0.007	1.05				5
	373.2	1.9410	1.7530	0.7336	0.073	-0.009	2.39	0.042	-0.008	6.26	5
Water + Nitromethane	323.2	3.1270	0.3031	0.1215	0.009	-0.001	3.20	0.040	-0.003	9.53	16
	313.2	2.7280	0.7054	0.1104	0.003	0.000	1.42	0.014	0.002	2.31	7
	296.2	2.7440	0.8837	0.0855	0.001	0.000	1.06	0.010	-0.001	1.95	7
	294.2	2.6560	1.0320	0.0948	0.001	0.000	1.20	0.013	0.000	2.69	7
Water + 2-Methylpyridine	318.2	2.7890	-0.3225	0.3813	0.001	0.000	1.27				10
	308.2	2.8360	-0.2918	0.3888	0.001	0.000	1.07				10
	298.2	2.8570	-0.3456	0.3832	0.001	0.000	2.18				10
Ethyl Acetate + Water	323.2	0.7413	3.6390	0.2428	0.008	0.000	2.20	0.013	0.001	2.23	9
	343.2	0.2463	3.9850	0.1826	0.017	-0.001	1.88	0.013	0.000	2.28	9
	353.2	0.2419	3.9770	0.1856	0.024	-0.001	1.90	0.014	0.001	2.56	9
Acetonitrile + Tert-Butanol	333.2	0.3370	0.6855	0.2293	0.003	0.000	0.39	0.004	0.001	0.75	11

TABLE C.I (Continued)

					BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
1,3-Butadiene +	305.0	1.3120	0.6366	0.5732	0.010	-0.001	0.38				16
Acetonitrile	329.9	1.2190	0.5703	0.5505	0.014	-0.002	0.30				22
Methyl tert-butyl ether + Acetonitrile	313.2	0.7046	0.8747	0.5588	0.001	0.000	0.21	0.007	-0.005	1.67	33
Methanol +	298.2	-0.1641	-0.1862	0.9000	0.001	0.000	1.13	0.006	0.000	0.98	19
Tert-Butanol	313.2	-0.1129	-0.2789	0.6659	0.002	-0.001	0.78				13
Trans-1,3-Pentadiene +	303.2	1.2410	0.8353	0.6068	0.014	-0.001	2.22				9
Acetonitrile	313.2	1.0290	0.8990	0.5925	0.006	0.000	0.69				9
Dimethyl Sulfide +	263.2	1.7230	0.6684	0.2832	0.004	-0.003	2.92				8
Methanol	273.2	1.8950	0.8983	0.4288	0.003	0.000	1.50				8
	288.2	1.8340	1.0480	0.5180	0.003	0.000	0.56				8
Methyl Mercaptan +	269.2	2.2820	0.8299	0.4998	0.004	-0.001	0.50				7
Methanol	278.2	2.0270	0.6531	0.4630	0.004	0.000	0.46				8
	288.2	1.9280	0.3879	0.3358	0.009	-0.001	0.70				8

TABLE C.I (Continued)

					BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
Methyl Mercaptan +	263.2	-0.2830	0.3331	0.9000	0.002	0.000	0.79				5
Dimethyl Sulfide	273.2	-0.4375	0.6728	0.9000	0.002	0.000	0.45				5
	288.2	-0.2191	0.1650	0.0100	0.004	-0.002	0.25				5
1-Butene +	310.9	-0.2350	0.3913	0.9000	0.006	-0.002	0.11	0.002	0.001	0.82	9
1,3-Butadiene	324.8	-0.0208	-0.0032	0.0100	0.027	0.008	0.36	0.004	0.001	1.19	9
	338.7	0.1852	-0.1268	0.9000	0.003	-0.001	0.02	0.001	0.000	0.18	9
Methanol +	311.0	1.0400	1.0290	0.0981	0.001	0.000	0.33	0.006	0.000	0.53	7
Dimethyl Disulfide	336.0	1.2230	0.9481	0.3682	0.001	0.000	0.13	0.011	-0.008	1.02	10

OVERALL MODEL STATISTICS

BUBBLE POINT PRESSURE

RMSE = 0.0074 Bar
BIAS = -0.0002 Bar
%AAD = 1.02
NO PTS = 797

VAPOR COMPOSITION

RMSE = 0.0160
BIAS = -0.0006
%AAD = 2.67
NO PTS = 418

TABLE C.II

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES AND VAPOR COMPOSITIONS OF NON-IDEAL SYSTEMS AT LOW PRESSURES USING THE (ϕ/ϕ) APPROACH (MWS MIXING RULES): CASE 3

						BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
Methanol +	318.2	-0.0827	0.8755	0.3692	0.5851	0.010	-0.006	2.83				7
Water	313.1	-0.1102	0.8179	0.3244	0.5371	0.003	-0.002	1.17	0.013	-0.010	1.46	11
	298.1	-0.0654	1.0790	0.1682	0.8032	0.005	-0.003	2.75	0.034	0.022	4.69	13
Ethanol +	298.2	0.3410	0.6888	-0.0892	0.9000	0.001	-0.001	1.47	0.063	0.056	11.69	10
Water	303.2	0.3540	0.6598	-0.1152	0.6570	0.003	-0.001	3.11				5
	308.2	0.3509	0.6320	-0.1174	0.7445	0.004	0.000	2.79				5
2-Propanol +	298.2	0.0626	1.5370	0.1698	0.5681	0.004	0.002	4.47	0.066	0.066	11.53	12
Water	328.2	0.0021	1.4990	0.6362	0.4345	0.002	0.000	0.57	0.016	0.014	2.60	9
Water +	323.2	0.4452	1.9300	0.8610	0.5895	0.004	0.000	3.24	0.110	-0.105	16.51	6
1-Butanol	343.2	0.2946	1.9030	1.3530	0.5337	0.008	-0.001	2.49	0.067	-0.066	10.40	6
	363.2	0.3642	1.8110	1.3740	0.6421	0.014	0.000	1.64	0.039	-0.038	5.87	6
	403.2	0.1882	1.9710	1.7480	0.5269	0.027	0.000	0.85	0.025	-0.015	3.00	6
Water +	343.2	0.3341	0.0537	1.5840	0.3010	0.010	0.000	3.25				17
2-Pentanol	363.2	0.1711	1.4310	1.8020	0.3533	0.014	-0.002	1.46				19

TABLE C.II (Continued)

SYSTEM	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			NO PTS
						RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	
Water +	294.2	-0.2023	-0.0126	3.1270	0.2999	0.004	-0.002	4.24	0.040	-0.030	4.07	6
1-Hexanol	313.2	-0.1904	-0.0562	3.0310	0.1319	0.000	0.000	1.23	0.078	-0.058	6.15	8
Allyl Alcohol +	294.2	0.0990	1.9760	2.4160	0.5759	0.000	0.000	0.22				4
Water	298.2	0.0953	1.7970	2.7870	0.5643	0.000	0.000	0.08				4
	303.2	0.0956	1.6320	3.0400	0.5498	0.000	0.000	0.54				4
	308.2	0.0887	1.5730	2.9270	0.5433	0.001	0.000	1.33				4
	313.2	0.0787	1.4730	2.9680	0.5124	0.000	0.000	0.27				4
Water +	278.2	-0.2646	0.8488	2.2260	0.2242	0.000	0.000	3.89	0.025	-0.020	2.12	8
2-Butoxyethanol	318.2	-0.2954	0.7318	2.3000	0.2447	0.003	-0.001	2.75	0.021	-0.017	1.86	8
	358.2	-0.2666	0.9020	2.3240	0.2871	0.005	-0.001	0.88	0.011	-0.008	1.04	7
Water + Cyclohexanol	363.2	0.0794	3.7410	2.2700	0.4281	0.010	0.000	1.84	0.080	-0.076	9.72	13
Water +	372.8	-0.5682	7.4920	1.7800	0.3693	0.027	-0.007	2.55	0.041	0.007	9.59	13
Acetic Acid	412.6	-0.1314	1.1580	1.0070	0.8938	0.038	-0.007	0.78	0.020	0.003	4.53	13
Water +	333.2	-0.0382	2.8760	2.2980	0.5058	0.008	-0.003	4.87	0.041	0.005	4.78	17
Propionic Acid	373.2	-0.2703	4.6990	2.0610	0.4050	0.013	-0.003	1.52	0.048	0.028	5.50	15

TABLE C.II (Continued)

						BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			
SYSTEM	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	NO PTS
Acetone +	373.2	0.0575	1.8580	1.2150	0.6575	0.044	0.005	1.10	0.028	0.019	9.80	22
Water	323.2	0.0000	2.2420	0.9619	0.6086	0.008	-0.003	0.93				15
	308.2	0.0131	2.1880	-0.0007	0.5536	0.007	-0.003	1.64	0.012	0.008	1.01	19
2-Butanone +	333.2	0.2826	2.5240	1.0900	0.6074	0.003	0.000	0.31				20
Water												
Diethyl Ether +	308.2	0.2432	3.9870	1.1300	0.4117	0.003	0.000	0.46				13
Water	298.2	0.2698	3.8600	1.9790	0.5072	0.012	0.000	2.00				13
Acetonitrile +	323.2	0.3862	3.4100	0.7865	0.6802	0.002	0.000	0.55				14
Water	333.2	0.3538	3.0790	0.9062	0.7095	0.002	0.000	0.29	0.041	0.022	5.78	14
Water +	333.2	0.0194	-4.2880	2.5870	0.2662	0.005	-0.001	5.75				12
Ethanolamine	351.2	0.0366	-3.3740	1.2450	0.2150	0.009	-0.005	5.44				12
	364.9	0.0352	-3.3030	1.1450	0.1804	0.012	-0.001	4.51				12
Tetrahydrofuran +	298.2	0.1220	2.5890	1.6590	0.5766	0.003	-0.001	1.39				19
Water												

TABLE C.II (Continued)

SYSTEM	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	BUBBLE POINT PRESSURE			VAPOR COMPOSITION OF COMPONENT 1			NO PTS
						RMSE (Bar)	BIAS (Bar)	%AAD	RMSE	BIAS	%AAD	
Acetaldehyde + Water	283.2	0.2555	9.6840	0.6774	0.4287	0.001	0.000	0.22				5
	293.2	0.2468	8.3890	0.2362	0.4994	0.005	0.000	0.52				5
	303.2	0.2292	2.6510	0.5501	1.2680	0.038	-0.019	1.82				5
	373.2	0.2382	0.4550	1.3090	1.3040	0.067	-0.004	1.97	0.032	0.016	4.42	5
Water + Nitromethane	323.2	-0.0001	0.6341	3.7370	0.2721	0.010	-0.002	3.95	0.083	-0.029	21.41	16
	313.2	-0.0001	0.6277	4.1130	0.2730	0.003	-0.001	2.13	0.081	-0.023	17.29	7
	296.2	-0.0001	0.5643	4.4510	0.2591	0.002	-0.001	2.34	0.085	-0.025	18.87	7
	294.2	-0.0001	0.6112	4.5470	0.2606	0.002	-0.001	3.04	0.087	-0.019	19.22	7
Water + 2-Methylpyridine	318.2	0.6470	2.0280	-0.2123	0.1005	0.001	0.000	1.11				10
	308.2	0.6969	2.3370	-0.2098	0.3021	0.001	0.000	1.76				10
	298.2	0.5850	3.1930	-0.1425	0.1978	0.001	0.000	1.98				10
Ethyl Acetate + Water	323.2	0.0796	3.0350	0.0601	0.3264	0.004	-0.001	1.08	0.043	0.038	7.86	9
	343.2	0.0366	3.2140	0.4665	0.3320	0.012	-0.001	1.25	0.037	0.029	7.53	9
	353.2	0.1026	3.1600	0.2548	0.3376	0.017	-0.002	1.17	0.034	0.025	7.27	9
Acetonitrile + tert-Butanol	333.2	0.2317	1.9230	-0.0087	0.9000	0.004	0.001	0.57	0.032	-0.021	5.91	11

TABLE C.II (Continued)

SYSTEM	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	BUBBLE POINT PRESSURE RMSE (Bar)	BUBBLE POINT PRESSURE BIAS (Bar)	BUBBLE POINT PRESSURE %AAD	VAPOR COMPOSITION OF COMPONENT 1 RMSE	VAPOR COMPOSITION OF COMPONENT 1 BIAS	VAPOR COMPOSITION OF COMPONENT 1 %AAD	NO PTS
1,3-Butadiene +	305.0	0.0221	2.1290	0.8441	0.5197	0.007	0.000	0.31				16
Acetonitrile	329.9	0.1109	1.7260	0.7515	0.6464	0.013	-0.001	0.29				22
Methyl tert-Butyl Ether + Acetonitrile	313.2	0.0995	1.1800	1.3940	0.7027	0.007	0.001	1.33	0.037	0.026	8.15	33
Methanol +	298.2	0.4154	-1.7240	0.0794	0.9000	0.006	-0.001	4.55	0.072	-0.038	16.22	19
tert-Butanol	313.2	0.3499	-1.4960	0.0053	0.9000	0.012	0.000	4.83				13
tr-1,3-Pentadiene +	303.2	-0.6116	3.2930	-0.2328	0.0370	0.023	0.003	3.80				9
Acetonitrile	313.2	-0.5970	3.3150	-0.1378	0.0403	0.019	0.004	1.90				9
Dimethyl Sulfide +	263.2	0.0443	2.7120	0.6012	0.3894	0.002	0.000	1.95				8
Methanol	273.2	0.0879	2.6620	0.8002	0.4564	0.003	0.000	1.33				8
	288.2	0.0109	2.9190	1.2100	0.4565	0.002	0.000	0.53				8
Methyl Mercaptan +	269.2	0.3181	3.4680	0.7034	0.6450	0.002	0.000	0.24				7
Methanol	278.2	0.1961	2.8070	0.6495	0.5470	0.005	-0.001	0.59				8
	288.2	0.2140	2.4290	0.5103	0.5277	0.010	-0.001	0.76				8

TABLE C.II (Continued)

SYSTEM	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	BUBBLE POINT PRESSURE RMSE (Bar)	BUBBLE POINT PRESSURE BIAS (Bar)	BUBBLE POINT PRESSURE %AAD	VAPOR COMPOSITION OF COMPONENT 1 RMSE	VAPOR COMPOSITION OF COMPONENT 1 BIAS	VAPOR COMPOSITION OF COMPONENT 1 %AAD	NO PTS
Methyl Mercaptan +	263.2	-0.1938	0.6533	0.0926	0.9000	0.001	0.000	0.57				5
Dimethyl Sulfide	273.2	-0.1936	0.6680	0.1240	0.9000	0.002	-0.001	0.46				5
	288.2	-0.2016	0.9301	0.1157	0.8997	0.009	-0.003	0.60				5
1-Butene +	310.9	-0.3260	0.8622	0.9888	0.8838	0.003	0.000	0.06	0.002	0.000	0.77	9
1,3-Butadiene	324.8	-0.1678	0.2207	0.3189	0.1052	0.021	0.006	0.27	0.003	0.000	0.92	9
	338.7	-0.0061	0.1967	-0.0934	0.9000	0.003	-0.001	0.02	0.000	0.000	0.12	9
Methanol +	311	0.0090	1.9060	2.2200	0.3596	0.003	0.000	0.92	0.018	0.002	1.86	7
Dimethyl Disulfide	336	0.2440	0.6603	1.7230	0.5309	0.001	0.000	0.08	0.006	-0.003	0.54	10

OVERALL MODEL STATISTICS

BUBBLE POINT PRESSURE

RMSE = 0.0091 Bar
BIAS = -0.0008 Bar
%AAD = 1.84
NO PTS = 797

VAPOR COMPOSITION

RMSE = 0.0406
BIAS = -0.0006
%AAD = 7.42
NO PTS = 418

TABLE C.III

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF ETHANE + HYDROCARBON SYSTEMS USING THE (ϕ/ϕ) APPROACH (VAN DER WAALS MIXING RULES): CASE 2

SOLVENT	TEMP (K)	C_{ij}	D_{ij}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	303.2	0.0168	-0.0141	0.230	-0.020	1.85	10
	323.2	0.0326	-0.0257	0.160	0.020	0.85	10
	343.2	0.0213	-0.0223	0.360	0.010	1.38	7
	363.4	0.0428	-0.0351	0.230	0.010	0.74	11
n-Decane	311.1	0.0119	-0.0059	0.080	-0.010	0.75	10
	344.4	0.0039	0.0000	0.300	0.090	1.59	7
	377.8	0.0092	-0.0121	0.090	-0.010	0.31	6
	411.1	0.0145	-0.0213	0.070	-0.010	0.29	7
n-Hexadecane	285.0	0.0284	-0.0160	0.340	-0.030	1.61	5
	305.0	0.0233	-0.0139	0.270	0.270	1.22	5
	325.0	0.0068	-0.0005	1.320	0.120	3.64	5
n-Docosane	320.0	0.0288	-0.0209	0.520	-0.072	1.63	6
	340.0	0.0315	-0.0215	1.570	-0.210	2.98	8
	360.0	0.0241	-0.0208	0.920	-0.134	2.07	6
n-Octacosane	348.2	-0.0007	-0.0197	0.180	-0.050	0.90	10
	373.2	0.0061	-0.0193	0.170	-0.020	1.28	7
	423.2	0.0098	-0.0264	0.140	-0.030	0.86	7
n-Hexatriacontane	373.2	-0.0208	-0.0198	0.060	-0.010	0.61	7
	423.2	-0.0175	-0.0287	0.260	-0.040	1.35	6
n-Tetratetracontane	373.2	-0.0296	-0.0256	0.170	-0.010	1.21	9
	423.2	-0.0807	-0.0197	0.150	-0.020	1.12	7
Benzene	323.2	0.0139	0.0286	0.110	0.020	0.72	7
	373.2	0.0040	0.0301	0.170	0.020	0.55	7
	423.2	0.0067	0.0203	0.100	0.010	0.24	7
	298.2	0.0190	0.0307	0.320	-0.040	1.28	7
Toluene	313.1	0.0158	0.0332	0.260	0.110	1.20	8

TABLE C.III (Continued)

SOLVENT	TEMP (K)	C_{ij}	D_{ij}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
	393.1	0.0100	0.0000	2.170	-1.360	3.38	9
	473.2	0.0100	0.0000	2.470	-1.300	2.76	9
Naphthalene	373.2	0.0240	0.0240	0.310	0.030	0.51	10
	423.2	0.0218	0.0203	0.190	0.010	0.35	7
Cyclohexane	323.2	-0.0012	0.0138	0.060	0.010	0.48	8
	373.2	0.0000	0.0060	0.100	0.000	0.34	7
	423.2	0.0098	0.0004	0.080	-0.010	0.16	6
Phenanthrene	383.2	0.0400	0.0175	0.620	0.040	1.04	6
	423.2	0.0404	0.0155	0.110	0.010	0.18	6
Pyrene	433.2	0.0576	0.0121	0.470	0.010	0.67	6

OVERALL MODEL STATISTICS

RMSE = 0.4297 Bar
BIAS = -0.0909 Bar
%AAD = 1.17
NO PTS = 266

TABLE C.IV

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF ETHANE + HYDROCARBON SYSTEMS USING THE (ϕ/ϕ) APPROACH (MWS MIXING RULES): CASE 3

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	303.2	-0.0084	-0.0889	0.1772	0.0880	0.279	-0.028	1.82	10
	323.2	0.0665	-0.0047	-0.0933	0.0100	0.187	0.001	0.93	10
	343.2	0.0297	-0.1499	0.0347	2.0520	0.363	0.016	1.37	7
	363.4	0.0000	0.1349	0.0000	0.0884	1.213	-0.275	2.27	11
n-Decane	311.1	-0.0021	-1.6610	0.5665	0.1829	0.090	0.000	0.69	10
	344.4	-0.0022	-1.6710	0.5494	0.2245	0.136	0.000	0.57	7
	377.8	0.0049	-1.6550	0.5040	0.2319	0.093	0.007	0.19	6
	411.1	-0.0070	-1.6800	0.5926	0.3521	0.071	-0.008	0.19	7
n-Hexadecane	285.0	0.0566	-1.7360	0.5025	0.2353	0.290	0.005	1.09	5
	305.0	0.0193	-1.7910	0.6380	0.5190	0.216	-0.020	0.85	5
	325.0	-0.0721	-2.0410	0.9332	0.6312	0.874	-0.016	1.46	5
n-Docosane	320.0	0.0524	-2.0510	0.7252	0.7251	0.070	-0.002	0.34	6
	340.0	0.0481	-2.1070	0.6811	0.6735	0.123	-0.005	0.50	8
	360.0	0.0568	-2.0430	0.6353	0.7027	0.144	-0.008	0.46	6
n-Octacosane	348.2	0.0250	-2.1260	0.6319	0.8454	0.177	0.005	0.89	10
	373.2	-0.0184	-2.1460	0.5808	0.7821	0.122	0.004	0.63	7

TABLE C.IV (Continued)

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
	423.2	-0.0420	-2.1640	0.5392	0.7982	0.079	0.001	0.25	7
n-Hexatriacontane	373.2	-0.5118	-2.1240	0.7677	1.0480	0.057	-0.001	0.37	7
	423.2	0.0291	-2.3080	0.5057	0.8643	0.124	-0.008	0.47	6
n-Tetratetracontane	373.2	-0.0271	-2.3760	0.5513	0.9840	0.251	0.002	0.92	9
	423.2	-0.3928	-2.3660	0.4764	0.8989	0.093	-0.002	0.61	7
Benzene	323.2	-0.0019	0.2051	0.4956	0.7838	0.068	0.013	0.43	7
	373.2	-0.0283	0.1575	0.3831	0.5795	0.050	0.001	0.15	7
	423.2	-0.0056	0.0089	0.3068	0.5366	0.117	-0.003	0.21	7
	298.2	-0.0055	0.3158	0.5773	0.5866	0.345	-0.113	0.97	7
Toluene	313.1	0.0031	-1.6790	1.6840	0.2476	0.136	0.006	0.38	8
	393.1	-0.0020	-3.1180	2.4670	0.1790	0.349	0.011	0.45	9
	473.2	0.0436	-2.1290	1.5900	0.2589	1.124	0.282	1.37	9
Naphthalene	373.2	-0.2128	0.9338	0.3908	0.0100	1.248	0.045	1.43	10
	423.2	-0.3094	0.0701	0.6753	0.0307	0.496	0.144	0.50	7
Cyclohexane	323.2	-0.0289	0.2716	0.0673	0.0100	0.042	0.001	0.21	8
	373.2	-0.0097	0.1711	0.0092	0.0837	0.115	-0.004	0.34	7
	423.2	0.0000	0.2439	0.0115	1.4510	0.097	-0.043	0.15	6

TABLE C.IV (Continued)

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
Phenanthrene	383.2	0.1987	1.1000	0.2353	0.0100	3.751	0.715	4.80	6
	423.2	0.1694	0.9156	0.2164	0.0100	1.528	0.426	2.13	6
Pyrene	433.2	0.6370	0.4979	0.3409	1.4280	0.485	0.048	0.74	6

OVERALL MODEL STATISTICS

RMSE = 0.4155 Bar
BIAS = 0.0258 Bar
%AAD = 0.88
NO PTS = 266

TABLE C.V

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF CARBON DIOXIDE + HYDROCARBON SYSTEMS USING THE (ϕ/ϕ) APPROACH (VAN DER WAALS MIXING RULES): CASE 2

SOLVENT	TEMP (K)	C_{ij}	D_{ij}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	277.9	0.1088	0.0215	0.170	0.039	0.96	8
	344.3	0.1240	0.0088	0.160	-0.002	0.47	8
	387.6	0.1671	-0.0261	0.220	0.004	0.48	7
n-Decane	310.9	0.0987	0.0168	0.500	-0.027	0.98	11
	410.9	0.1222	-0.0135	0.080	0.000	0.09	6
	510.9	0.1333	0.0034	0.350	-0.021	0.81	6
n-Hexadecane	463.1	0.0461	-0.0003	0.210	0.023	0.60	4
	542.9	0.1308	-0.0307	0.110	-0.001	0.22	4
	623.6	0.1970	-0.0318	0.050	0.000	0.14	4
n-Docosane	323.2	0.1034	-0.0046	0.280	-0.005	0.68	14
	348.2	0.0982	-0.0095	0.400	-0.026	1.02	19
	373.2	0.0854	-0.0080	0.490	-0.016	1.42	11
n-Octacosane	348.2	0.1031	-0.0126	0.090	0.000	0.16	8
	423.2	0.0827	-0.0198	0.890	-0.077	1.95	7
	573.5	-0.0525	-0.0048	0.380	-0.013	1.20	5
n-Hexatriacontane	373.2	0.0624	-0.0133	0.370	-0.018	0.76	10
	423.2	0.0612	-0.0220	0.740	-0.054	0.90	8
n-Tetratetracontane	373.2	0.0494	-0.0162	0.360	-0.023	0.70	7
	423.2	0.0207	-0.0221	0.490	-0.039	0.81	7
Benzene	298.2	0.0675	0.0132	0.680	-0.223	1.08	8
	344.3	0.0582	0.0246	7.220	1.054	2.88	16
	413.6	0.0525	0.0210	0.930	0.036	0.70	9
Toluene	353.4	0.0707	0.0287	0.270	-0.070	1.62	8
	373.2	0.0678	0.0316	0.320	-0.080	2.19	7
	393.2	0.0516	0.0474	0.610	-0.100	2.29	7

TABLE C.V (Continued)

SOLVENT	TEMP (K)	C_{ij}	D_{ij}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
Naphthalene	373.2	0.0790	0.0292	0.200	-0.006	0.29	7
	423.2	0.0739	0.0277	0.270	-0.002	0.40	7
Cyclohexane	348.2	0.0968	0.0532	0.330	0.060	0.77	6
	373.2	0.0989	0.0436	0.090	0.010	0.17	7
	423.2	0.1066	0.0328	0.060	0.000	0.06	7
Phenanthrene	383.2	0.0996	0.0207	0.330	-0.049	0.76	7
	423.2	0.0937	0.0185	0.170	0.000	0.28	7
Pyrene	433.2	0.1150	0.0140	0.440	0.030	0.76	7

OVERALL MODEL STATISTICS

RMSE = 0.7802 Bar
BIAS = 0.0433 Bar
%AAD = 0.96
NO PTS = 264

TABLE C.VI

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF CARBON DIOXIDE + HYDROCARBON SYSTEMS USING THE (ϕ/ϕ) APPROACH (MWS MIXING RULES): CASE 3

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	277.9	0.0723	0.7746	0.8973	0.0100	0.110	-0.009	0.63	8
	344.3	0.1178	-0.1319	0.8195	0.0124	0.172	-0.001	0.49	8
	387.6	0.1717	-0.3998	0.7128	0.0100	0.233	0.007	0.52	7
n-Decane	310.9	0.0779	3.0030	0.5106	0.0100	1.272	0.015	3.24	11
	410.9	0.2315	1.0740	0.2262	0.1290	0.204	-0.009	0.30	6
	510.9	0.1297	0.9910	0.2320	0.0111	0.306	0.011	0.77	6
n-Hexadecane	463.1	0.0569	0.0126	0.2756	0.0577	0.208	0.024	0.59	4
	542.9	0.4361	0.7813	-0.0073	0.7529	0.327	-0.069	0.66	4
	623.6	0.2323	0.8440	0.1363	1.5000	0.278	-0.064	0.61	4
n-Docosane	323.2	0.2777	9.1190	0.4450	0.0251	0.390	-0.035	0.89	14
	348.2	0.6952	4.8840	0.2827	0.0115	0.485	-0.038	1.31	19
	373.2	0.8019	3.8120	0.1979	0.0107	0.539	-0.042	1.47	11
n-Octacosane	348.2	0.7375	-2.4560	1.6260	1.0050	0.066	0.000	0.15	8
	423.2	0.3615	-2.3500	0.9982	0.9227	0.778	-0.069	1.75	7
	573.5	0.0293	-2.1400	0.4083	0.6882	0.309	0.024	1.16	5

TABLE C.VI (Continued)

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Hexatriacontane	373.2	0.3455	-2.7030	1.2370	0.8817	0.174	-0.004	0.44	10
	423.2	0.0176	-2.7180	1.0290	0.8748	0.201	0.001	0.29	8
n-Tetratetracontane	373.2	-0.0036	-2.2740	1.2860	1.2680	0.297	-0.033	0.60	7
	423.2	0.0712	-2.2690	0.8700	1.1950	0.083	-0.002	0.20	7
Benzene	298.2	0.1073	-0.5483	0.8887	0.4725	0.593	-0.105	0.99	8
	344.3	0.0614	-0.4436	0.8053	0.2503	0.197	0.003	0.16	16
	413.6	0.0522	-0.3646	0.5380	0.5564	0.852	-0.017	0.73	9
Toluene	353.4	0.2968	-0.0035	0.6429	3.0780	0.250	-0.008	0.85	8
	373.2	0.3864	0.0280	0.6021	4.8200	0.443	-0.009	1.13	7
	393.2	0.3319	0.1598	0.6912	4.2120	0.537	0.005	0.98	7
Naphthalene	373.2	0.1688	2.0070	0.7200	1.4800	0.119	-0.001	0.21	7
	423.2	0.0885	3.7130	0.6046	1.5960	0.202	-0.002	0.33	7
Cyclohexane	348.2	0.1129	0.2722	0.9060	0.6028	0.305	-0.009	0.62	6
	373.2	0.1436	0.0767	0.7819	0.8828	0.062	0.001	0.11	7
	423.2	0.1518	-0.0855	0.6255	1.1080	0.063	0.000	0.07	7
Phenanthrene	383.2	0.9982	1.6170	0.5293	2.8620	0.347	0.010	0.66	7
	423.2	0.9283	8.2670	0.3632	4.1230	0.184	-0.001	0.30	7

TABLE C.VI (Continued)

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
Pyrene	433.2	0.8043	2.4980	0.2351	0.0104	0.420	-0.010	0.58	7

OVERALL MODEL STATISTICS

RMSE = 0.3574 Bar
BIAS = -0.0141 Bar
%AAD = 0.78
NO PTS = 264

TABLE C.VII

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF NITROGEN + HYDROCARBON SYSTEMS USING THE (ϕ/ϕ) APPROACH (VAN DER WAALS MIXING RULES): CASE 2

SOLVENT	TEMP (K)	C_{ij}	D_{ij}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	250.0	0.0387	0.0334	0.290	0.020	0.53	9
	277.0	0.0421	0.0332	0.660	0.050	2.13	12
	311.1	0.0272	0.0360	1.300	0.020	0.90	16
	344.4	0.0290	0.0361	0.200	-0.050	0.53	12
n-Decane	310.9	0.1094	0.0007	3.440	-1.200	3.56	22
	344.3	0.1112	-0.0001	5.240	-0.820	3.67	30
	410.9	0.1390	0.0097	4.240	0.310	2.80	20
n-Hexadecane	462.7	0.1868	-0.0010	0.550	0.030	0.42	8
	543.5	0.1321	0.0091	0.370	0.020	0.40	7
	623.7	0.0827	0.0466	0.600	0.090	0.76	7
n-Eicosane	323.2	0.3076	0.0015	0.230	0.050	0.15	8
	373.2	0.2832	0.0014	0.340	0.050	0.42	6
	423.2	0.2703	0.0000	0.280	0.030	0.35	6
n-Octacosane	348.2	0.3928	0.0032	0.380	0.020	0.36	7
	373.2	0.4001	0.0024	0.580	0.050	0.55	6
	423.2	0.3679	0.0041	0.290	-0.020	0.22	6
n-Hexatriacontane	373.2	0.3961	0.0113	0.380	0.040	0.40	6
	423.2	0.4193	0.0114	0.300	0.030	0.32	6
Benzene	348.2	-0.0007	0.0634	0.980	0.110	0.70	6
	373.2	-0.0051	0.0619	2.590	-0.170	1.18	6
	398.2	-0.0835	0.0892	0.790	-0.090	0.44	7
Toluene	323.2	-0.1349	0.1149	6.690	-0.409	2.74	6
	348.2	0.2029	0.0127	7.820	-0.668	5.70	6
Cyclohexane	366.4	-0.0017	0.0453	4.140	-0.280	6.47	9
	410.8	-0.0365	0.0592	1.310	0.190	1.77	9

TABLE C.VII (Continued)

OVERALL MODEL STATISTICS

RMSE = 2.2353 Bar
BIAS = -0.2055 Bar
%AAD = 1.91
NO PTS = 243

TABLE C.VIII

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF NITROGEN + HYDROCARBON SYSTEMS USING THE (ϕ/ϕ) APPROACH (MWS MIXING RULES): CASE 3

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	250.0	0.4476	-0.1059	0.5746	1.1080	0.253	-0.004	0.48	9
	277.0	0.1174	0.4348	0.5313	0.9640	1.008	-0.027	2.64	12
	311.1	-0.3177	0.6030	0.7588	1.0470	1.298	-0.036	0.88	16
	344.4	-0.3243	0.5423	0.6343	0.0565	0.414	-0.002	0.73	12
n-Decane	310.9	0.3572	10.2300	0.3153	0.2715	4.599	-0.042	1.99	22
	344.3	0.2838	10.9900	0.2845	0.2989	5.918	-0.150	2.83	30
	*410.9	0.2491	10.5400	0.2772	0.3240	4.278	0.481	2.64	19
n-Hexadecane	462.7	0.1500	1.4570	0.1206	0.0119	0.605	-0.034	0.43	8
	543.5	0.2610	1.1800	0.1033	0.2288	0.528	-0.009	0.35	7
	623.7	0.5266	1.3460	0.1133	0.1959	2.253	0.122	1.10	7
n-Eicosane	323.2	0.3378	5.4090	0.3469	0.0134	0.216	0.005	0.15	8
	373.2	0.2648	3.5390	0.2555	0.0100	0.410	-0.016	0.36	6
	423.2	0.2379	2.5270	0.2051	0.0663	0.306	-0.003	0.30	6
n-Octacosane	348.2	0.4801	8.3360	0.3724	0.0101	0.371	-0.008	0.33	7
	373.2	0.4398	7.0360	0.3451	0.0281	0.621	-0.017	0.48	6
	423.2	0.5137	4.5330	0.3042	0.0731	0.257	-0.002	0.19	6

TABLE C.VIII (Continued)

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Hexatriacontane	373.2	0.7969	11.3900	0.4683	0.0116	0.240	-0.005	0.18	6
	423.2	0.8362	7.3200	0.4308	0.0486	0.245	-0.002	0.15	6
Benzene	348.2	0.5579	-2.9530	2.2230	0.0979	1.172	-0.027	0.60	6
	373.2	-0.1652	-2.9300	2.2450	0.0498	1.994	-0.105	0.72	6
	398.2	-0.1826	-3.1770	2.1890	0.0128	1.465	-0.010	0.53	7
Toluene	323.2	0.7075	12.2100	0.0017	0.0830	3.946	-0.253	1.70	6
	348.2	0.4085	7.2900	0.0083	0.0864	6.422	-1.151	5.42	6
Cyclohexane	366.4	0.3887	1.7660	0.1766	0.1229	4.910	0.524	7.17	9
	410.8	-0.1141	1.9150	0.2012	0.0359	1.303	-0.175	1.78	9

OVERALL MODEL STATISTICS

RMSE = 2.2749 Bar
BIAS = -0.0551 Bar
%AAD = 1.57
NO PTS = 223

* - Isotherm with non-convergent point(s) which were discarded from the data set. Isotherm not included in overall analysis.

TABLE C.IX (Continued)

SOLVENT	TEMP (K)	C_{ij}	D_{ij}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
Naphthalene	373.2	0.3905	0.0000	1.970	-0.760	2.22	6
	423.2	0.4127	0.0000	1.170	-0.400	1.46	8
Cyclohexane	310.9	-0.5594	0.1601	10.990	4.614	2.39	13
	344.3	-0.5148	0.1719	5.260	-0.141	1.18	14
	377.6	-0.2350	0.1365	1.220	-0.026	0.31	13
	410.9	0.1334	0.0743	2.830	-0.111	0.80	13
Phenanthrene	398.2	0.3921	-0.0002	1.420	-0.500	1.11	7
	423.2	0.3995	0.0000	1.620	-0.600	1.32	6
	448.2	0.4100	0.0005	1.040	-0.430	1.07	6
	473.2	0.0090	0.0398	0.660	-0.090	0.45	6
Pyrene	433.2	0.4367	0.0016	1.720	-0.710	1.80	6

OVERALL MODEL STATISTICS

RMSE = 1.8092 Bar
BIAS = 0.0936 Bar
%AAD = 1.02
NO PTS = 274

TABLE C.X

RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES OF HYDROGEN + HYDROCARBON SYSTEMS USING THE (ϕ/ϕ) APPROACH (MWS MIXING RULES): CASE 3

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Butane	327.7	-0.0952	-0.0116	1.0690	1.7150	1.403	-0.048	1.35	13
	361.0	0.1210	2.4860	0.4725	0.1179	1.539	-0.056	1.27	11
	394.3	0.1156	4.0190	0.5672	0.1180	1.671	-0.085	1.50	12
n-Decane	462.5	0.9112	3.6200	0.1173	0.0498	2.543	0.079	1.46	7
	503.4	0.9112	3.6200	0.1173	0.0498	7.307	-2.441	8.97	7
	543.0	1.0588	3.6320	0.1079	0.0102	1.694	0.035	0.87	7
n-Hexadecane	461.7	0.4945	2.1000	0.1687	0.0108	0.483	0.012	0.55	7
	542.3	0.5086	1.8920	0.1581	0.0274	0.324	0.042	0.29	7
	*622.9	0.9468	2.4010	0.1936	0.0378	0.980	0.064	0.63	6
	664.1	1.3420	8.6200	0.0930	0.0569	2.828	0.111	2.15	8
n-Eicosane	323.2	0.7797	2.6750	0.3903	0.0278	0.232	0.002	0.21	7
	373.2	0.5800	0.5499	0.3449	0.2669	0.377	-0.003	0.51	9
	423.2	0.5947	-0.3153	0.2876	0.0204	0.171	0.011	0.26	6
n-Octacosane	348.2	0.5136	9.4330	0.1194	0.0100	0.186	0.004	0.22	6
	373.2	0.3775	8.2040	0.0953	0.0237	0.056	0.000	0.06	5
	423.2	0.1392	5.3570	0.0578	0.0654	0.359	-0.004	0.43	9

TABLE C.X (Continued)

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
n-Hexatriacontane	373.2	-0.0079	8.1850	0.0692	0.0808	0.512	0.077	0.37	6
	423.2	0.0039	0.1896	0.0486	0.3550	0.522	-0.163	0.67	6
Benzene	323.2	0.9250	4.7730	0.3173	0.0508	0.058	0.000	0.08	6
	373.2	1.1679	4.1700	0.2283	0.0880	0.205	0.008	0.32	6
	*423.2	1.2739	3.6770	0.1524	0.1034	0.130	0.006	0.17	5
Toluene	461.9	1.1374	5.6860	0.0887	0.0927	0.968	-0.043	0.64	5
	502.2	1.1374	5.6860	0.0887	0.0927	5.042	2.035	1.70	7
	542.2	1.1374	5.6860	0.0887	0.0927	7.773	1.536	3.48	6
Naphthalene	373.2	1.1192	1.9590	0.7386	0.0348	0.403	0.000	0.39	6
	423.2	1.1380	1.1270	0.6694	0.1132	0.731	0.003	0.55	8
Cyclohexane	310.9	1.0330	7.1300	0.6939	0.2132	7.097	-0.154	2.07	13
	344.3	1.0338	9.2240	0.6523	0.2169	6.244	-0.029	1.47	14
	377.6	0.9591	11.0400	0.6220	0.2258	3.405	0.103	1.06	13
	410.9	0.7279	13.2100	0.6293	0.2272	1.937	0.064	0.53	13
Phenanthrene	398.2	0.6374	3.9530	0.6450	0.0511	0.663	-0.012	0.45	7
	423.2	0.7630	3.3750	0.6131	0.0657	0.695	-0.031	0.60	6
	448.2	0.7200	2.8970	0.5892	0.0803	0.141	-0.005	0.13	6
	473.2	0.8449	2.5190	0.5684	0.1107	0.729	-0.001	0.31	6

TABLE C.X (Continued)

SOLVENT	TEMP (K)	C_{ij}	τ_{12}	τ_{21}	α_{12}	RMSE (Bar)	BIAS (Bar)	%AAD	NO PTS
Pyrene	433.2	1.2043	4.3010	0.5838	0.0106	0.344	0.001	0.27	6

OVERALL MODEL STATISTICS

RMSE = 2.0805 Bar
BIAS = 0.0192 Bar
%AAD = 1.13
NO PTS = 261

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* - Isotherm with non-convergent point(s) which were discarded from the data set. Isotherm not included in overall analysis.

2

VITA

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Master of Science

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