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# Accurate Vaporizing Gas-Drive Minimum Miscibility Pressure Prediction

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## ABSTRACT

Prediction of The Minimum Miscibility Pressure (MMP) of the Vaporizing Gas Drive (VGD) process is modeled using an equation of state with different mixing rules joined with a newly formulated expression for the unlike-three-body interactions between the injection gas and the reservoir fluid. The comparison of the numerical results with the available experimental data indicates that an equation of state alone overestimates the MMP. However, when the equation of state is joined with the unlike-three-body interaction term, the MMP will be predicted accurately. The proposed technique is used to develop a simple and reliable correlation for the accurate vaporizing gas drive MMP prediction

## INTRODUCTION

The Ternary or pseudoternary diagram is a useful way to visualize the development of miscible displacement in enhanced oil recovery. The phase behavior of a reservoir fluid for which the exact composition is never known can be represented approximately on a triangular diagram by grouping the components of the reservoir fluid into three pseudocomponents. Such diagram is called pseudoternary diagram.

The scope of this paper involves the use of the Peng-Robinson equation of state coupled with coherent mixing and combining rules derived from statistical mechanical considerations, and the implementation of the three body effects in the evaluation of the phase behavior of ternary systems and the prediction of the minimum miscibility pressure of simulated reservoir fluids. To support the application of the model, it was preferable to obtain phase behavior data for true ternary systems

such as carbon dioxide-n-butane-n-decane and methane-n-butane-n-decane, which are rigorously described by ternary diagrams. Moreover, experimental vapor-liquid data for the above systems are available at pressures and temperatures which fall within the range of the majority of oil reservoirs.

The utility of the Peng-Robinson (PR) equation of state has been tested<sup>1,2</sup> with limited success in predicting the phase behavior and minimum miscibility pressures of simulated reservoir fluids. By using the PR equation of state an overprediction of the MMP of the methane-n-butane-n-decane system was observed and it was believed that this was due to the limitations of the PR equation which does not accurately predict the phase behavior of the methane-n-butane-n-decane system in the critical region. In addition the prediction of the vapor-liquid coexistence curves of the carbon dioxide-n-butane-n-decane systems was not satisfactory in all ranges of pressures and compositions.

The ultimate objective of this paper is to show the impact of the mixing and combining rules on the prediction of the phase envelopes and the contribution of the three body-effects on phase behavior predictions near the critical region.

## THE VAN DER WAALS MIXING RULES

From the conformal solution theory of statistical mechanics it can be shown that pair-intermolecular potential energy function of any two molecules of a mixture can be related to the potential energy function of a reference fluid by the following expression:

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References and illustrations at end of paper

$$u_{ij}(r) = f_{ij} u_0(r/h_{ij})^{1/3} \quad (1)$$

In the above equation  $u_0$  is the potential energy function of the reference pure fluid,  $f_{ij}$  is the conformal molecular energy parameter and  $h_{ij}^{1/3}$  is the conformal molecular length parameter of interactions between molecules  $i$  and  $j$  of the mixture. By using Eq.1 in the statistical mechanical virial or energy equations of state and application of the conformal solution approximation to the radial distribution functions of components of a mixture<sup>3</sup> it can be shown that

$$f_x h_x = \sum_i^n \sum_j^n x_i x_j f_{ij} h_{ij} \quad (2)$$

$$h_x = \sum_i^n \sum_j^n x_i x_j h_{ij} \quad (3)$$

where  $h_x$  and  $f_x$  are the conformal solution parameters of a hypothetical pure fluid which can represent the mixture and  $x_i$ ,  $x_j$  are the mole fractions. This means that for the extension of applicability of a pure fluid equation of state to mixtures one has to replace molecular energy and length parameters of the equation of state with the above mixing rules.

Equations 2 and 3 are identical with the mixing rules which were originally proposed by van der Waals<sup>4</sup> for the van der Waals equation of state as it was applied to simple mixtures.

In order to apply the van der Waals mixing rules in different equations of state, one has to consider the following guidelines of the conformal solution theory of statistical mechanics:

- (i) The van der Waals mixing rules are for constants of an equation of state.
- (ii) Equation 2 is a mixing rule for parameters that are proportional to (molecular length)<sup>3</sup>, (molecular energy) and Equation 3 is a mixing rule for parameters that are proportional to (molecular length)<sup>3</sup>

As an example the Peng-Robinson<sup>5</sup> equation of state which has received a wide acceptance in process engineering calculations is chosen in this investigation to perform vapor-liquid equilibrium calculations.

In the Peng-Robinson equation of state

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (4)$$

where

$$a(T) = a(T_c) \{1 + \kappa(1-T_r^{1/2})\}^2 \quad (5)$$

$$a(T_c) = 0.45724 R^2 T_c^2 / P_c \quad (6)$$

$$b = 0.07780 RT_c / P_c \quad (7)$$

the characteristic constant  $\kappa$  is given by the following relationship:

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (8)$$

It is customary, for the mixture, to calculate parameters  $a$  and  $b$  with the following expressions which are known as their mixing rules

$$a = \sum_i^n \sum_j^n x_i x_j a_{ij} \quad (9)$$

$$b = \sum_i^n x_i b_i \quad (10)$$

$$a_{ij} = (1 - \xi_{ij}) (a_i a_j)^{1/2} \quad (11)$$

This set of mixing rules is however inconsistent with the guidelines dictated by the conformal solution theory of statistical mechanics.

In order to apply the van der Waals mixing rules correctly in the Peng-Robinson equation of state, we must separate thermodynamic variables from constants of the equation of state. Thus, we can write the Peng-Robinson equation of state in the following form:

$$Z = \frac{v}{v-b} - \frac{c/RT + d - 2\sqrt{cd/RT}}{(v+b) + (b/v)(v-b)} \quad (12)$$

where  $c = a(T_c)(1+k)^2$  and  $d = a(T_c)k^2/RT_c$

This new form indicates that this equation of state has three independent constants which are  $b$ ,  $c$ , and  $d$ . Parameters  $b$  and  $d$  are proportional to (molecular length)<sup>3</sup> or ( $b=h$  and  $d=h$ ), while parameter  $c$  is proportional to (molecular length)<sup>3</sup> (molecular energy) or ( $c=fh$ ). Thus, the mixing rules for  $c$ ,  $b$ , and  $d$  will be

$$c = \sum_i^n \sum_j^n x_i x_j c_{ij} \quad (13)$$

$$b = \sum_i^n \sum_j^n x_i x_j b_{ij} \quad (14)$$

$$d = \sum_i^n \sum_j^n x_i x_j d_{ij} \quad (15)$$

The combining rules for the unlike interaction parameters  $b$ ,  $c$  and  $d$  that are consistent with the above mixing rules will be

$$b_{ij} = (1-l_{ij})^3 \left[ \frac{b_{ii}^{1/3} + b_{jj}^{1/3}}{2} \right]^3 \quad (16)$$

$$d_{ij} = (1-m_{ij})^3 \left[ \frac{d_{ii}^{1/3} + d_{jj}^{1/3}}{2} \right]^3 \quad (17)$$

$$c_{ij} = (1-k_{ij}) [c_{ii} \cdot c_{jj} / b_{ii} \cdot b_{jj}]^{1/2} b_{ij} \quad (18)$$

In Equations 16-18 parameters  $k_{ij}$ ,  $l_{ij}$  and  $m_{ij}$  are the binary interaction parameters that can be adjusted to provide the best fit to the experimental data. In the next section we will discuss the shortcoming of using mixing rules for multicomponent mixtures (three components and more) and we will propose the concept of unlike three-body interactions to correct this problem.

### THEORY OF THE THREE BODY FORCES

In a fluid system the total intermolecular potential energy of the interacting molecules may be written in the following form:

$$U = \sum_{i<j}^N u(ij) + \sum_{i<j<k}^N u(ijk) + \dots \quad (19)$$

In the above equation  $u(ij)$  is the pair intermolecular potential energy between molecules  $i$  and  $j$ , and  $u(ijk)$  is the triplet intermolecular potential energy between molecules  $i$ ,  $j$  and  $k$ . It is shown<sup>6</sup> that the contribution of the triplet intermolecular interaction energy to the total intermolecular potential energy is of the order of 5 to 10%. However, higher order terms (four body interactions and higher) in Equation 19 are negligible. Moreover, when a third order quantum mechanical perturbation to the energy of interaction is carried out<sup>7,8</sup>, it can be shown that the leading term in the three-body interaction energy is the dipole-dipole-dipole term which is known as the Axilrod-Teller triple-dipole dispersion energy. The Axilrod-Teller potential is given by the following expression:

$$u(ijk) = \frac{\nu_{ijk}(1 + 3\cos\gamma_i \cos\gamma_j \cos\gamma_k)}{(r_{ij}r_{jk}r_{ik})^3} \quad (20)$$

where  $i$ ,  $j$  and  $k$  are the three molecules forming a triangle with sides  $r_{ij}$ ,  $r_{jk}$  and  $r_{ik}$  and interior angles  $\gamma_i$ ,  $\gamma_j$  and  $\gamma_k$ . For the evaluation of the triple-dipole constant  $\nu_{ijk}$  it is possible to show<sup>9</sup> that

$$\nu_{ijk} = \frac{3h}{\pi(4\pi\epsilon_0)^2} \int_0^\infty \alpha_i(i\omega) \alpha_j(i\omega) \alpha_k(i\omega) d\omega \quad (21)$$

where  $\alpha_i(i\omega)$  is the dipole polarizability of molecule  $i$  at the imaginary frequency  $i\omega$ ,  $h$  is the Planck constant and  $\epsilon_0$  is the vacuum permittivity. Several approximate expressions for the triple-dipole constant  $\nu_{ijk}$  have been proposed; however, the expression which is very often associated with the Axilrod-Teller potential function has the following form:

$$\nu_{ijk} \approx \frac{3}{2} \frac{(i_j + i_k) \alpha_i \alpha_j \alpha_k}{(i_j + i_k)(i_j + i_k)(i_j + i_k)} \quad (22)$$

where  $i_j$  is the first ionization potential and  $\alpha_i$  is the static polarizability of molecule  $i$ .

In Equation 20  $\nu_{ijk}$  will be a positive quantity, indicating repulsion, provided the molecules form an acute triangle, and it will be negative, indicating attraction, when the molecules form an obtuse triangle. Contribution of three-body effects to the Helmholtz free energy of a pure fluid using the statistical mechanical superposition approximation for the molecular radial distribution function is described by a Padé approximant<sup>6</sup>

$$A^{3b} = \frac{N\nu}{d^9} \frac{f_1(\eta)}{f_2(\eta)} \quad (23)$$

where

$$f_1(\eta) = 9.87749\eta^2 + 11.76739\eta^3 - 4.20030\eta^4 \quad (24)$$

$$f_2(\eta) = 1 - 1.12789\eta + 0.73166\eta^2 \quad (25)$$

$$\eta = (\pi/6)(nd^3/V) \quad (26)$$

in which  $N$  is the number of molecules in volume  $V$  and  $d$  is a hard core molecular diameter. As a result the following relation holds for the Helmholtz free energy of pure fluids:

$$A = A^{2b} + A^{3b} \quad (27)$$

where  $A^{2b}$  is the Helmholtz free energy due to pair intermolecular interactions, and  $A^{3b}$  is the Helmholtz free energy due to triplet intermolecular interactions.

Basic statistical mechanical equations of state which incorporate in their formulations the concept of pair intermolecular interactions can be used to derive the expression for the Helmholtz free energy

due to pair interactions  $A^{2b}$ . Then if we replace the resulting  $A^{2b}$  in Equation 27 will have an expression which can be used for realistic fluids<sup>10</sup>. However, for such equations of state the intermolecular potential energy parameters are not available for highly asymmetric compounds.

In extending Equation 27 to mixtures one can either use an exact mixture theory or a set of mixing rules. In a multicomponent mixture, in addition to binary interaction parameters there will be numerous three-body parameters  $\nu_{ijk}$ 's to be dealt with. For example, in a binary mixture, in addition to binary parameters, we will have four ternary parameters ( $\nu_{111}$ ,  $\nu_{112}$ ,  $\nu_{122}$  and  $\nu_{222}$ ) which are all different from each other. In a ternary mixture we will have the following ternary parameters ( $\nu_{111}, \dots, \nu_{123}, \dots,$  and  $\nu_{333}$ ) which add up to nine ternary parameters. The excessive number of interaction parameters and the lack of experimental data for these parameters demonstrate the difficulty which presently exist in the practical utilization of such statistical mechanical equation of state. As a result in the present report we are using the Peng-Robinson equation of state which is a fairly accurate empirical equation for thermodynamic property calculations of hydrocarbon mixtures. However, when an empirical equation of state is used for pure fluid it would be rather difficult to separate contributions of the two-body and three-body interactions into the equation of state.

An empirical equation of state is usually joined with a set of mixing and combining rules when its application is extended to mixtures. By a comparison of a mixture empirical equation of state with a statistical mechanical equation of state we can conclude that, for pure fluid and binary mixtures, an empirical equation of state can represent mixture properties correctly since the energy of interaction which is related to  $\nu_{112}$  and to  $\nu_{122}$  is accounted for by the empirical equation of state through the binary interaction parameters which are used in the combining rules. However, when we use a mixture equation of state which is based on the above concept of mixing rules for multicomponent mixtures (ternary and higher systems), there will be a deficiency in the mixture property representation. This deficiency is due to the lack of consideration of any unlike three-body interaction term in such empirical equations of state. This deficiency can be corrected by adding the contribution of the unlike three-body term, resulting from the Axilrod-Teller potential, to the empirical equation of state. Consequently for the Helmholtz free energy of a multicomponent mixture we can write

$$A_m^{3b} = A_m^e(a,b) + \sum_{i,j,k} \sum_{l} x_i x_j x_k A_{ijkl}^{3b}, \quad i \neq j \neq k \quad (28)$$

where

$$A_{ijk}^{3b} = \frac{N_{ijk}}{d^9} f_1(d) \quad (29)$$

in which  $d$  is the mixture average hard core molecular diameter, and  $A_m^e(a,b)$  is the Helmholtz free energy evaluated with the mixture empirical equation of state.

For example, for a binary mixture Equation 28 becomes

$$A_m = A_m^e(a,b) \quad m=2 \quad (30)$$

and for a ternary mixture we have

$$A_m = A_m^e(a,b) + x_1 x_2 x_3 A_{123}^{3b} \quad m=3 \quad (31)$$

while for a four component mixture Equation 28 would be

$$A_m = A_m^e(a,b) + x_1 x_2 x_3 A_{123}^{3b} + x_1 x_2 x_4 A_{124}^{3b} + x_1 x_3 x_4 A_{134}^{3b} + x_2 x_3 x_4 A_{234}^{3b} \quad m=4 \quad (32)$$

It is a proven fact that unlike three-body interaction terms are the major part of the three-body potential in multicomponent mixtures<sup>11</sup>. As a result the three-body correction terms in the above equations would make a substantial improvement specially in the region of equimolar mixture.

#### VAPORIZING GAS DRIVE AND MINIMUM MISCIBILITY PRESSURE

The vaporizing gas drive mechanism is a process used in enhanced oil recovery to achieve dynamic miscible displacement or multiple contact miscible displacement. Miscible displacement processes rely on multiple contact of injected gas and reservoir oil to develop an in-situ vaporization of intermediate molecular weight hydrocarbons from the reservoir oil into the injected gas and create a miscible transition zone<sup>12</sup>.

The miscible agents which are used in such a process may include natural gas, inert gases and carbon dioxide. Dynamic miscibility with CO<sub>2</sub> has a major advantage since it can be achieved at a lower pressure than with natural gas or inert gases.

For a given fluid system (crude oil and a miscible agent) and temperature, the minimum pressure at which miscibility can be achieved through multiple contacts is referred to as the minimum miscibility pressure. The minimum miscibility pressure can also be defined as the minimum pressure at which the critical tie line (tangent to the binodal curve at the critical point) passes through the point representing the oil composition (Figure 1). Dynamic miscibility can be achieved when the reservoir fluid lies to the right of the limiting tie line.

In evaluating a petroleum reservoir field for possible CO<sub>2</sub> or natural gas flooding certain data are required which can be measured in the laboratory. In the absence of measurements such information can be estimated from fundamentals and theoretical considerations. The required information include the MMP, PVT data, asphaltene precipitation, viscosity reduction, the swelling of crude oil. It is obvious that accurate predictions of PVT data and MMP have important consequences for the design of a miscible displacement process. In the following section a mathematical model is presented for the evaluation of the minimum miscibility pressure.

#### Mathematical Formulation of the MMP

The governing equations of the critical state of a three-component system<sup>13</sup> are given by the following determinant equations:

$$U = \begin{vmatrix} \frac{\partial^2 g}{\partial x_1^2} & \frac{\partial^2 g}{\partial x_1 \partial x_2} \\ \frac{\partial^2 g}{\partial x_1 \partial x_2} & \frac{\partial^2 g}{\partial x_2^2} \end{vmatrix} = 0 \quad (33)$$

$$V = \begin{vmatrix} \frac{\partial^2 g}{\partial x_1^2} & \frac{\partial^2 g}{\partial x_1 \partial x_2} \\ \frac{\partial U}{\partial x_1} & \frac{\partial U}{\partial x_2} \end{vmatrix} = 0 \quad (34)$$

where the partial derivatives of the molar Gibbs free energy  $g(P,T,x_i)$  are obtained at constant  $P$ ,  $T$  and  $x_3$ . When the above determinant equations are solved for the critical compositions, the tangent to the binodal curve at the critical point will be obtained as the following:

$$\frac{x_1^c - x_1}{x_2^c - x_2} = \frac{dP_n}{dx_2} \quad \text{at critical point} \quad (35)$$

where  $x_1^c$  and  $x_2^c$  are the critical compositions of the light and intermediate components, respectively.  $P_n$  is the interpolating polynomial of the binodal curve and the first derivative of the interpolating polynomial at the critical point is approximated by a central difference formula. It should be pointed out that a good estimate of the critical point of a mixture can be obtained from the coexisting curves and combined with Equation 35 to generate the critical tie line.

#### VAPOR-LIQUID EQUILIBRIUM CALCULATIONS

When applying a single equation of state to describe both liquid and vapor phases, the success of the vapor-liquid equilibrium predictions will depend on the accuracy of the equation of state and on the mixing rules which are used.

In the equilibrium state, the intensive properties - temperature, pressure and chemical potentials of each component - are constant in the overall system. Since the chemical potentials are functions of temperature, pressure and compositions, the equilibrium condition

$$\mu_i^V(T, P, \{y\}) = \mu_i^L(T, P, \{x\}) \quad i=1, 2, \dots, n \quad (36)$$

can be expressed by

$$y_i \phi_i^V = x_i \phi_i^L \quad i=1, 2, \dots, n \quad (37)$$

The expression for the fugacity coefficient  $\phi_i$  depends on the equation of state that is used and is the same for the vapor and liquid phases

$$RT \ln \phi_i = \int_V^{\infty} [(\partial P / \partial n_i)_{T, V, n_j} - (RT/V)] dV - RT \ln Z \quad (38)$$

With the use of the correct version of the van der Waals mixing rules, the following expression for the fugacity coefficient will be derived:

$$\begin{aligned} \ln \phi_i = & ((2 \sum x_j b_{ij} - b) / b) (Z-1) - \ln(Z-B) - (A / (2\sqrt{2} B)) \\ & ((2 \sum x_j c_{ij} + 2RT \sum x_j d_{ij} - 2\sqrt{2} (RT) (c \sum x_j d_{ij} \\ & + d \sum x_j c_{ij}) / \sqrt{cd}) / C - (2 \sum x_j b_{ij} - b) / b) \\ & (\ln((Z + (1+\sqrt{2})B) / (Z + (1-\sqrt{2})B))) \quad (39) \end{aligned}$$

where

$$\begin{aligned} A &= CP / (RT)^2 \\ B &= bP / RT \\ C &= c + RTd - 2\sqrt{cdRT} \end{aligned}$$

The original Peng-Robinson equation of state, Equation 4, was used in the derivation of Equation 39. However, with the implementation of the three body effects the mixture equation of state will be

$$P = (\delta A / \delta V)_{T, n} = P^e + x_1 x_2 x_3 \frac{\eta \beta}{b^3 v} \left( \frac{f_1' f_2 - f_1 f_2'}{f^2} \right) \quad (40)$$

where  $P^e$  is the expression for the empirical equation of state and

$$\beta = (8/27) \pi N_0^4 v_{123} \quad (41)$$

$$f_1' = (\delta f_1 / \delta \eta) = 19.75498\eta + 35.30217\eta^2 - 16.80120\eta^3 \quad (42)$$

$$f_2' = (\delta f_2 / \delta \eta) = -1.12789 + 1.46332\eta \quad (43)$$

The co-volume parameter,  $b$ , is related to  $\eta$  with the following relation:

$$\eta = (b/4v) \quad (44)$$

Now if we derive the fugacity coefficient from the integral form, Equation 38, and using Equation 40, we obtain for the PR equation of state with the original mixing rules the following expression:

$$\begin{aligned} \ln \phi_i = & (b_i/b) (P^e v - RT) / RT - \ln(P(v-b) / RT) \\ & - (a(2 \sum x_j a_{ij} / a - b_i/b) / (2\sqrt{2} bRT)) \\ & \ln((v + (1+\sqrt{2})b) / (v + (1-\sqrt{2})b)) \\ & + d(x_1 x_2 x_3 A_{123}^{3b}) / dn_i \quad (45) \end{aligned}$$

while the following expression is derived when the PR equation of state is used with the correct version of the van der Waals mixing rules:

$$\ln \phi_1 = ((2 \sum x_j b_{1j} - b) / b) (P^0 v / RT - 1) - \ln(P(v-b) / RT) \\ (c / (2\sqrt{2RTb})) ((2 \sum x_j c_{1j} + 2RT \sum x_j d_{1j} - 2\sqrt{RT}) \\ (c \sum x_j d_{1j} + d \sum x_j c_{1j}) / \sqrt{cd}) / C - (2 \sum x_j b_{1j} - b) / b \\ (\ln((v + (1+\sqrt{2})b) / (v + (1-\sqrt{2})b))) \\ + d (\sum x_2 x_3 A_{123}^{3b}) / dn_1 \quad (46)$$

With the aid of a computational algorithm Equations 37 through 46 are used to generate the binodal curves of binary and ternary systems as it is discussed below.

### RESULTS AND DISCUSSION

In the present calculations experimental binary vapor-liquid equilibrium data are used in the evaluation of the binary interaction parameters which minimize the following objective function:

$$OF = \sum_{i=1}^M \left[ \frac{P(\text{exp}) - P(\text{cal})}{P(\text{exp})} \right]^2_i \quad (47)$$

where  $M$  is the number of experimental data considered,  $P(\text{exp})$  and  $P(\text{cal})$  are the experimental and calculated bubble point pressures, respectively. A three parameter search routine is used to evaluate the binary interaction parameters of the correct version of the van der Waals mixing rules. The values of the binary interaction parameters of all the systems studied in this paper are reported in Table 1.

In Figure 2 the experimental and calculated results are compared for the methane-n-decane system which has a big influence on the prediction of the methane-n-butane-n-decane ternary system. In this case both mixing rules provide a good correlation of the experimental results; however, a bigger deviation, overprediction, is observed for the original mixing rules in the vicinity of the critical point. The carbon dioxide-n-decane system is illustrated in Figure 3 where we can see that the PR equation with the classical mixing rules fails to properly correlate the VLE data in all ranges of pressures and compositions while an excellent correlation is obtained with the correct mixing rules.

For asymmetric mixtures it has been shown that PR equation of state could not represent the sharp changes of slopes near the mixture critical region. This same problem can be also observed in a simple ternary mixture of methane-ethane-propane<sup>16</sup> as it is demonstrated in Figure 4. However, by incorporating the three-body effects it is shown in

this figure that the deviation of the PR equation around the critical point is substantially corrected. Figure 5 shows the phase behavior of the methane-n-butane-n-decane system<sup>17</sup>. Since the value of the triple-dipole constant  $\nu_{123}$  is obtained from an approximate expression, an adjustable parameter,  $\epsilon$ , is introduced in Equation 23 as the following:

$$\nu_{ijk} \approx \epsilon \frac{3}{2} \frac{(i+j+k) i_j j_l k \alpha_i \alpha_j \alpha_k}{(i+j)(j+k)(i+k)} \quad (48)$$

In this equation,  $\epsilon$  is adjusted to provide the best correlation possible of the ternary system. In Figure 5 the value of  $\epsilon$  is found to be equal to 0.5. The carbon dioxide-n-butane-n-decane system<sup>18</sup> is shown in Figure 6 where the phase behavior prediction with the correct version of the van der Waals mixing rule is clearly superior than with the classical mixing rules. The chain-dotted line is for the PR equation with the correct mixing rules and including the three-body effects with  $\epsilon=1$ . Figure 7 illustrates the contribution of the three-body effects on the phase behavior prediction of the ternary system in the vicinity of the critical region which is very important for the prediction of the MMP. The PR equation with the classical mixing rules and including the three body-effects with  $\epsilon=0.5$  is represented by the solid lines while the PR equation with the same mixing rules but without the three-body effects overpredicts the MMP, dashed lines. It should be pointed out that in this case the critical point is evaluated from the coexisting curves and the binodal curve is approximated with a quadratic polynomial around the critical point. In Figure 8 the critical point is obtained from Equations 29 and 30 and the quadratic polynomial around the critical point is obtained with two additional points from the binodal curve. In this case we also observe an overprediction of the MMP from the PR equation and the classical mixing rules.

### CONCLUSION

As a conclusion the following may be pointed out:

(i) For a successful prediction of phase behavior of ternary and multicomponent systems, we must first be able to correlate binary data of species constituting the mixture correctly. In the present report this has been achieved by utilizing the correct version of the van der Waals mixing rules for the PR equation of state. As a result, the binary VLE data are correlated with an accuracy which was not achieved previously with the PR equation.

(ii) To improve prediction of the phase behavior

of ternary and multicomponent mixtures around the critical region it is necessary to incorporate the three-body effects in the equation of state calculation. The contribution of the three-body effects around the critical point must not be confused with the "critical phenomena" effect<sup>19</sup>. Deviations of the PR equation of state from experimental data of ternary systems around the critical point are generally much bigger than what the "non-classical" effect due to "critical phenomena" can cause. The authors have demonstrated that a large portion of this deviation can be corrected by incorporating the unlike-three-body effects in the phase behavior calculations. In most instances studied the non-classical contribution is so small that for the scale of the graphs and the accuracy of the available experimental data it is insignificant.

(iii) The utilization of the concept of statistical thermodynamics of multicomponent mixtures has provided us with a strong tool of improving the correlation and predictive capabilities of the existing empirical engineering thermodynamic models.

(iv) The ternary mixture computational technique presented here based on the incorporation of the corrected version of the van der Waals mixing rules and the three-body effects can be readily extended to multicomponent calculations. The authors have developed a number of computer packages which are capable of performing such calculations. In the forthcoming publications results of such calculations for multicomponent systems will be also reported.

#### NOMENCLATURE

$\xi$  = Binary interaction parameter

$\eta$  = Reduced density

$\mu$  = Chemical potential

$\omega$  = Acentric factor

P = Pressure

R = Universal gas constant

r = Intermolecular distance

T = Temperature

v = Molar volume

x = Mole fraction

Z = Compressibility factor

Superscripts or subscripts

c = Critical state

i = Component identification

L = Liquid state

m = Mixture property

r = Reduced property

V = Vapor state

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Table 1. Values of binary interaction parameters for the different mixing rules.

System	Reference	Temperature (Kelvin)	Pressure Range (bars)	Binary Interactions Parameters			
				Correct Mixing Rules			Original Mixing Rules
				$k_{12}$	$l_{12}$	$m_{12}$	$\xi_{12}$
Methane - n-Butane	[14]	344.26	10-103	-0.0492	-0.0848	-0.0178	0.0139
Methane - n-Decane	[14]	344.26	1-120	0.0691	-0.6300	-0.0824	0.0440
n-Butane - n-Decane	[14]	344.26	1-9	0.0846	0.0195	-0.0261	0.0100
Carbon Dioxide- n-Butane	[14]	344.26	11-66	0.0087	-0.0957	0.0008	0.1351
Carbon Dioxide- n-Decane	[15]	344.26	13-128	0.2054	-0.0650	-0.0792	0.1075

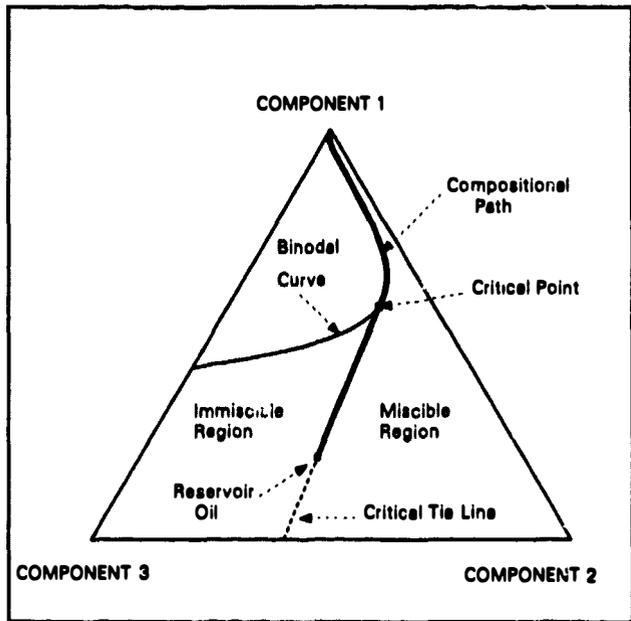


Fig. 1—Vaporizing gas-drive miscibility/mmp.

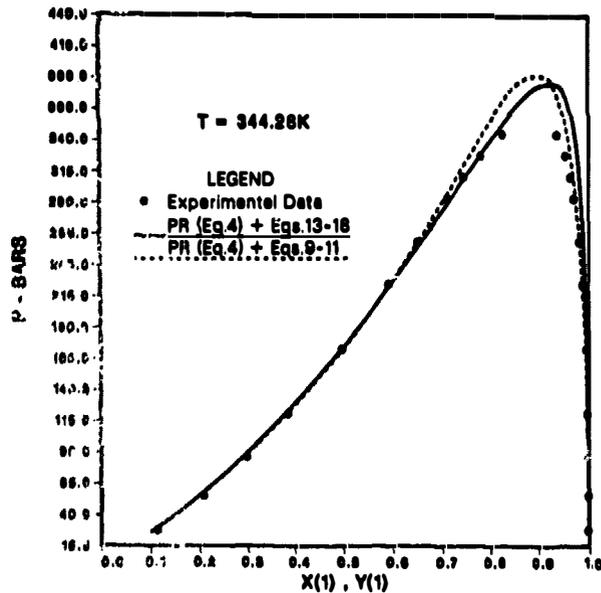


Fig. 2—Equilibrium pressure-composition diagram for  $\text{CH}_4\text{-n-C}_{10}\text{H}_{22}$ .

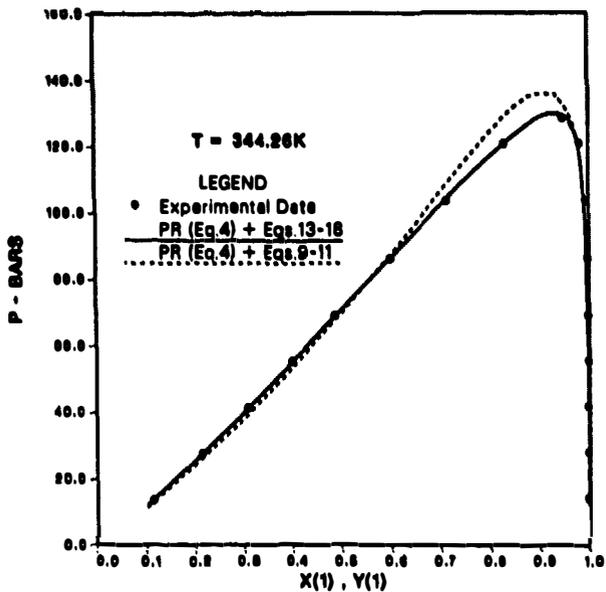


Fig. 3—Equilibrium pressure-composition diagram for  $\text{CO}_2\text{-n-C}_{10}\text{H}_{22}$ .

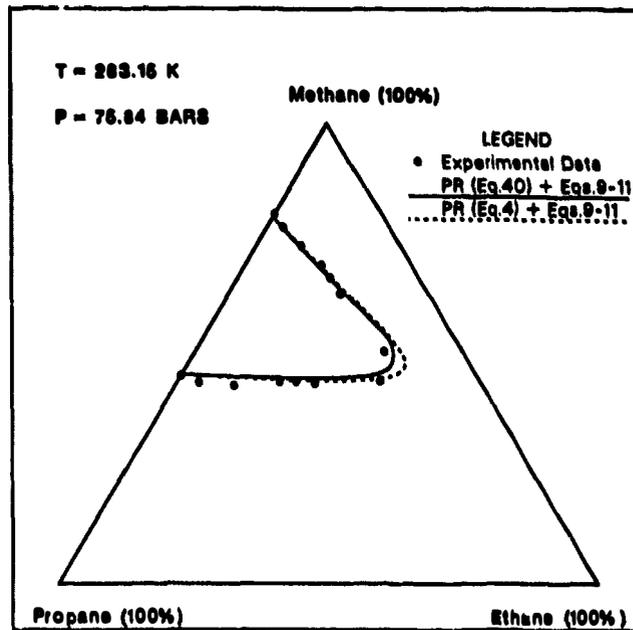


Fig. 4—Vapor-liquid equilibrium composition diagram for  $\text{CH}_4\text{-C}_2\text{H}_6\text{-C}_3\text{H}_8$ .

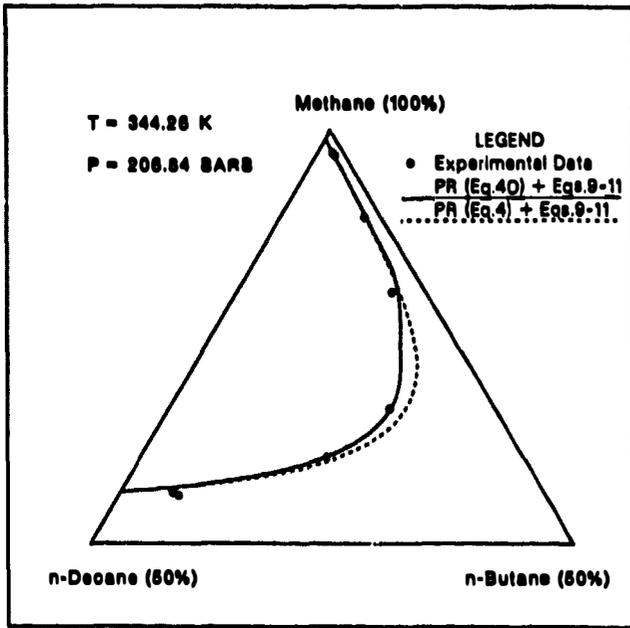


Fig. 6—Vapor-liquid equilibrium composition diagram for  $CH_4$ - $n-C_4H_{10}$ - $n-C_{10}H_{22}$ .

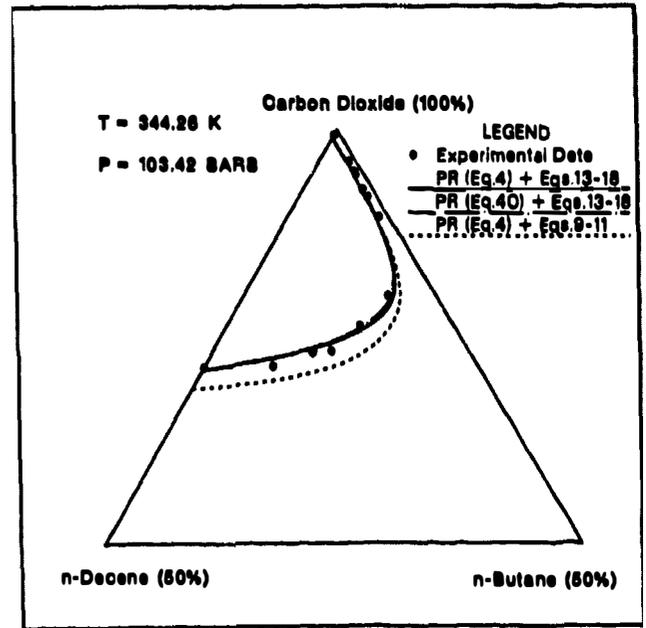


Fig. 6—Vapor-liquid equilibrium composition diagram for  $CO_2$ - $n-C_4H_{10}$ - $n-C_{10}H_{22}$ .

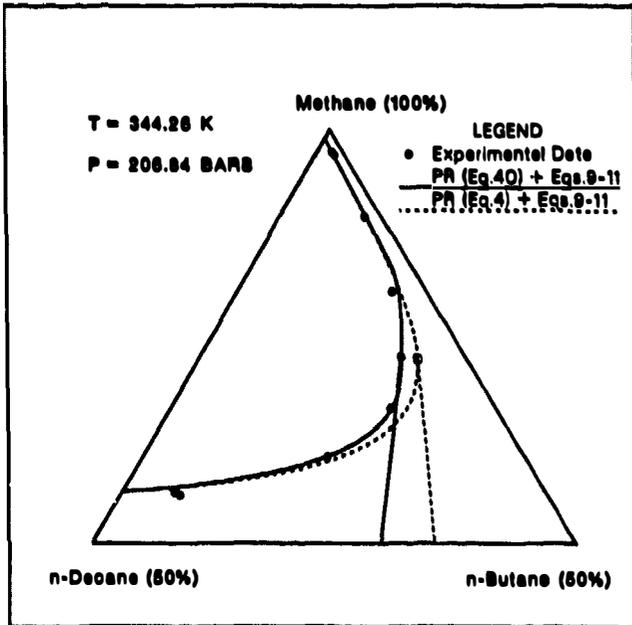


Fig. 7—Phase behavior and critical tie lines of  $CH_4$ - $n-C_4H_{10}$ - $n-C_{10}H_{22}$ .

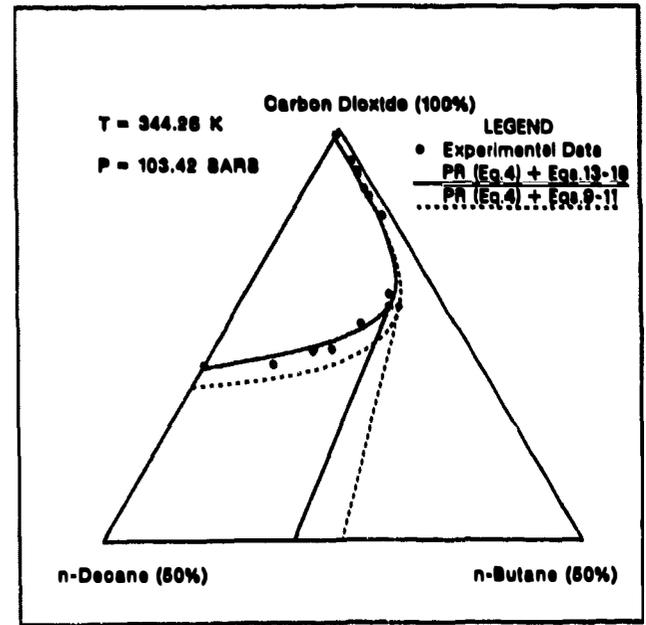


Fig. 8—Phase behavior and critical tie lines of  $CO_2$ - $n-C_4H_{10}$ - $n-C_{10}H_{22}$ .