

Minimum Miscibility Pressure Prediction With Equations of State

El-Houri Benmekki and G.Ali Mansoori, SPE, U. of Illinois at Chicago

Summary. Prediction of the minimum miscibility pressure (MMP) of the vaporizing gas drive (VGD) process is modeled by use of an equation of state (EOS) 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 EOS alone overestimates the MMP. When the EOS is joined with the correct version of the van der Waals mixing rules and the unlike three-body interaction term, however, the MMP will be predicted accurately.

Introduction

The ternary or pseudoternary diagram is a useful way to visualize the development of miscible displacement in EOR. 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 a diagram is called a pseudoternary diagram.

The scope of this paper involves the use of the Peng-Robinson (PR) EOS, along with coherent mixing and combining rules derived from statistical mechanical considerations. Also discussed is the implementation of the three-body effects in the evaluation of the phase behavior of ternary systems and in the prediction of the MMP 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 CO₂/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 that fall within the range of the majority of oil reservoirs.

The usefulness of the PR EOS has been tested^{1,2} with limited success in predicting the phase behavior and MMP's of simulated reservoir fluids. With the PR EOS, an overprediction of the MMP of the methane/n-butane/n-decane system was observed and it was believed to be the result of 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 CO₂/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.

van der Waals Mixing Rules

It can be shown from the conformal solution theory of statistical mechanics that the 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:

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

where

- u_o = potential energy function of reference pure fluid,
- f_{ij} = conformal molecular energy parameter, and
- $h_{ij}^{1/3}$ = conformal molecular length parameter of interactions between Molecules i and j of mixture.

By use of Eq. 1 in the statistical, mechanical, virial, or energy EOS, and in the application of the conformal solution approximation to

the radial distribution functions of components of a mixture,³ it can be shown that

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

and

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

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

As an example, the PR⁴ EOS, which has received wide acceptance in process engineering calculations, is chosen in this investigation to perform vapor/liquid equilibrium calculations.

In the PR EOS,

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}, \quad (4)$$

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

$$a = \sum_i^n \sum_j^n x_i x_j a_{ij}, \quad (5)$$

$$b = \sum_i^n x_i b_i, \quad (6)$$

and

$$a_{ij} = (1 - \xi_{ij})(a_{ii} a_{jj})^{1/2}. \quad (7)$$

To apply the van der Waals mixing rules correctly in the PR EOS, we must separate thermodynamic variables from constants of the EOS. Thus, we can write the PR EOS in the following form:

$$z = \frac{V}{V-b} - \frac{c/RT + d - 2\sqrt{cd/RT}}{(V+b) + (b/V)(V-b)}, \quad (8)$$

This new form indicates that this EOS has three independent constants, b , c , and d . Parameters b and d are proportional to (molecular length)³, or $b \propto h$ and $d \propto h$, while parameter c is proportional to (molecular length)³ × (molecular energy), or $c \propto fh$. Thus, the mixing rules for c , b , and d will be

$$c = \sum_i^n \sum_j^n x_i x_j c_{ij}, \dots \dots \dots (9)$$

$$b = \sum_i^n \sum_j^n x_i x_j b_{ij}, \dots \dots \dots (10)$$

and

$$d = \sum_i^n \sum_j^n x_i x_j d_{ij}, \dots \dots \dots (11)$$

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

$$b_{ij} = (1 - l_{ij})^3 \left(\frac{b_{ii}^{1/3} + b_{jj}^{1/3}}{2} \right)^3, \dots \dots \dots (12)$$

$$d_{ij} = (1 - m_{ij})^3 \left(\frac{d_{ii}^{1/3} + d_{jj}^{1/3}}{2} \right)^3, \dots \dots \dots (13)$$

and

$$c_{ij} = (1 - k_{ij})(c_{ii}c_{jj}) / (b_{ii}b_{jj})^{1/2} b_{ij}, \dots \dots \dots (14)$$

In Eqs. 12 through 14, 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. 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:

$$U = \sum_{i < j}^N u(ij) + \sum_{i < j < k}^N u(ijk) + \dots, \dots \dots (15)$$

where $u(ij)$ 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 shown⁵ that the contribution of the triplet intermolecular interaction energy to the total intermolecular potential energy is on the order of 5 to 10%. However, higher-order terms (four-body interactions and higher) in Eq. 15 are negligible. Moreover, when a third-order quantum mechanical perturbation to the energy of interaction is carried out,^{6,7} 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

$$u(ijk) = \frac{\nu_{ijk}(1 + 3 \cos \gamma_i \cos \gamma_j \cos \gamma_k)}{(r_{ij}r_{jk}r_{ik})^3}, \dots \dots \dots (16)$$

where i , j , and k are the three molecules that form a triangle with sides r_{ij} , r_{jk} , and r_{ik} and interior angles γ_i , γ_j , and γ_k . For the evaluation of the triple-dipole constant ν_{ijk} it is possible to show⁸ that

$$\nu_{ijk} = \frac{3h}{\pi(4\pi\epsilon_0)^2} \int_0^\infty \alpha_i(i\omega)\alpha_j(i\omega)\alpha_k(i\omega)d\omega, \dots \dots \dots (17)$$

where

$\alpha_i(i\omega)$ = dipole polarizability of Molecule i at the imaginary frequency, $i\omega$,

h = Planck constant, and

ϵ_0 = vacuum permittivity.

Several approximate expressions for ν_{ijk} have been proposed however, the expression often associated with the Axilrod-Teller potential function has the following form:

$$\nu_{ijk} \approx \frac{3(I_i + I_j + I_k)I_i I_j I_k \alpha_i \alpha_j \alpha_k}{2(I_i + I_j)(I_j + I_k)(I_i + I_k)}, \dots \dots \dots (18)$$

where I_i is the first ionization potential and α_i is the static polarizability of Molecule i .

In Eq. 16, u_{ijk} will be a positive quantity (indicating repulsion) provided that the molecules form an acute triangle; 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 approximant⁶:

$$A^{3b} = \frac{N\nu f_1(\rho_r)}{d^9 f_2(\rho_r)}, \dots \dots \dots (19)$$

where

$$f_1(\rho_r) = 9.87749\rho_r^2 + 11.76739\rho_r^3 - 4.20030\rho_r^4, \dots \dots (20)$$

$$f_2(\rho_r) = 1 - 1.12789\rho_r + 0.73166\rho_r^2, \dots \dots \dots (21)$$

and

$$\rho_r = (\pi/6)(nd^3/V), \dots \dots \dots (22)$$

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:

$$A = A^{2b} + A^{3b}, \dots \dots \dots (23)$$

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

An empirical EOS is usually joined with a set of mixing and combining rules when its application is extended to mixtures. By comparing a mixture empirical EOS with a statistical mechanical EOS, we can conclude that for pure fluid and binary mixtures an empirical EOS can represent mixture properties correctly because the energy of interaction related to ν_{112} and ν_{122} is accounted for by the empirical EOS through the binary interaction parameters used in the combining rules. When we use a mixture EOS, however, that 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 caused by lack of consideration of any unlike three-body interaction term in such empirical EOS. This deficiency can be corrected by adding the contribution of the unlike three-body term resulting from the Axilrod-Teller potential to the empirical EOS. Consequently, for the Helmholtz free energy of a multicomponent mixture we can write

$$A_e = A_m^e(a, b) + \sum_i^n \sum_j^n \sum_k^n x_i x_j x_k A_{ijk}^{3b}, \quad i \neq j \neq k, \dots \dots \dots (24)$$

where

$$A_{ijk}^{3b} = \frac{N\nu_{ijk} f_1(d)}{d^9 f_2(d)}, \dots \dots \dots (25)$$

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 EOS.

Vaporizing Gas Drive and MMP

The vaporizing-gas-drive mechanism is a process used in EOR 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 thus to create a miscible transition zone.⁹

The miscible agents used in such a process may include natural gas, inert gases, and CO₂. Dynamic miscibility with CO₂ has a major advantage because it can be achieved at a lower pressure than with natural 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 MMP. The MMP 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 (Fig. 1). Dynamic miscibility can be achieved when the reservoir fluid lies to the right of the limiting tie-line.

In the evaluation of a petroleum reservoir field for possible CO₂ or natural gas flooding, certain data are required that can be measured in the laboratory. In the absence of measurements, such information can be estimated from fundamentals and theoretical considerations. The required information includes the MMP, PVT data, asphaltene precipitation, viscosity reduction, and 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. A mathematical model is presented for the evaluation of the MMP.

Evaluation of the Critical Tie-Line. The governing equations of the critical state of a three-component system¹⁰ are given by the following determinant equations:

$$D1 = \begin{vmatrix} \delta g^2 / \delta x_1^2 & \delta g^2 / (\delta x_1 \delta x_2) \\ \delta g^2 / (\delta x_1 \delta x_2) & \delta g^2 / \delta x_2^2 \end{vmatrix} = 0 \quad \dots \dots \dots (26)$$

and

$$D2 = \begin{vmatrix} \delta g^2 / \delta x_1^2 & \delta g^2 / (\delta x_1 \delta x_2) \\ \delta D1 / \delta x_1 & \delta D1 / \delta x_2 \end{vmatrix} = 0, \quad \dots \dots \dots (27)$$

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:

$$\frac{x_1^c - x_1}{x_2^c - x_2} = \frac{dP_n}{dx_2} \quad \dots \dots \dots (28)$$

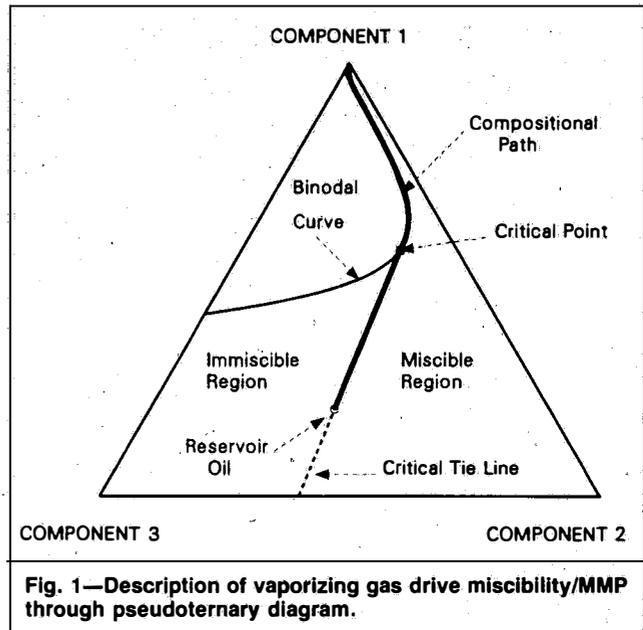


Fig. 1—Description of vaporizing gas drive miscibility/MMP through pseudoternary diagram.

at the critical point, 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 Eq. 28 to generate the critical tie-line.

Phase-Behavior Calculations

The expression for the fugacity coefficient, ϕ_i , depends on the EOS used and is the same for the vapor and liquid phases:

$$RT \ln \phi_i = \int_V^\infty [(\partial p / \partial n_i)_{T, V, n_j} - (RT/V)] dV - RT \ln z. \quad \dots \dots (29)$$

With the implementation of the three-body effects, the mixture EOS will be

$$p = (\delta A / \delta V)_{T, n} = p^e + x_1 x_2 x_3 \frac{\rho_r \beta}{b^3 V} \left(\frac{f'_1 f'_2 - f_1 f'_2}{f^2} \right), \quad \dots \dots \dots (30)$$

where p^e is the empirical EOS,

$$\beta = (8/27) \pi N_{Av}^4 v_{123}, \quad \dots \dots \dots (31)$$

$$f'_1 = (\delta f_1 / \delta \rho_r) = 19.75498 \rho_r + 35.30217 \rho_r^2 - 16.80120 \rho_r^3, \quad \dots \dots \dots (32)$$

and

$$f'_2 = (\delta f_2 / \delta \rho_r) = -1.12789 + 1.46332 \rho_r, \quad \dots \dots \dots (33)$$

TABLE 1—VALUES OF BINARY INTERACTION PARAMETERS FOR THE DIFFERENT MIXING RULES

System	Reference	Temperature (K)	Pressure Range (bars)	Binary Interaction Parameters			
				Correct Mixing Rules			Original Mixing Rules
				k_{12}	l_{12}	m_{12}	ξ_{12}
Methane/n-Butane	11	344.26	10 to 103	-0.0492	-0.0848	-0.0178	0.0139
Methane/n-Decane	11	344.26	1 to 120	0.0691	-0.6300	-0.0824	0.0440
n-Butane/n-Decane	11	344.26	1 to 9	0.0846	0.0195	-0.0261	0.0100
CO ₂ /n-Butane	11	344.26	11 to 66	0.0087	-0.0957	0.0008	0.1351
CO ₂ /n-Decane	12	344.26	13 to 128	0.2054	-0.0650	-0.0792	0.1075

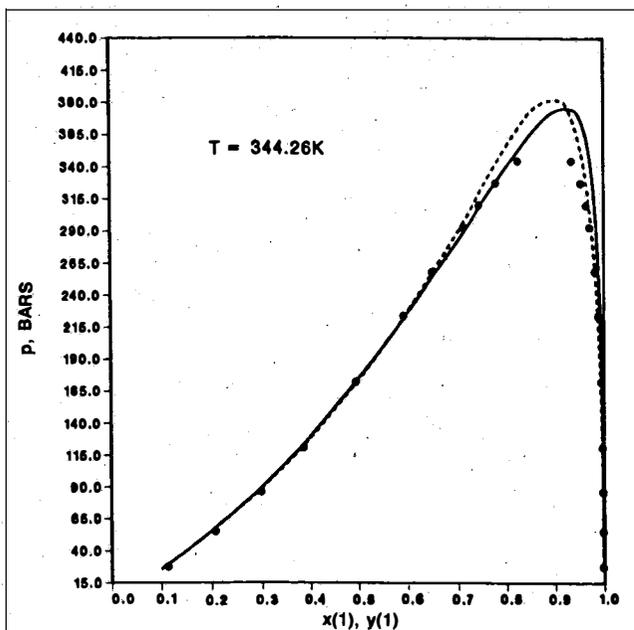


Fig. 2—Prediction of equilibrium pressure/composition diagram for $\text{CH}_4/\text{nC}_{10}\text{H}_{22}$ and comparison with experimental data. Dashed line represents calculations with the original mixing rules; solid line represents calculations with the present mixing rules; dots represent experimental data.¹¹

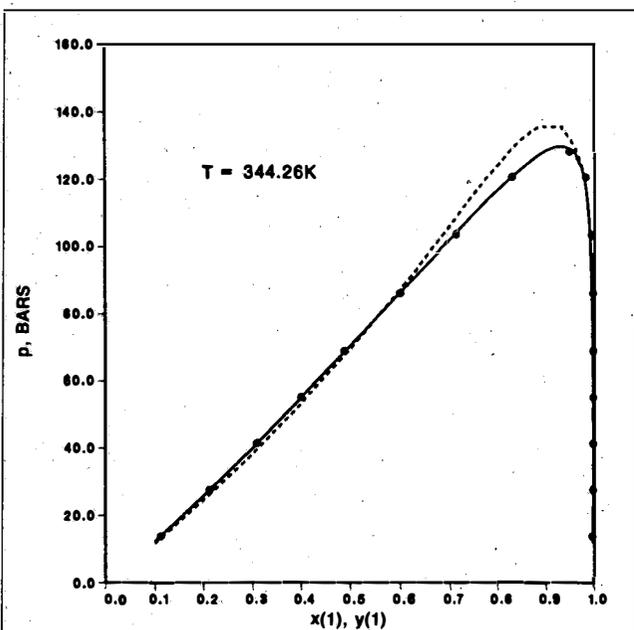


Fig. 3—Prediction of equilibrium pressure/composition diagram for $\text{CO}_2/\text{nC}_{10}\text{H}_{22}$ and comparison with experimental data. Dashed line represents calculations with the original mixing rules; solid line represents calculations with the present mixing rules; dots represent experimental data.¹¹

In Eq. 30, N_{Av} is the Avogadro number.

The covolume parameter b is related to ρ_r with the following relation:

$$\rho_r = (b/4V) \dots \dots \dots (34)$$

Results and Discussion

In these calculations, experimental binary vapor/liquid equilibrium data are used in the evaluation of the binary interaction parameters

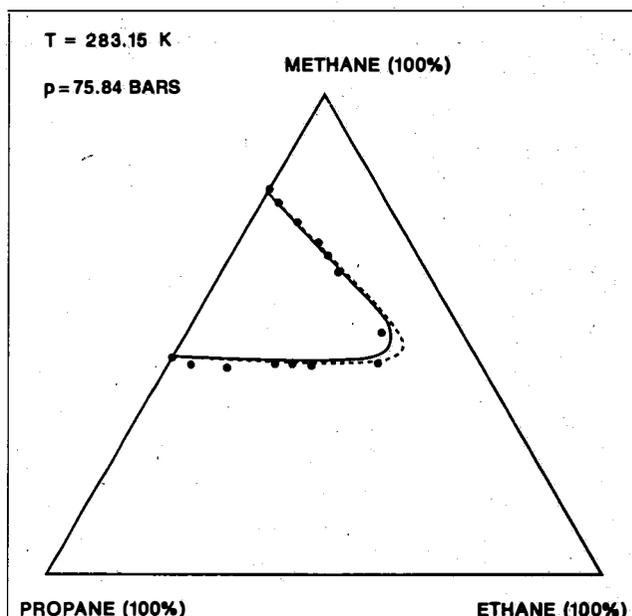


Fig. 4—Prediction of equilibrium pressure-composition diagram for $\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ and comparison with experimental data. Dashed line represents calculations with original mixing rules; solid line represents calculations with the present mixing rules; dots represent experimental data.¹³

that minimize the following objective function:

$$OF = \sum_{i=1}^M \left(\frac{p_{\text{exp}} - p_{\text{cal}}}{p_{\text{exp}}} \right)^2 \dots \dots \dots (35)$$

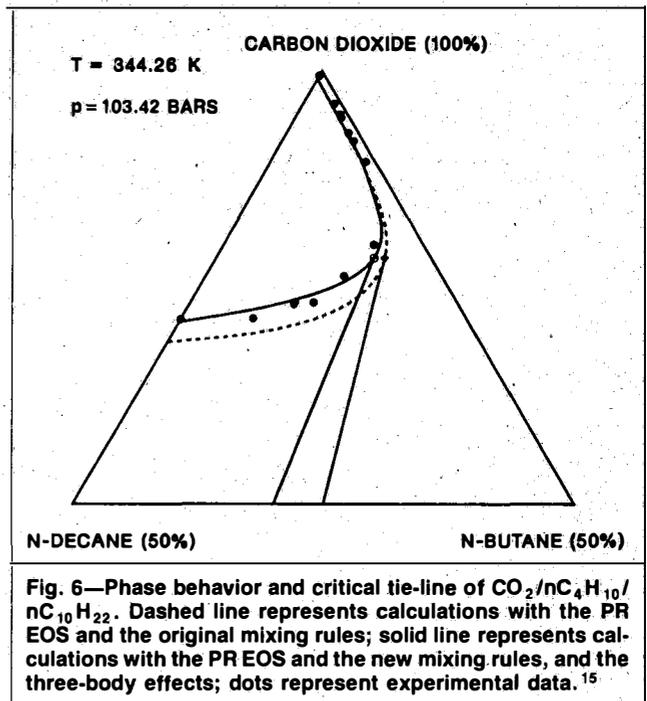
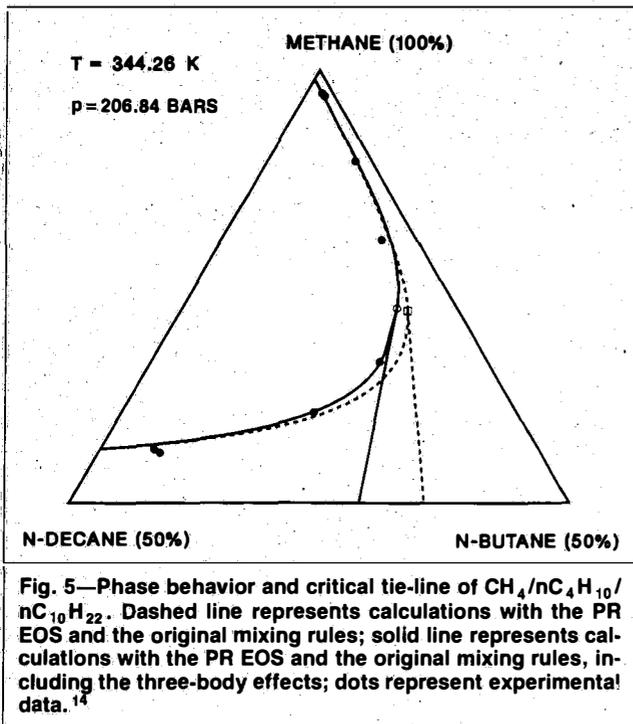
where M is the number of experimental data considered, and p_{exp} and p_{cal} are the experimental and calculated bubblepoint pressures, respectively. A three-parameter search routine is used to evaluate the binary interaction parameters of the correct version of the van der Waals mixing rules. The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

The experimental and calculated results in Fig. 2 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 $\text{CO}_2/\text{n-decane}$ system is illustrated in Fig. 3, where we can see that the PR equation with the classic mixing rules fails to correlate the VLE data properly 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 the PR EOS could not represent the sharp slope changes near the mixture critical region. This problem can also be observed in a simple ternary mixture of methane/ethane/propane, as demonstrated in Fig. 4. When the three-body effects are incorporated, however, this figure shows that the deviation of the PR equation around the critical point is substantially corrected. Because the value of the triple-dipole constant ν_{123} is obtained from an approximate expression, an adjustable parameter, ϵ , is introduced in Eq. 18 as

$$\nu_{ijk} = \epsilon \frac{3(I_i + I_j + I_k)I_i I_j I_k \alpha_i \alpha_j \alpha_k}{2(I_i + I_j)(I_j + I_k)(I_i + I_k)} \dots \dots \dots (36)$$

where ϵ is adjusted to provide the best correlation possible of the ternary system. Fig. 5 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 MMP. The PR equation with the classic 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 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. The value of ϵ is found to be equal to 1.0 for the CO₂/nC₄H₁₀/nC₁₀H₂₂ system. In Fig. 6, the critical point is obtained from Eqs. 26 and 27, 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 from the classic mixing rules.

Conclusions

1. For 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. This has been achieved here by using the correct version of the van der Waals mixing rules for the PR EOS. As a result, the binary vapor/liquid equilibrium data are correlated with an accuracy that was not achieved previously with the PR equation.
2. 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 EOS calculation. The contribution of the three-body effects around the critical point must not be confused with the "critical phenomena" effect.¹⁶ Deviations of the PR EOS from experimental data of ternary systems around the critical point are generally much bigger than what the "nonclassical" effect resulting from "critical phenomena" can cause.
3. Use of the concept of statistical thermodynamics of multicomponent mixtures has provided us with a strong tool for improving the correlation and predictive capabilities of the existing empirical engineering thermodynamic models.

Nomenclature

- a, b, c, d* = parameters
A = Helmholtz free energy from intermolecular interaction
d = molecular diameter
D = determinate equation
f_{ij} = conformal molecular energy parameter

- f_x* = conformal solution parameter of a hypothetical pure fluid
g = Gibb's free energy
h = Planck constant
h_{ij} = conformal molecular length parameter
h_x = conformal solution parameters of a hypothetical pure fluid
I = ionization potential
M = number of experimental data
N = number of molecules in volume
p = pressure
p^e = empirical EOS
p_{exp} = experimental bubblepoint pressure
p_{cal} = calculated bubblepoint pressure
P_n = interpolating polynomial at the critical point
r = intermolecular distance
R = universal gas constant
T = temperature
u_{ij} = pair intermolecular potential energy
u_o = potential energy function of the reference pure fluid
U = total intermolecular potential energy
V = molar volume
x = mole fraction, liquid phase
y = mole fraction, vapor phase
z = compressibility factor
 α = static polarizability
 γ = interior angle of triangle formed by three molecules
 ϵ_0 = vacuum permittivity
 κ = parameter of PR EOS
 ν = triple dipole constant
 ξ = binary interaction parameter
 ρ = density
 ρ_r = reduced density
 ϕ_i = fugacity coefficient

Subscripts

- i, j, k* = component identification
m = mixture property
r = reduced property

Superscripts

- c = critical state
 e = empirical correlation

Acknowledgments

We are indebted to Abbas Firoozabadi of Stanford U. for his advice during the preparation of this work. This research is supported by the Gas Research Inst., Contract No. 5086-260-1244.

References

1. Kuan, D.Y. *et al.*: "Multicomponent Carbon Dioxide/Water/Hydrocarbon Phase Behavior Modeling: A Comparative Study," *SPE* (Jan. 1986) 61-72.
2. Firoozabadi, A. and Aziz, K.: "Analysis and Correlation of Nitrogen and Lean Gas Miscibility Pressure," *SPE* (Aug. 1986) 100-10.
3. Mansoori, G.A.: "Mixing Rules for Cubic Equations of State," ACS Symposium Series (1986) No. 300, 314-30.
4. Peng, D.Y. and Robinson, D.B.: "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fund.* (1976) 15, 59-64.
5. Barker, J.A., Henderson, D., and Smith, W.R.: "Three Body Forces in Dense Systems," *Physical Review Letters* (1968) 21, 134-36.
6. Axilrod, B.M. and Teller, E.: "Interaction of the van der Waals Type Between Three Atoms," *J. Chem. Phys.* (1943) 11, 299-300.
7. Axilrod, B.M.: "Triple-Dipole Interaction. I. Theory," *J. Chem. Phys.* (1951) 19, 719-29.
8. Maitland, G.C. *et al.*: *Intermolecular Forces*, Clarendon Press, Oxford (1981) Chap. 2.
9. Stalkup, F.I.: *Miscible Displacement*, Monograph Series, SPE, Richardson, TX (1984) 8, 127-36.
10. Peng, D.Y. and Robinson, D.B.: "A Rigorous Method for Predicting the Critical Properties of Multicomponent Systems from an Equation of State," *AIChE J.* (1977) 23, 137-44.
11. Sage, B.H. and Lacey, W.N.: *Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide and Carbon Dioxide*, API, New York City (1955).
12. Reamer, H.H. and Sage, B.H.: "Phase Equilibrium in Hydrocarbon Systems. Volumetric and Phase Behavior of the n-Decane-Carbon Dioxide System," *J. Chem. Eng. Data* (1963) 8, 508-13.
13. Price, A.R. and Kobayashi, R.: "Low Temperature Vapor-Liquid Equilibrium in Light Hydrocarbon Mixtures: Methane-Ethane-Propane System," *J. Chem. Eng. Data* (1959) 4, 40-52.
14. Reamer, H.H., Fiskin, J.M., and Sage, B.H.: "Phase Equilibria in Hydrocarbon Systems: Phase Behavior in the Methane-n-Butane-n-Decane System," *Ind. Eng. Chem.* (1949) 41, 2871-75.
15. Metcalfe, R.S. and Yarborough, L.: "The Effect of Phase Equilibria on the CO₂ Displacement Mechanism," *SPE* (Aug. 1979) 242-52.
16. Hahne, F.J.N.: *Critical Phenomena*, Springer-Verlag, Berlin, Heidelberg (1983).

SI Metric Conversion Factors

$$\begin{array}{lcl} \text{bar} \times 1.0^* & \text{E}+05 & = \text{Pa} \\ ^\circ\text{R} \times 5/9 & & = \text{K} \end{array}$$

*Conversion factor is exact.

SPE

Original SPE manuscript received for review Oct. 5, 1986. Paper accepted for publication June 8, 1987. Revised manuscript received Oct. 5, 1987. Paper (SPE 15677) first presented at the 1986 SPE Annual Technical Conference and Exhibition held in New Orleans, Oct. 5-8.