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Predicting Retrograde Phenomena and Miscibility Using Equation of State

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ABSTRACT

While the knowledge about the retrograde condensation and condensing-gas drive phenomena is not new their utilization in production-stimulation and simulation of the natural gas and NGL reservoirs has been delayed due to the lack of accurate predictive computer algorithms. In this report the groundwork for accurate computation and prediction of the behavior of reservoir fluids under retrograde condensation and in condensing-gas-drive conditions are presented. It is shown that through equations of state one can predict the following properties of the reservoir fluid systems:

- (i) The minimum miscibility conditions and solubilities of intermediate and heavy hydrocarbons in miscible solvents.
- (ii) The effect of mixed miscible solvents and entrainers on lowering the minimum miscibility pressure of heavy components of reservoir fluids.
- (iii) The role of variations in temperature, pressure, and solvent composition on the miscibility and solubilities.
- (iv) Flash (dew point and bubble point) calculation for complex reservoir fluids in VLE and VLLE cases.

INTRODUCTION

Retrograde condensation and condensing-gas-drive phenomena have important applications in NGL production and processing¹⁻⁴. The knowledge about retrograde condensation and condensing-gas drive is not new. However, the application of this knowledge has been delayed due to the lack of accurate predictive equations of state. Recently under a contract with the Gas Research Institute the groundwork for accurate prediction of the behavior of reservoir fluids under retrograde condensation and in condensing-gas-drive conditions are developed at the University of Illinois at Chicago⁴⁻¹². It is shown that by using

equations of state it is possible to calculate accurately the minimum miscibility conditions and solubility of heavy and intermediate hydrocarbons in miscible solvents (gases and gaseous mixtures) and phase behavior (dew point and bubble point in VLE and VLLE cases) of complex reservoir fluids. The basis of these developments lie in statistical mechanical mixing rules and the conformal solution theory of polar fluid mixtures.

RETROGRADE PHENOMENA: Retrograde condensation has important applications in enhanced oil and gas recovery, industrial separation of chemical compounds, and processing of fossil fuels^{1,4,13}. The phenomena was first recognized in 1879 by Hannay and Hogarth^{1,14}. They discovered that solid compounds could be dissolved in dens gases having densities near that of a liquid. The interest in this process is because of the appreciable increase in solvent power of dens fluids at temperatures and pressures above, but not far removed from, their critical point. A dens gas can be an effective solvent for a condensed compound (solute) which remains in the condensed state (liquid or solid) at the supercritical conditions of the solvent. This requires a large molecular weight and size difference between the dens gas solvent and the condensed solute. Thermodynamic modeling and prediction of solubilities of heavy solutes in dens gas solvents has been hampered due to the lack of thermodynamic models of asymmetric mixtures.

MINIMUM MISCIBILITY CONDITION: The vaporizing gas drive is used in enhanced oil and gas condensate recovery to achieve dynamic miscible displacement or multiple contact miscible displacement³. Miscible displacement relies on multiple contact of injected gas and reservoir fluid to develop an in-situ vaporization of intermediate molecular weight hydrocarbons from the reservoir fluid into the injected gas and create a miscible transition zone⁴. The miscible cases which are used in such a process may include natural gas, inert gases, and carbon dioxide. For a given reservoir fluid and a miscible agent system at a given temperature, the minimum pressure at which miscibility can be achieved through multiple contact is referred to as the minimum miscibility pressure (MMP).

References and figures at end of paper.

THERMODYNAMIC MODELING

In order to describe and model the retrograde and condensing gas drive phenomena and predict the minimum miscibility conditions accurately one has to utilize the theory of conformal solution of asymmetric mixture and the theory of many-body interactions.

THEORY OF CONFORMAL SOLUTION

MIXING RULES: There has been substantial progress made in recent years to improve conformal solution mixing rules¹⁵⁻²². Utilizing such mixing rules for calculation of mixture thermodynamic properties requires to combine them with an equation of state. There exist varieties of cubic equations of state available in the literature. The Peng-Robinson (PR) equation of state

$$z = v/(v-b) - a(T)/[v(v+b)+b(v-b)] \quad (1)$$

where

$$a(T) = a_c \{1 + k(1 - T_r^{1/2})\}^2, \quad (2)$$

$$a_c = a(T_c) = 0.45724 R^2 T_c^2 / P_c,$$

$$k = 0.37464 + 1.54226 \omega - 0.26992 \omega^2, \quad (3)$$

$$b = 0.0778 R T_c / P_c \quad (4)$$

is one such equation of state which is used in the present paper. We will limit our calculations and discussions to the PR equation of state with the understanding that similar computations can be performed with other equations of state such as SRK, etc. In order to utilize conformal solution mixing rules for the PR equation of state we first need to separate thermodynamic variables from constants of this equation of state. For this purpose we may write this equation of state in the following form¹⁷

$$Z = v/(v-b) - [(A/RT + C - 2(AC/RT)^{1/2}) / (v+b) + (b/v)(v-b)] \quad (5)$$

where

$$A = a_c(1+k)^2 \quad (6)$$

$$C = a_c k^2 / RT_c \quad (7)$$

This form of the equation of state indicates that there exist three independent constants (A, C, and b) in the equation. In Table I the mixing rules for these parameters are based on different conformal solution theories of mixtures. The combining rules for the unlike interaction parameters of this equation of state are

$$A_{ij} = (1 - k_{ij}) b_{ij} (a_{ii} a_{jj} / b_{ii} b_{jj})^{1/2} \quad (8)$$

$$b_{ij} = (1 - l_{ij}) (b_{ii}^{1/3} + b_{jj}^{1/3})^3 / 8 \quad (9)$$

$$C_{ij} = (1 - m_{ij}) (C_{ii}^{1/3} + C_{jj}^{1/3})^3 / 8 \quad (10)$$

In the present report we use the van der Waals (vdW) conformal solution mixing rules which are the simplest among the successful conformal solution mixing rules. It will be demonstrated that when the vdW mixing rules are combined with Equation 5 accurate retrograde condensation and condensing gas drive calculations can be made.

THEORY OF MANY-BODY INTERACTIONS:

In a fluid system the total intermolecular potential energy of the interacting molecules is expressed in the following form^{5,6,23-25}.

$$U = \sum_{i < j}^N \sum U^{(2)}(ij) + \sum_{i < j < k}^N \sum \sum U^{(3)}(ijk) + \dots \quad (11)$$

In this expression $u^{(2)}(ij)$ is the pair intermolecular potential energy between molecules i and j , $u^{(3)}(ijk)$ is the triplet intermolecular potential energy between molecules i , j , and k , etc. It is shown that²³⁻²⁵ 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) of Equation 11 are negligible. Moreover it is 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 as expressed by the following expression²⁶:

$$u^{(3)}(ijk) = \frac{v_{ijk}(1 + 3\cos \gamma_i \cos \gamma_j \cos \gamma_k)}{(r_i r_j r_k)^3} \quad (12)$$

where i , j and k are the three molecules forming a triangle with sides r_{ij} , r_{jk} and r_{ik} and interior angles γ_i , γ_j and γ_k and v_{ijk} is the triple-dipole constant. Contribution of this three-body effects to the Helmholtz free energy of a pure fluid is

$$A^{3b} = N v d f_1(\eta) / f_2(\eta) \quad (13)$$

where

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

$$f_2(\eta) = 1 - 1.12789 \eta^2 + 0.73166 \eta^3,$$

$$\eta = (\pi/6) (Nd^3/V),$$

N is the number of molecules in volume V and d is a hard core molecular diameter.

An equation of state, such as Equation 1 with a choice of mixing rules is based on binary interactions. The parameters A_{ij} , b_{ij} , and C_{ij} of this equation of state are derived from pure component properties while parameters A_{ij} , b_{ij} , and C_{ij} are derived from binary data of i and j . However, it has been shown that in utilizing such equations of state, even with better mixing rules, to predict ternary and multi-component system phase behavior, the results deviate from experimental data^{27,28}. This is specially observed for ternary mixtures around the critical point for which there is sufficient experimental data available.

The reason for the deviation of prediction of the equation of state around the ternary mixture critical point can be described as the following: In a ternary mixture, in addition to the kinds of interactions which exist between molecules in binary mixtures, there also exists an interaction which we would call the unlike-three-body interaction which happens when there are three molecules of three different kinds interacting in a mixture. Considering the fact that there exist no such terms in an equation of state, such as the two parameter cubic equations of state, we would expect that the unlike three-body interaction contribution to the equation of state will not be accounted for when the equation of state is based on the pure component and binary mixture data. Symbolically we will define the unlike-three-body interaction contribution to compressibility of a ternary mixture by $x_1 x_2 x_3 \Delta Z(v_{123}, T, N)$ where v_{123} is a parameter corresponding to the unlike-three-body interaction. As a result the equation of state of a mixture must be written in the following form:

$$Z_m = Z_m(v, T, a_{11}, a_{12}, \dots, a_{nn}, x_1, x_2, \dots, x_n) + \sum_i \sum_j \sum_k x_i x_j x_k \Delta Z(v_{ijk}, T, N); (i \neq j \neq k) \quad (14)$$

The second term in the right hand side of this equation includes all the unlike-three-body interaction between every three different molecules in the mixture.

The basic question to be answered at this stage is how to arrive at an expression for the unlike-three-body interaction term? This problem has been addressed in the statistical mechanical theory of many-body interactions. Starting with the work of Axilrod and Teller in the development of algebraic expressions for three-body intermolecular interactions energy and the development of an analytic expression for the unlike three-body interaction Helmholtz free energy using the perturbation theory of statistical mechanics^{26,29}. Details of the theory are given elsewhere²⁶. However, the final expression for the unlike Helmholtz free energy is as the following²⁴:

$$A_{ijk} = N d^{-9} v_{ijk} f_1(\eta)/f_2(\eta) \quad (15)$$

Knowing the unlike-three-body interaction Helmholtz free energy we can now calculate other thermodynamic properties. For example as a result the correct compressibility factor of a mixture will be

$$Z_m = Z_m^{emp} + \sum_i \sum_j \sum_k x_i x_j x_k (\eta\beta/b^3 v) (f_1 f_2 - f_1 f_2)/f_2^2 \quad (16)$$

where Z_m^{emp} is the expression for the empirical equation of state and

$$\beta = (8/27)\pi N_0^4 \eta_{ijk}$$

$$f_1 = (df_1/d\eta) = 19.75498 \eta + 35.30217 \eta^2 - 16.80120 \eta^3$$

$$f_2 = (df_2/d\eta) = -1.12789 + 1.46332 \eta$$

The co-volume parameter, b , is related to η as

PHASE EQUILIBRIUM CALCULATIONS: In the present calculations we compare the results of the above formulations with the PR equation of state for mixtures. In the calculations reported here it is assumed that the equation of state is valid for all the phases in equilibrium. The following equilibrium conditions between fugacities of the phases are assumed to hold:

$$f_i^I(T,P,(x)) = f_i^{II}(T,P,(x)) = \dots = f_i^N(T,P,(x)); \quad i=1,2,\dots,n$$

which can be expressed with respect to the fugacity coefficients of the phases as the following

$$\phi_i^I x_i^P = \phi_i^{II} x_i^P = \dots = \phi_i^N x_i^P \quad i = 1, 2, \dots, n \quad (17)$$

where I, II, ..., N represent the phases in equilibrium. For a mixture of three components exhibiting two liquid-phases and a vapor phase, the following algorithm is used in the phase equilibrium calculations⁶:

- 1) Overall mass balance $L_A + L_B + V = 1$
- 2) Species Mass Balance $x_{Ai} L_A + x_{Bi} L_B + y_{Bi} V = z_i$
- 3) Component Restrictive Equations $Sx_{Ai} = Sx_{Bi} = Sy_i = 1$
- 4) Equilibrium Criteria $f_{Ai} = f_{Bi} = f_i \quad i = 1, 2, 3$

where the subscripts A and B are used to identify the two liquid phases in equilibrium. The equilibrium constants or distribution coefficients of components between phases are defined as:

$$K_{Ai} = y_i/x_{Ai}; \quad K_{Bi} = y_i/x_{Bi}$$

As a result we obtain

$$\begin{aligned} x_{Ai} &= z_i / (L_A(1-K_{Ai}) + L_B(K_{Ai}/K_{Bi}-K_{Ai}) + K_{Ai}) \\ x_{Bi} &= z_i K_{Ai}/K_{Bi} / (L_A(1-K_{Ai}) + L_B(K_{Ai}/K_{Bi}-K_{Bi}) + K_{Ai}) \\ y_i &= z_i K_{Ai} / (L_i(1-K_{Ai}) + L_i(K_{Ai}/K_{Bi}-K_{Ai}) + K_{Ai}) \end{aligned}$$

Three different objective functions can be used:

- 1) Liquid-liquid-vapor bubble point calculation $Sx_{Ai} - Sx_{Bi} = Sy_i - 1 = 0$
- 2) Liquid-liquid-vapor dew point calculations $Sx_{Ai} - Sy_i = Sx_{Bi} - 1 = 0$
- 3) Liquid-liquid-vapor dew point calculations $Sx_{Ai} - Sy_i = Sx_{Bi} - 1 = 0$

MATHEMATICAL FORMULATION AND PREDICTION OF THE MMP

The governing equations of the critical state of a three-component system are given by the following determinant equations⁶:

$$U = \begin{vmatrix} \partial^2 g / \partial x_1^2 & \partial^2 g / \partial x_1 \partial x_2 \\ \partial^2 g / \partial x_1 \partial x_2 & \partial^2 g / \partial x_2^2 \end{vmatrix} = 0 \quad (18)$$

and

$$V = \begin{vmatrix} \partial^2 g / \partial x_1^2 & \partial^2 g / \partial x_1 \partial x_2 \\ \partial^2 g / \partial x_1 & \partial^2 g / \partial x_2^2 \end{vmatrix} = 0 \quad (19)$$

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:

$$\frac{x_1^c - x_1}{x_2^c - x_2} = \frac{dP_n}{dx_2} \quad (\text{at the critical point}) \quad (20)$$

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. With the implementation of the three-body effects the mixture equation of state will be

$$P = (\partial A / \partial V)_{T,n} = P^{emp} + x_1 x_2 x_3 (\eta\beta/b^3 v) (f_1 f_2 - f_1 f_2)/f_2^2$$

where P^{emp} is the expression for the empirical equation of state. The fugacity coefficient will take the following form:

$$\ln f_i = \ln f_i^{emp} + \partial(x_1 x_2 x_3 A_{123}^{3b}) / \partial n_i \quad (21)$$

With the aid of a computational algorithm the above equations are used to generate the binodal curves of binary and ternary systems.

VAPORIZING GAS DRIVE MMP PREDICTION: The substantial limitations of the PR and other cubic equations of state using empirical mixing rules are reported by Kuan³⁰ and by Firoozabadi³¹ in predicting the phase behavior and minimum miscibility pressures of simulated reservoir fluids. According to these investigators by using the empirical mixing rules an over-prediction of the MMP of hydrocarbon systems was observed. The mixture equation of state discussed above is applied to predict the minimum miscibility pressure of simulated reservoir fluids.

The first and simplest ternary system which is analyzed here is the mixture of methane + ethane + propane as reported on Figure 1. According to this figure while the Peng-Robinson equation of state (dashed line) is capable of predicting the behavior of binary VLE data of methane + propane, it fails to predict the VLE behavior (solid dots) around the critical point of the ternary mixture. With the consideration of three-body forces (solid line) the proposed technique is capable of predicting the VLE behavior of this ternary mixture.

The next ternary system analyzed was carbon dioxide + n-decane + n-butane as reported on Figure 2. According to the figure the PR equation of state (dashed lines) again fails to predict the binary data (solid dots) of these components. With the consideration of three-body forces (solid line in ternary diagram) the proposed technique is capable of predicting the VLE behavior of this ternary mixture quite well. Also reported on this figure are the large errors which would occur on locating the tangent at the critical point which passes through the reservoir fluid composition at the MMP condition.

THE SELF-CONSISTENT PSEUDOIZATION TECHNIQUE⁷

Let us assume the equation of state which is considered for phase equilibrium calculation to be in the following form:

$$Z = Z(v, T, a_m, b_m) \quad (22)$$

where its mixing rules can be shown by the following general expressions:

$$a_m = a_m(x_i, x_j, a_{ij}); \quad i, j = 1, \dots, c \quad (23)$$

$$b_m = b_m(x_i, x_j, b_{ij}); \quad i, j = 1, \dots, c \quad (24)$$

and with the following combining rules:

$$a_{ij} = (1 - k_{ij})(a_{ii} a_{jj})^{1/2} \quad (25)$$

$$b_{ij} = (1 - l_{ij})(b_{ii} + b_{jj})/2 \quad (26)$$

Provided one knows the exact number of components of the mixture this equation of state can be used for phase equilibrium calculation of that mixture. In the proposed technique it is assumed that one can group the (c) components of the mixture to (s) pseudo-components (for example s=3 when one wants to represent the data in a ternary diagram). Then the mixing rules can be shown in the following forms:

$$a_m = a_m(\xi_i, \xi_\phi, \alpha_{i\phi}); \quad i, \phi = 1, \dots, s \quad (27)$$

$$b_m = b_m(\xi_i, \xi_\phi, \beta_{i\phi}); \quad i, \phi = 1, \dots, s \quad (28)$$

and with the following combining rules:

$$\alpha_{i\phi} = (1 - \kappa_{i\phi})(\alpha_{ii} \alpha_{\phi\phi})^{1/2} \quad (29)$$

$$\beta_{i\phi} = (1 - \lambda_{i\phi})(\beta_{ii} + \beta_{\phi\phi})/2 \quad (30)$$

It should be pointed out that contrary to the case of Eqs 25 and 26 parameters $\kappa_{i\phi}$ and $\lambda_{i\phi}$ will be in general non-zero parameters for both cases of $i \neq \phi$ and $i = \phi$. When $i = \phi$ parameters $\kappa_{i\phi}$ and $\lambda_{i\phi}$ will be called "Lumping Parameters" and when $i \neq \phi$ parameters $\kappa_{i\phi}$ and $\lambda_{i\phi}$ will be called "Pseudo-binary Interaction Parameters". In Eqs. 27 and 28 ξ_i and ξ_ϕ are "Group Mole Fractions" and α_{ii} , $\alpha_{\phi\phi}$, β_{ii} , $\beta_{\phi\phi}$ are pseudo-component parameters associated with each group. At this stage we have to address three questions: (i) How to define the pseudo-component parameters? (ii) How to calculate the lumping parameters? (iii) How to calculate the pseudo-binary interaction parameters?

(i) **Definition of pseudo-component Parameters** - In the present technique one can use any of the available techniques without loss of generality. So long as the same pseudo-component calculation technique is used for defining pseudo-components the present technique will predict the same phase behavior for the multi-component system under consideration.

(ii) **Calculation of Lumping Parameters** - These parameters are calculated by assuming that a pseudo-compound with equation of state parameters a^{ps}_{ii} and b^{ps}_{ii} can represent properties of a lumped group of compounds. Parameters a^{ps}_{ii} and b^{ps}_{ii} are then calculated by matching properties of a pseudo-compound with the mixture properties of the group of compounds which are lumped together.

(iii) **Calculation of Pseudo-Binary Interaction Parameters** - After the pseudo-component parameters are defined and the lumping parameters are calculated pseudo-binary interaction parameters can be calculated by matching the properties of every pseudo-binary mixture with a true multi-component mixture consisting of all the compounds appearing in the pseudo-binary mixture.

First Application: A synthetic oil of 10 components³² for which the composition is given in Table 2 is selected to test the proposed technique. When the heavy-end fractions are described by the molecular weight, the specific gravity, and the boiling point, empirical correlations^{2,33} are used to estimate the properties (critical pressure and temperature and acentric factor) of the fractions. A lumping configuration is selected such that the synthetic mixture is reduced to 3 pseudo-components, consisting of [C₁] (methane), [C₂-C₆] (ethane to hexanes), and [C₇₊] (heptanes and heavier fractions).

Figure 3 shows the P-X diagram of the [C₂-C₆]+[C₇₊] pseudo-binary system where the symbols represent the calculation with the exact compositional description of the synthetic mixture. The dash-dotted line is the calculation with 2 pseudo-components but without the pseudo-binary interaction parameters and lumping parameters. The dashed line is the result with two pseudo-components and the pseudo-binary interaction parameter, but, without the lumping parameters. The solid line is obtained with two pseudo-components, the pseudo-binary interaction parameter and the lumping parameters. Exact multicomponent calculation is shown by (x). In Figure 4 the P-X diagram of the [C₁]+[C₇₊] pseudo-binary system is reported where only the pseudo-binary interaction parameter is evaluated to match the exact calculation represented by the symbols. For this particular example two lumping parameters are only needed, one lumping parameter for the [C₂-C₆] group and a second lumping parameter for the [C₇₊] group.

Figures 5-7 are for prediction of the phase behavior of a vaporizing gas drive process with CO₂ as the injected gas and the synthetic oil as the reservoir oil. Prediction with the pseudoization technique is represented by the solid line. Exact multi-component calculation is shown by (x). The objective here is to test the performance of the proposed technique at different pressures and in all ranges of composition of solvent and oil. The P-X diagrams shown in Figures 5 and 6 are used to evaluate the binary interaction parameters between CO₂ and the pseudo-components of the synthetic mixture. The predicted pseudo-ternary diagram for this system is shown in Figure 7 where it is demonstrated that the agreement between the exact calculation and the lumping technique is excellent.

Second Application: A P-T phase envelope of a gas condensate³⁴ system (high in methane and low in heavy hydrocarbons) with the composition as in Table 3 is constructed and it is reported by Figure 8. In this calculation 4 pseudo-components are chosen which are [CH₄], [N₂], [CO₂, C₂-C₅], and [C₆₊]. Also, a P-X diagram of carbon dioxide-reservoir oil³⁴ system (low in methane and high in heavier hydrocarbons) with the composition as in Table 4 is constructed using the same 4 pseudo-components and it is reported by Figure 9. In both of these cases the results of calculations obtained with the present self-consistent approach are in very good agreement with the exact multi-component calculations.

Third Application: The final application is to establish a relationship between the cricondenbar locus of P-X diagram of a mixture and the phase separation regions of the pseudo-ternary diagram of the same mixture. This kind of relationship is of significant importance in application of pseudoization techniques in high pressure processes such as extraction of heavy compounds from mixtures by dense gases and miscible flood enhanced oil recovery.

In the present computation we categorize our mixture by three pseudo-components [heavy (3), intermediate (2), and light (1)] and we study the P-X diagrams by varying the ratio of compositions of heavy and intermediates. Rather than plotting various P-X diagrams the locus of the cricondenbars of such mixtures versus $C=X(2)/[X(2)+X(3)]$ are reported by Figures 10 and 11. Also reported in Figures 10 and 11 are the pseudo-ternary diagrams related to the same mixtures at different pressures. The major difference between Figures 10 and 11 is the difference in shapes of the cricondenbar loci. These two shapes (one a decreasing function of C and the other having a minimum point) are the only possible trends that one can produce by choosing all possible relative compositions for the light, intermediate, and heavy fractions of a mixture.

THEORY OF PHASE EQUILIBRIUM OF CONTINUOUS MIXTURES

Development of compositional reservoir simulators is presently hampered due to the complexity of the existing computational algorithms of reservoir fluid phase behavior calculations. Through the application of the theory of polydisperse fluid mixtures a number of algorithms for phase behavior calculations are developed⁹⁻¹¹. In this part of the present report we introduce one such algorithm. In this algorithm reservoir fluid is considered to consist of a continuous mixture with a defined molecular weight/composition distribution function. Computational computer time required for the new algorithm is shown to be one order of magnitude smaller than the existing algorithms. Comparisons of experimental data with the calculated results indicate good agreement between the two.

For a mixture with many components being continuous in character, the compositions can be described by a density distribution function, $F(I, I_0, \eta)$ whose independent variable I is

some measurable property such as molecular weight, boiling point or density with a mean value of I_0 and a variance of η . The normalization of the density distribution function is given by

$$\int_I F(I) dI = 1 \quad (31)$$

In case the mixture is in part continuous and contain sufficiently large amounts of components which should be considered as discrete components Equation(31) will be valid for the continuous fraction of the mixture while for the whole mixture the following normalizing condition will hold:

$$\sum_I^d x_i + x_c = 1 \quad (32)$$

where x_i and x_c are the mole fraction of component i and the continuous fraction, respectively and d is the total number of discrete components in the mixture. Regarding the material balance of component I in a flash calculation we get

$$z_c F_I(I) = x_c \Phi_L F_L(I) + y_c \Phi_V F_V(I) \quad (33)$$

The distribution functions, $F_I(I)$, $F_L(I)$, $F_V(I)$, are not additive and as a result they can not possess the same functional forms in a specific flash calculation scheme.

In order to extend continuous thermodynamics to engineering applications, we introduce a general phase equilibrium calculation technique which is based on THE MINIMIZATION OF THE TOTAL GIBBS FREE ENERGY ALGORITHM¹⁰. Using this technique, flash calculations of complex mixtures containing discrete components and a continuous fraction, which could have a wide molecular weight distribution, can be performed. For a system in equilibrium (constant T and P), for any differential "virtual displacement" occurring in the system, a general criterion should be imposed on the system such that the total Gibbs free energy is minimal.

$$(dG)_{T,P} = 0 \quad (34)$$

To restrict our consideration only to the vapor-liquid equilibrium, we write the total Gibbs free energy of the system as:

$$G = G_L + G_V \quad (35)$$

For a mixture consisting of discrete components and a one-family continuous fraction, we derive an expression of the Gibbs free energy for the liquid phase;

$$G_L = \int_V [P - N_L RT/v_L] dv - RT \sum_i^d N_i \ln [v_i/N_i RT] - N_c RT \int_I F_L(I) \ln [v_L/N_c RT F_L(I)] dI + P v_L + G_L^0 \quad (36)$$

where G_L^0 is the Gibbs free energy of the reference state. A similar expression will hold for the vapor phase. Since, the system is in phase equilibrium, thus, according to Equation (34), all of the first derivatives of the total Gibbs free energy with respect to the system variables must be equal to zero. i.e.

$$(\partial G / \partial \eta_L)_{T,P,x_i,y_i,\eta_V,I_0,L,I_0,V} = 0 \quad (37)$$

$$(\partial G / \partial \eta_V)_{T,P,x_i,y_i,\eta_L,I_0,L,I_0,V} = 0 \quad (38)$$

$$\left(\frac{\partial G}{\partial I_{oL}}\right)_{T,P,x_i,y_i,\eta_L,\eta_V,I_{oV}} = 0 \quad (39)$$

$$\left(\frac{\partial G}{\partial I_{oV}}\right)_{T,P,x_i,y_i,\eta_L,\eta_V,I_{oL}} = 0 \quad (40)$$

To perform flash calculations for a system composed of discrete components and a continuous fraction, Eq's. (5) and (6), coupled with Eq's.(37)-(40), will form a set of nonlinear equations which must be solved simultaneously. To illustrate the application of this technique let us assume the PR equation of state

$$P = RT/(v-b) - a(T)/[v(v+b)+b(v-b)] \quad (41)$$

$$a(T) = a(T_c)[1+k(1-T_r^{1/2})]^2, \\ a(T_c) = 0.45724R^2T_c^2/P_c, \\ b = 0.0778 RT_c/P_c \quad (42)$$

$$k = 0.37464 + 1.54226 \omega - 0.26992\omega^2 \quad (43)$$

with its empirical mixing rules

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (44)$$

$$b = \sum_i x_i b_i \quad (45)$$

$$a_{ij} = (1-k_{ij})(a_i a_j) \quad (46)$$

is valid. In order to extend this equation of state to a mixture containing d discrete components and a continuous fraction with a wide molecular weight distribution, we need to rewrite the mixing rules as the following forms:

$$a = \sum_i \sum_j x_i x_j a_{ij} + 2 \sum_i x_i x_c \int_0^I F(I) a(i,I) dI + \\ x_c^2 \int_0^I \int_0^I F(I) F(J) a(I,J) dJ dI \quad (47)$$

$$b = \sum_i x_i b_i + x_c \int_0^I F(I) b(I) dI \quad (48)$$

where

$$a(i,I) = a_i^{1/2} a^{1/2}(I) (1-k_{iI});$$

$$a(I,J) = a^{1/2}(I) a^{1/2}(J) (1-k_{IJ})$$

The parameters $a^{1/2}(I)$ and $b(I)$ can be accurately represented by third-order polynomials with respect to molecular weight I for a homologous series of paraffinic hydrocarbons as given below 9,10:

$$a^{1/2}(I) = \alpha_1 + \alpha_2 I + \alpha_3 I^2 + \alpha_4 I^3 \quad (49)$$

where

$$\alpha_1 = 0.4771 + 0.0157T^{1/2};$$

$$\alpha_2 = 0.1055 + 0.0017T^{1/2};$$

$$\alpha_3 = -0.4066 \times 10^{-4} + 0.2960 \times 10^{-5} T^{1/2};$$

$$\alpha_4 = 0.2700 \times 10^{-6} - 0.1318 \times 10^{-8} T^{1/2}$$

and

$$b(I) = \beta_1 + \beta_2 I + \beta_3 I^2 + \beta_4 I^3 \quad (50)$$

where

$$\beta_1 = 0.0071, \beta_2 = 0.0013, \beta_3 = -0.1371 \times 10^{-5}$$

and

$$\beta_4 = 0.9686 \times 10^{-8} \quad (51)$$

We may further introduce an exponential-decay distribution function

$$F(I) = (1/\eta) \exp[-(I-I_c)/\eta] \quad (52)$$

which is proper to describe the composition of gas-condensate fluids.⁹⁻¹¹ Knowing that methane constitute a large fraction of every gas-condensate system, it is appropriate to treat the system as a mixture of methane and a continuous fraction of the rest of hydrocarbons. As a result, by substituting Equation (41) into Equation (35) and considering Equation (52) as the continuous fraction distribution function, the total Gibbs free energy of the system will be

$$G = \Phi_L g_L + \Phi_V g_V \quad (53)$$

where

$$g_L = -RT \ln(v_L - b_L) + \{a_L/[2.828b_L]\} \ln[(v_L - 0.414b_L)/(v_L + 2.414b_L)] - RT(x_1 - x_1 \ln x_1 + x_c \ln x_c) + v_L RT/[v_L - b_L] - a_L v_L/[v_L(v_L + b_L) + b_L(v_L - b_L)]$$

and g_V will have a similar expression. The expressions for a_L and b_L are as the following:

$$a_L = x_1^2 a_{11} + x_c^2 a_{cL}^2 + 2x_1 x_c (a_{11})^{1/2} (a_{cL})^{1/2} a_{1L} \quad (54)$$

with

$$a_{1L} = \exp(-70/\eta_L)(q_1 + q_2 \eta_L + q_3 v_L^2 + q_4 \eta_L^3 + q_5 \eta_L^4);$$

$$a_{cL} = [\eta_1 + h_2(I_c + \eta_L) + v_3(I_c^2 + 2I_c \eta_L + 2\eta_L^2) + \eta_4(I_c^3 + 3I_c^2 \eta_L + 6I_c \eta_L^2 + 6\eta_L^3)]^2 - 0.02\{(a_{22})^{1/2}[\exp(-70/\eta_L) - \exp(-84/\eta_L)] +$$

$$(a_{33})^{1/2}[\exp(-84/\eta_L) \exp(98/\eta_L)]\}(s_1 + s_2 \eta_L + s_3 \eta_L^2 + s_4 \eta_L^3);$$

$$q_1 = -0.0579\alpha_1 - 5.344\alpha_2 - 10.257\alpha_3 - 1.662 \times 10^2 \alpha_4;$$

$$q_2 = 0.441 \times 10^{-4} \alpha_1 - 0.0491 \alpha_2 - 10.257 \alpha_3 - 1.662 \times 10^2 \alpha_4;$$

$$q_3 = 0.8822 \times 10^{-4} \alpha_2 + 2.5308 \alpha_3 - 34.398 \alpha_4;$$

$$q_4 = 2.6466 \times 10^{-4} \alpha_3 - 0.393 \alpha_4;$$

$$q_5 = 1.0586 \alpha_4;$$

$$s_1 = \alpha_1 + \alpha_2 \times 10^2 + \alpha_3 \times 10^4 + \alpha_4 \times 10^6;$$

$$s_2 = \alpha_2 + 2v_3 \times 10^2 + 3\alpha_4 \times 10^4;$$

$$s_3 = 2\alpha_3 + 6\alpha_4 \times 10^2; \quad s_4 = 6.0 \alpha_4$$

and

$$b_L = x_1 b_1 + x_c [\beta_1 + \beta_2(I_c + \beta_L) + \beta_3(I_c^2 + 2I_c \beta_L + 2\beta_L^2) + \beta_4(I_c^3 + 3I_c^2 \beta_L + 6I_c \beta_L^2 + 6\beta_L^3)]$$

In the above equations b_1 is the (b) parameter of the equation of state for methane and a_{11} , a_{22} , and a_{33} are the (a) parameter of the equation of state for methane, ethane, and propane, respectively. Similar relations will hold for parameters a_v and b_v . To perform flash calculations, we need to substitute Equation (53) into Equations (37)-(40). Since for gas-condensates $I_{of} = I_{oL} = I_{oV}$, Equation (39) and Equation (40) will vanish. We only need to solve Equations (37) and (38), simultaneously and considering the fact that pressure and temperatures in the two phases remain identical. In what follows the proposed algorithm is used for calculation of properties of two gas-condensate systems.

COMPARISON OF CALCULATED AND EXPERIMENTAL RESULT : In our calculations, we perform flash calculations for the a gas-condensate system³⁵ in which the crude oil composition, equilibrium condensate phase equilibrium data and liquid-vapor volume ratios at different pressures are given.

The gas-condensate systems is treated as a fluid with a discrete component of methane and a continuous fraction of other hydrocarbons. The continuous fraction is described by an exponential-decay distribution function starting from the molecular weight of ethane. For calculation of the binary interaction parameter k_{ij} of gas-condensate systems, the following procedure is used; (i) It is assumed that $k_{ij} = 0$ for all binary pairs except for methane- C_{7+} , ethane- C_{7+} , and propane- C_{7+} interactions. (ii) It is assumed that $k_{ij} = 0.01$ for ethane- C_{7+} and propane- C_{7+} binary pairs as proposed by Katz and Firoozabadi³⁶. (iii) Du and Mansoori¹¹ produced the following expression relating the pair-interaction parameter of methane- C_{7+} to molecular weight of hydrocarbons will be derived.

$$k_{1,i} = -0.0579 + 0.4411 \times 10^{-4} M w_i \quad (55)$$

The gas condensate³⁵ system is treated as a discrete mixture of methane (with a mole fraction of 0.74133) and a continuous fraction of other hydrocarbons. The continuous fraction is described by an exponential distribution function (with a variance of $\eta = 48.9$). In Figures (12-14) the component mole fraction equilibrium ratio, (K value), liquid volume percent (with respect to total volume of the system), and the P-T diagram as calculated by the present technique are compared with the experimental data³⁵. Dots are the experimental data while the solid lines are the results of the proposed continuous mixture phase equilibrium algorithm. As shown in Figures (12-14), the flash calculations performed by using the proposed technique are in good agreement with the experimental data.

This technique provides a general and convenient procedure for performing flash calculations for a complex mixture consisting of both discrete and continuous components. This technique can also reduce the required computer time and overcome the complexity for solving a multitude of simultaneous equations. The present technique is applicable to varieties of complex reservoir fluid mixtures, equations of state, mixing rules, and combining rules.

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Table 1. Conformal solution mixing rules for the PR equation of state

RMA Theory	$A = [\sum_i \sum_j x_i x_j A_{ij} b_{ij}]^{3/2} / [\sum_i \sum_j x_i x_j A_{ij} b_{ij}^3]^{1/2}$ $b = [\sum_i \sum_j x_i x_j A_{ij} b_{ij}]^3 / \sum_i \sum_j x_i x_j A_{ij} b_{ij}]^{1/2}$ $C = [\sum_i \sum_j x_i x_j A_{ij} C_{ij}^3 / \sum_i \sum_j x_i x_j A_{ij} C_{ij}]^{1/2}$
vdW Theory	$A = \sum_i \sum_j x_i x_j A_{ij}$ $b = \sum_i \sum_j x_i x_j b_{ij}$ $C = \sum_i \sum_j x_i x_j C_{ij}$
HSE Theory	$A = \sum_i \sum_j x_i x_j A_{ij}$ $b = [\sum_i \sum_j x_i x_j A_{ij}]^2 / \sum_i \sum_j x_i x_j A_{ij}^2 / b_{ij}$ $C = [\sum_i \sum_j x_i x_j A_{ij}]^2 / \sum_i \sum_j x_i x_j A_{ij}^2 / C_{ij}$
DEX Theory	$A = \sum_i \sum_j x_i x_j A_{ij} \{ 1 - [(A_{ij}/b_{ij})(b/A) - 1] \xi \}$ $b = \sum_i \sum_j x_i x_j b_{ij}$ $C = \sum_i \sum_j x_i x_j C_{ij}$
CSA Theory	$A = \sum_i \sum_j x_i x_j A_{ij}$ $1 + \Delta_{xx} = B^* / \sum_i \sum_j x_i x_j B^* _{ij}$ $B^*_{ij} = x_i (d_{ij} + x_j \Delta_{xx} b_{ij} / b)$ $C = \sum_i \sum_j x_i x_j C_{ij}$
$\Delta_{xx} = pRT\kappa_{Txx} - 1 = -1 + RT / \{ RTv^2 / (v-b)^2 - 2Av^3 / (v^2 + b^2)^2 \}$ $\xi = \{ [A - \sqrt{(ACRT)}] / (2bRT\sqrt{2}) \} \ln \{ (v+b-b\sqrt{2}) / (v+b+b\sqrt{2}) \} + \sqrt{(ACRT)} / \{ 2[\sqrt{(ACRT)} - A] \}$	

Table 2. Synthetic oil composition used for the first application

Components	Molar Percentage
Methane	35
Ethane	3
Propane	4
n-Butane	6
n-Pentane	4
n-Hexane	3
n-Heptane	5
n-Octane	5
n-Decane	30
n-Tetradecane	5

Table 3. Gas condensate composition used for the second application

Components	Molar Percentage
Methane	76.34
Ethane	8.86
Propane	4.29
i-Butane	0.79
n-Butane	1.26
i-Pentane	0.56
n-Pentane	0.58
Hexane ⁺	4.06
Nitrogen	0.94
Carbon dioxide	2.32

Table 4. Reservoir oil composition used for the second application

Components	Molar Percentage
Methane	32.54
Ethane	9.09
Propane	7.73
i-Butane	1.36
n-Butane	4.28
i-Pentane	1.67
n-Pentane	2.30
Hexane ⁺	38.41
Nitrogen	1.19
Carbon dioxide	0.63

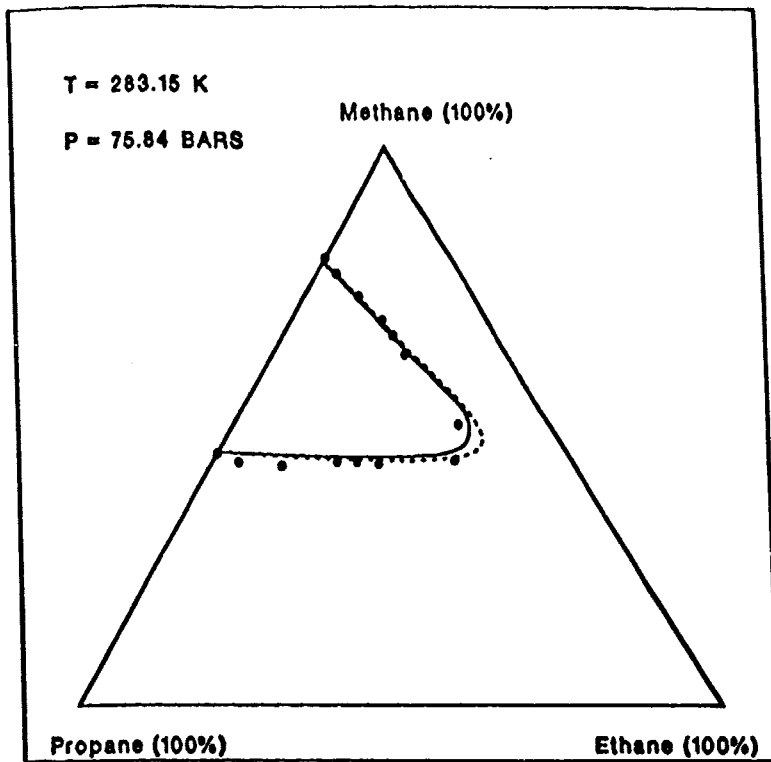


Figure 1. Ternary mixture of methane + ethane + propane. According to this figure while the Peng-Robinson equation of state (dashed line) is capable of predicting the behavior of binary VLE data of methane + propane, it fails to predict the VLE behavior (solid dots) around the critical point of the ternary mixture. With the consideration of three-body forces (solid line) the proposed technique is capable of predicting the VLE behavior of this ternary mixture.

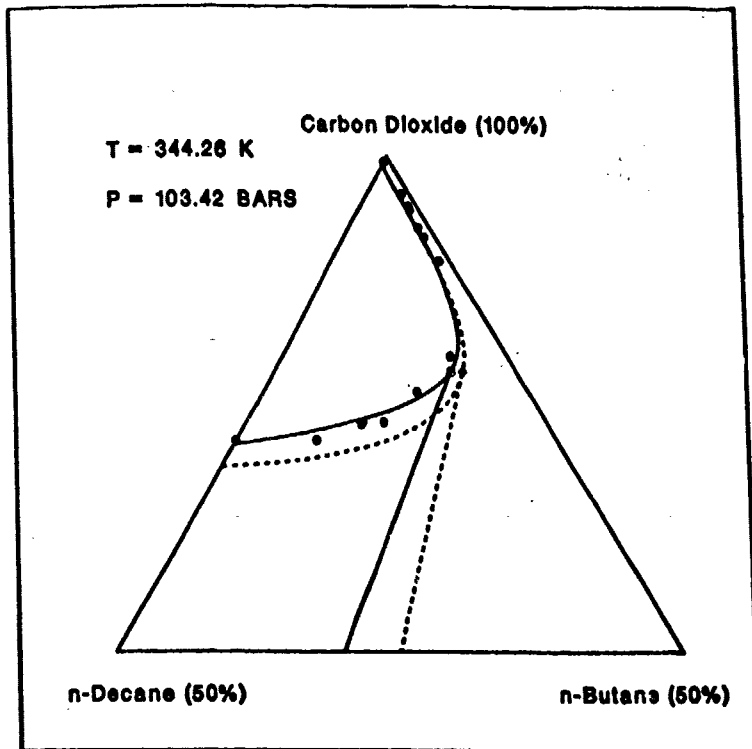


Figure 2. Ternary mixtures of carbon dioxide, n-decane, and n-butane. According to the binary figures the PR equation of state (dashed lines) fails to predict the binary data (solid dots) of these components. With the consideration of conformal solution mixing rules (solid lines) we are capable of predicting the binary mixtures and the ternary mixtures away from the ternary critical point. With the consideration of three-body forces (solid line in ternary diagram) the proposed technique is capable of predicting the VLE behavior of this ternary mixture quite well.

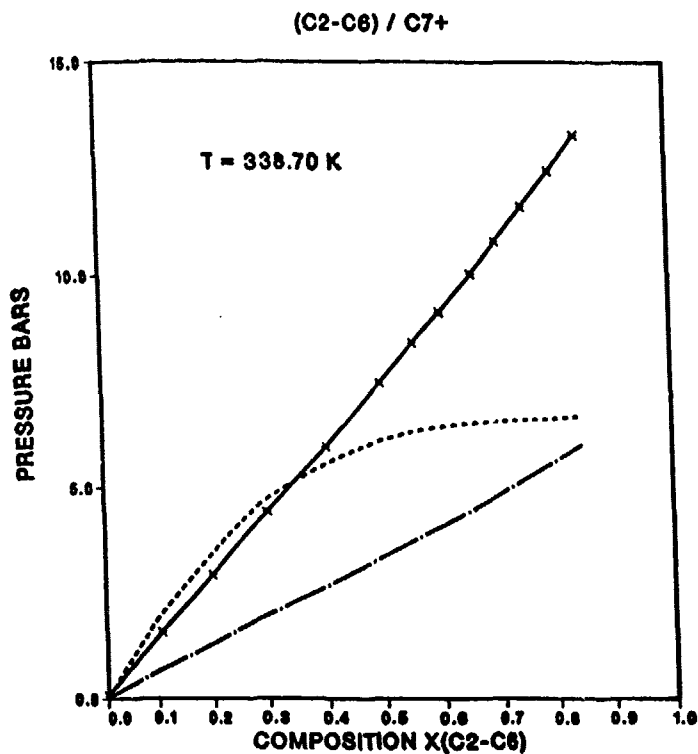


Figure 3. The P-X diagram for the [C₂-C₆]+[C₇₊] pseudo-binary system at 338.70 K. Calculation with two pseudo-components but without the lumping and the pseudo-binary interaction parameters is represented by the dashed-dotted line. Calculation with two pseudo-components and the pseudo-binary interaction parameter but without the lumping parameters is shown by the dashed line. Calculation with two pseudo-components including the lumping and pseudo-binary interaction parameters is shown by the solid line. Exact multi-component calculation is shown by (x).

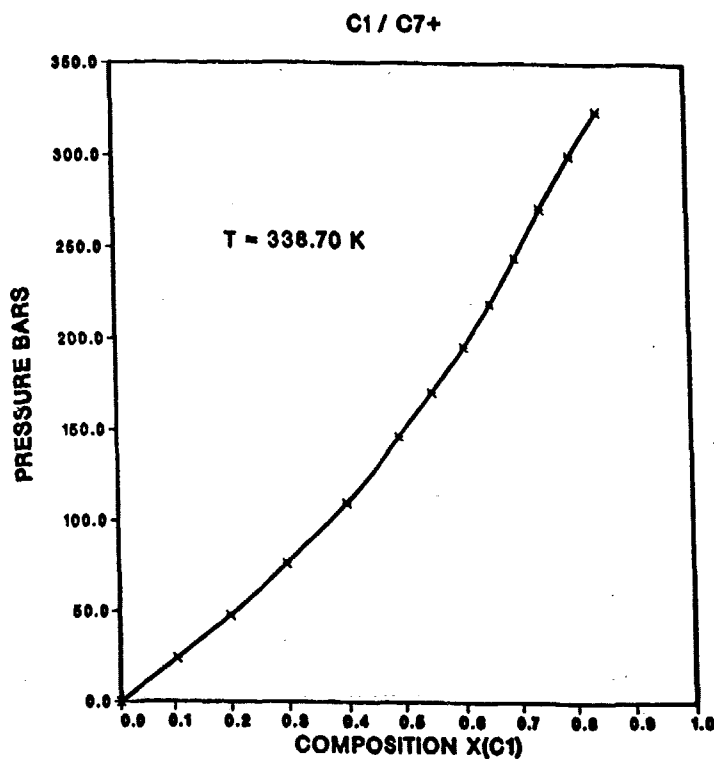


Figure 4. The P-X diagram for the [C₁]+[C₇₊] pseudo-binary system at 338.70 K. Calculation with two pseudo-components and including the lumping and pseudo-binary interaction parameters is shown by the solid line. Exact multi-component calculation is shown by (x).

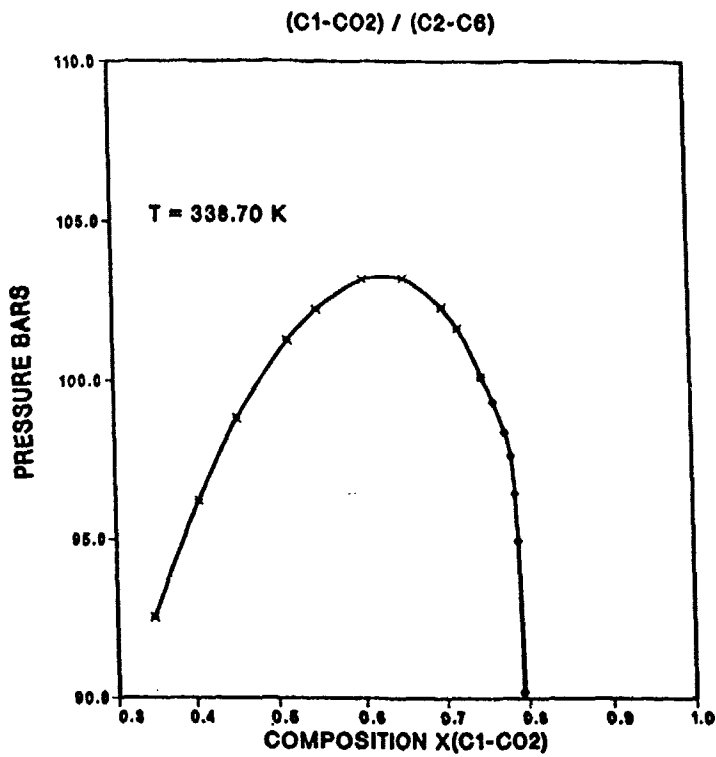


Figure 5. The P-X diagram for the $[C_1-CO_2]/[C_2-C_6]$ system at 338.70 K. Calculation with pseudoization technique is shown by the solid line. Exact multicomponent calculation is shown by (x) and (o).

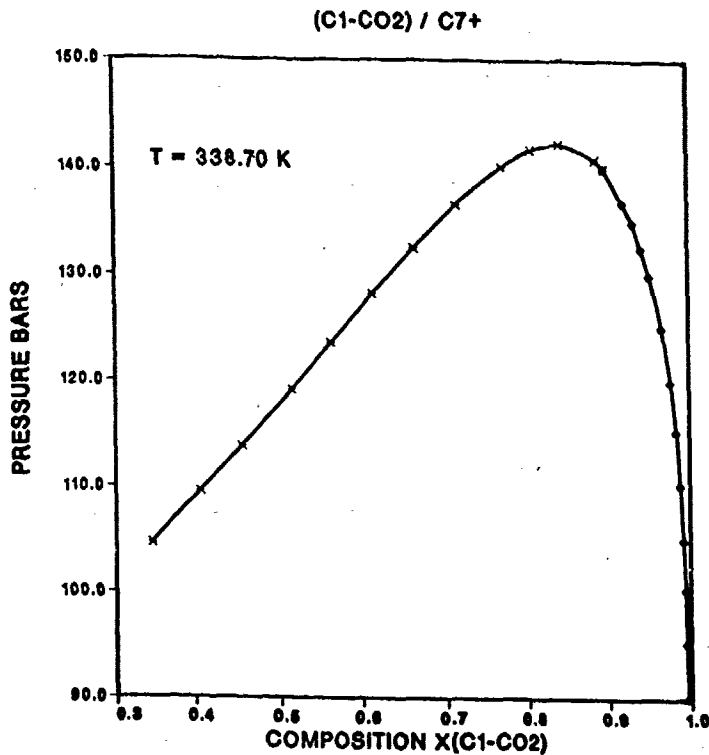


Figure 6. The P-X diagram for the $[C_1-CO_2]/[C_7+]$ system at 338.70 K. Calculation with pseudoization technique is shown by the solid line. Exact multicomponent calculation is shown by (x) and (o).

CO₂ / SYNTHETIC OIL

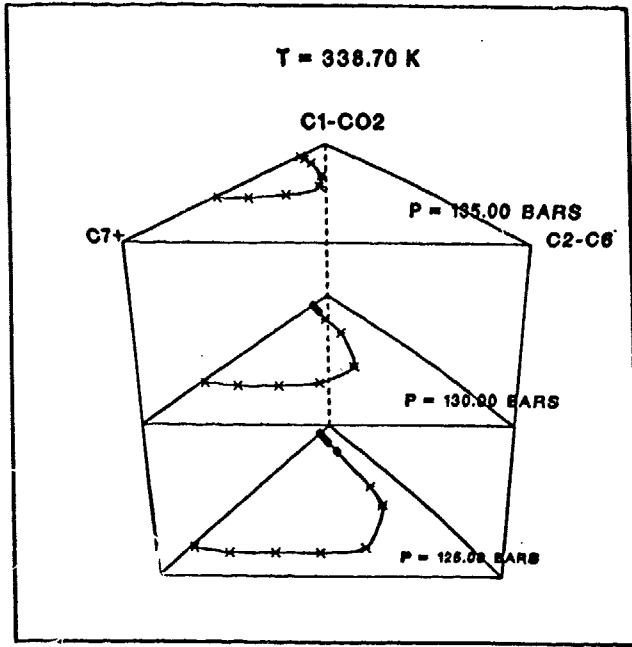


Figure 7. Pseudo-ternary diagram for CO₂/Synthetic Oil at different pressures. Prediction with the pseudoization technique is represented by the solid line. Exact multi-component calculation is shown by (x).

PHASE ENVELOPE OF GAS CONDENSATE

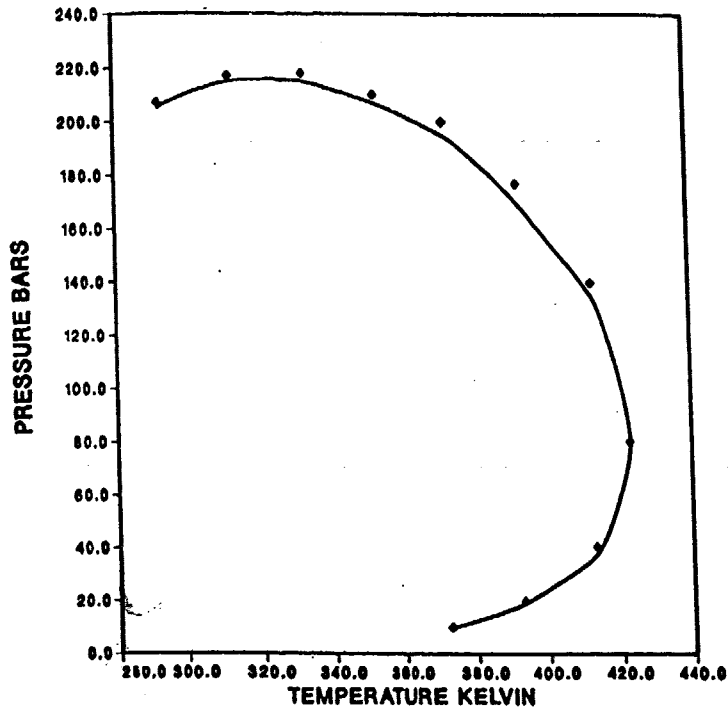


Figure 8. Phase envelope of gas condensate at 369.85 K. Prediction with the pseudoization technique is shown by the solid line. Exact multicomponent calculation is shown by (x).

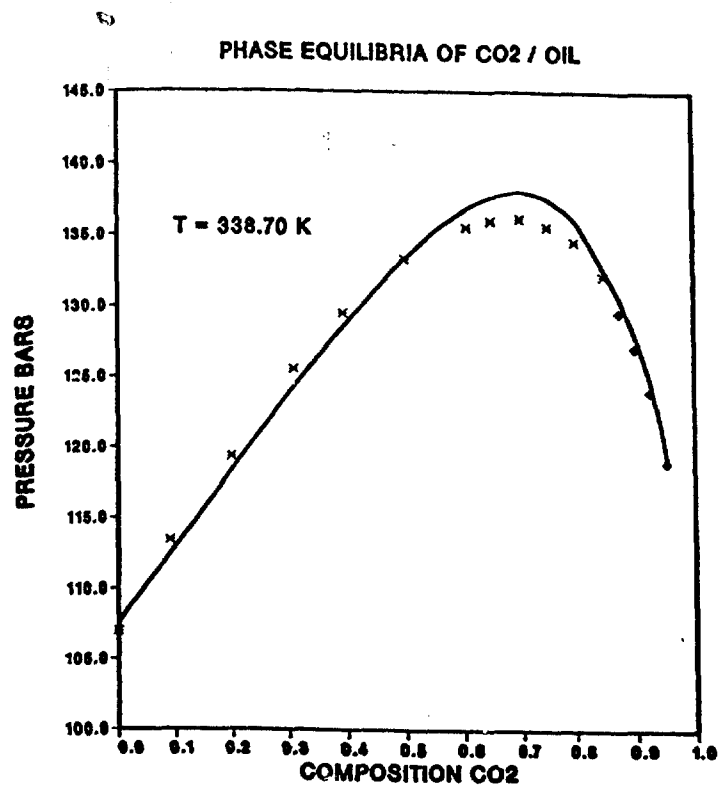


Figure 9. The P-X diagram of carbon dioxide-reservoir oil system (low in methane and high in heavier hydrocarbons) with the composition as in Table 4 constructed using the same 4 pseudo-components as in Figure 13. Prediction with the pseudoization technique is shown by the solid line. Exact multicomponent calculation is shown by (x).

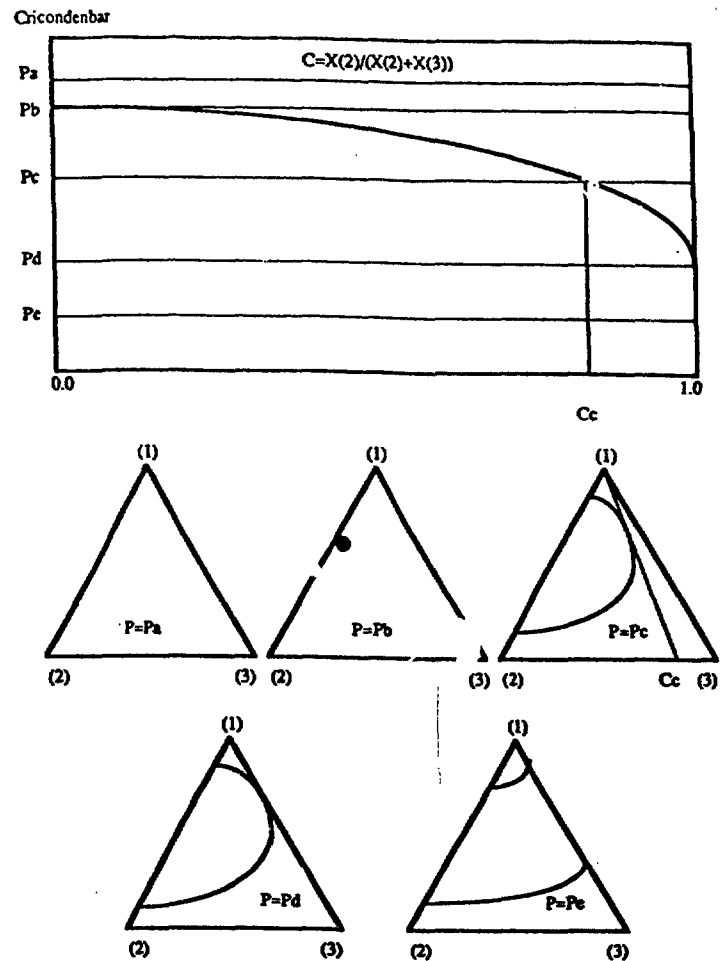


Figure 10. Phase diagram relationship between P-X and ternary diagrams for systems exhibiting only one phase envelope in the pseudo-ternary representation. This is the first of the two possible relationship between criocondenbar locus of P-X diagram and phase separation regions in pseudo-ternary diagram.

Cricondenbar

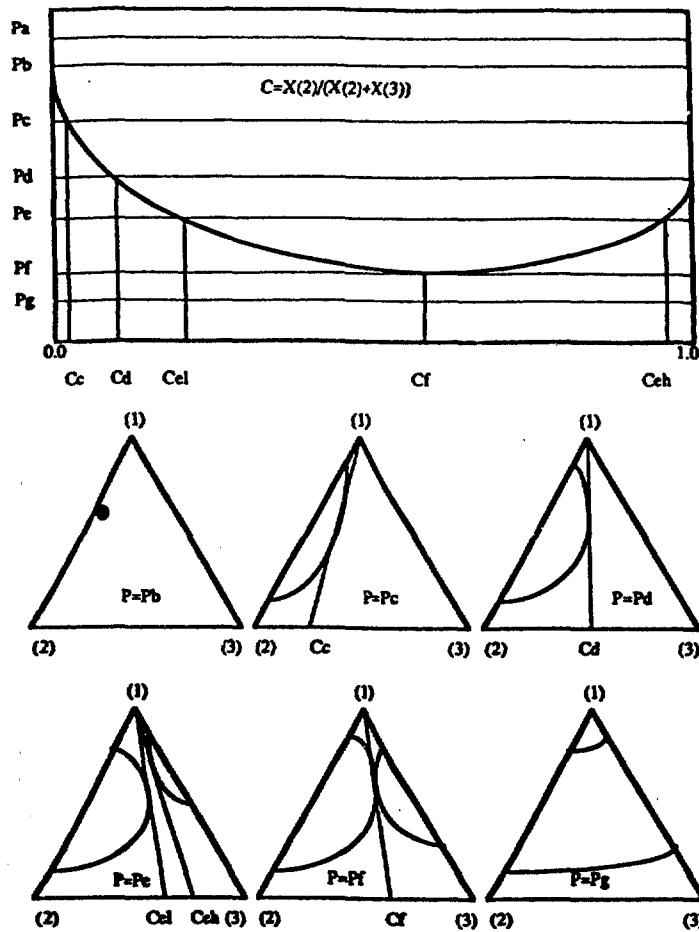


Figure 11. Phase diagram relationship between P-X and ternary diagrams for systems which may exhibit two closed phase envelopes in the pseudo-ternary representation. This is the second of the two possible relationship between cricondenbar locus of P-X diagram and phase separation regions in pseudo-ternary diagram.

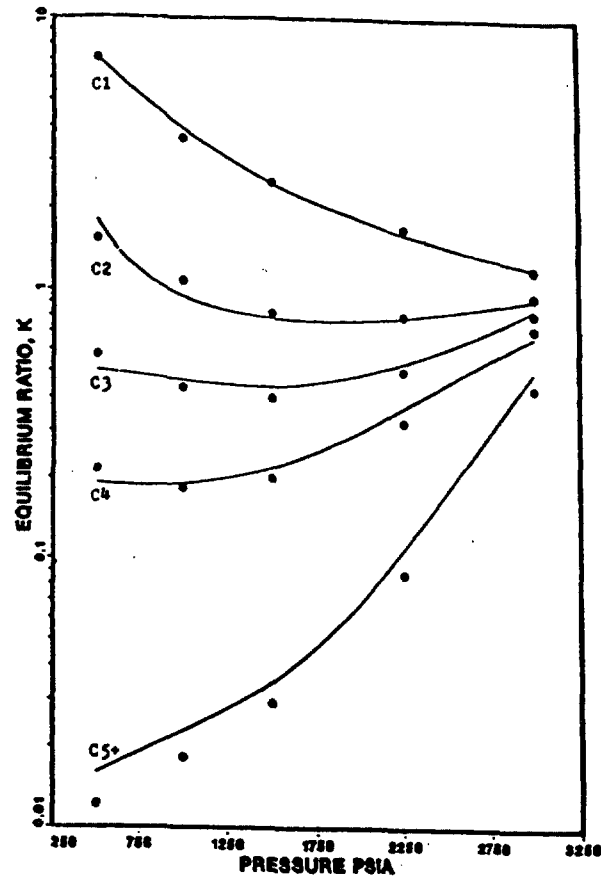


Figure 12. Component mole fraction equilibrium ratio, K-values, of a gas condensate fluid³⁵ at 100°F. Dots are the experimental data while the solid lines are the results of the proposed continuous mixture phase equilibrium algorithm.

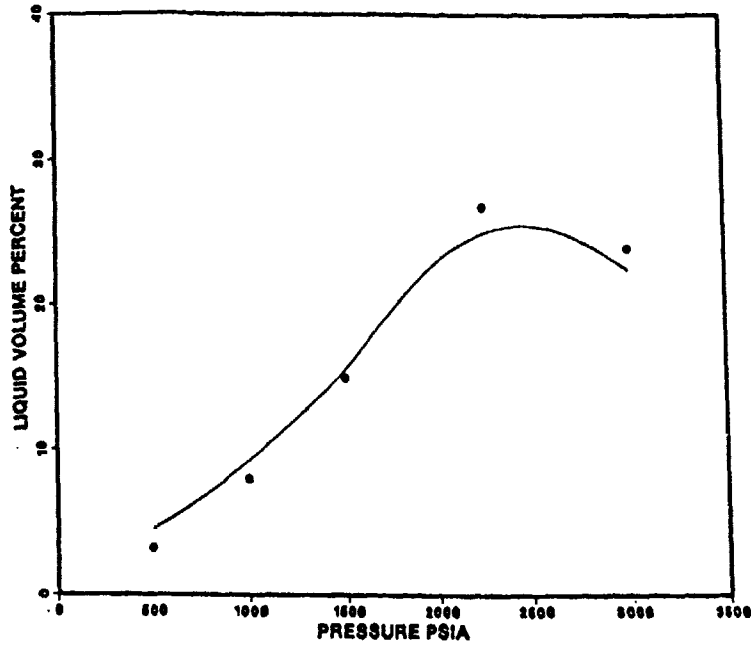


Figure 13. Liquid volume percent of a gas condensate fluid³⁵ at 100°F. Dots are the experimental data while the solid lines are the results of the proposed continuous mixture phase equilibrium algorithm.

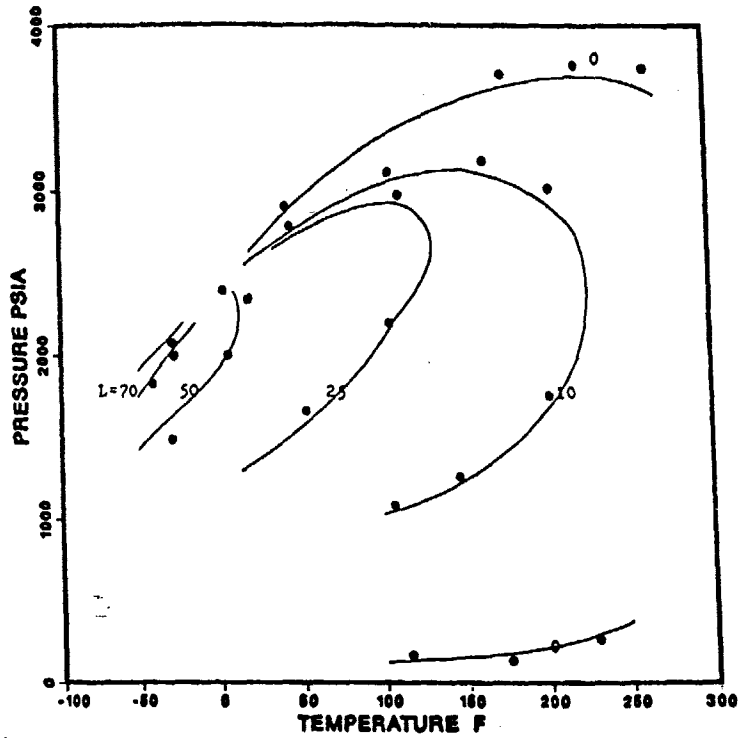


Figure 14. PT diagram of a gas condensate fluid³⁵. Dots are the experimental data while the solid lines are the results of the proposed continuous mixture phase equilibrium algorithm.