Pseudoization Techniques and Heavy Fraction Characterization with Equation of State Models

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ABSTRACT

A pseudoization technique is developed which is independent of the kind of mixing rules used for characterizing the parameters of the equations of state. This technique uses a pseudobinary representation to evaluate a lumping parameter which accounts for the mixture-like character of the pseudocomponent. This is to reduce original mixture characterization to a minimum number of components. The method is versatile and can be used to tune the equation of state to any laboratory PVT data. The validity of the technique is demonstrated by several sample calculations such as phase split isotherms and phase envelopes of a gas condensate and other reservoir oils. The pseudoternary diagram representation of solvent-oil systems are predicted and they are shown to be in agreement with the original mixture characterization. Accuracy of prediction of such pseudoternary diagrams, which are widely used in vaporizing-gas-drive enhanced oil recovery processes, is demonstrated as a further test of the proposed method.

INTRODUCTION

The computational efficiency and cost of simulation of processes involving complex fossil fuels (petroleum, coal-liquids, etc.) using equations of state depend a great deal on the number of components (real and pseudocomponents) chosen to describe the fluid under study. In general the number of components necessary to describe such complex fluids is higher than ten. The computer capacity of storage and computation time increase considerably with the increase in the number of components. Several methods have been reported to characterize pseudocomponents and heavy-end fractions (Hong 1982; Mehra et al. 1982; Withson 1983; Gonzalez et al. 1986; Wu and Batycky 1986). Most of these methods are based on arbitrary mixing rules and empirical pseudoization techniques where the pseudocomponents are treated as pure components. None of the methods-proposed to date seem to offer an advantage over the other available techniques. More recently, a semi-empirical concept has been proposed to account for the mixture-like character of the pseudocomponent (Schlijper 1986). This concept has brought about improvement in describing phase behavior of complex fluids. In the present report, a new technique is presented that uses a nonlinear regression-based phase behavior program to characterize pseudocomponents. The method takes into consideration the effect of temperature in calculating the lumping parameters by adjusting critical properties of the pseudocomponents evaluated from mixing rules.

In the second section of this report a review of the available methods for evaluating the properties of pseudocomponents is presented. In the third section an algorithm for the evaluation of the lumping parameters and the pseudobinary interaction parameters is described. Finally, in the fourth section computational results are presented for a synthetic oil mixture, a gas condensate system, and a reservoir oil.

PSEUDOCOMPONENT PROPERTIES

In lumping components into pseudocomponents to represent a complex many-component fluid one can use mixing rules to determine the pseudocomponent properties for substitution into the equation of state. These properties include critical temperature (T_c), critical pressure (P_c), critical volume (V_c), critical compressibilty factor (Z_c), acentric factor (ω), molecular weight (MW), and binary interaction parameters (k_{ij}). There are numerous sets of mixing rules available in the literature to characterize pseudocomponents.

Kay's rules (Kay 1938) are the simplest form of mixing rules by which the pseudocomponent properties are obtained by summing the products of the component properties and a weighting factor which is usually the relative molar fraction for the group of components used in a pseudocomponent,

$$P_{cm} = \sum_i^m x_i P_{ci} \tag{1}$$

$$T_{cm} = \sum_i^m x_i T_{ci} \tag{2}$$

$$V_{cm} = \sum_i^m x_i V_{ci} \tag{3}$$

$$\omega_m = \sum_i^m x_i \omega_i \tag{4}$$

$$MW_m = \sum_i^m x_i MW_i \tag{5}$$

In connection with evaluation of cross-parameters, a_{ij}, of cubic equations of state and the cross-second virial coefficient, B_{ij}, of the virial equation, Prausnitz and Gunn (1958) adopted the Lorentz-Berthelot type combining rules. The complete system of pseudocomponent properties includes:

$$T_{cij} = (T_{ci}T_{cj})^{0.5} \tag{6}$$

$$V_{cij}^{1/3} = \frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2} \tag{7}$$

$$T_{cm} = \sum_{i}^{m}\sum_{j}^{m} x_i x_j (1-k_{ij})(T_{ci}T_{cj})^{0.5} \tag{8}$$

$$V_{cm}^{1/3} = \frac{1}{2}\sum_{i}^{m}\sum_{j}^{m} x_i x_j \left(V_{ci}^{1/3} + V_{cj}^{1/3}\right) \tag{9}$$

$$Z_{cm} = 0.5(Z_{ci} + Z_{cj}) \tag{10}$$

$$\omega_m = 0.5(\omega_i + \omega_j) \tag{11}$$

$$P_{cm} = \frac{Z_{cm} R T_{cm}}{V_{cm}} \tag{12}$$

An alternate procedure for characterizing pseudocomponents has been developed by Mehra et al. (1982) as the following:

$$T_{cm} = \frac{1}{8}\frac{1}{V_{cm}}\sum_{i}^{m}\sum_{j}^{m} x_i x_j \left(V_{ci}^{1/3} + V_{cj}^{1/3}\right)^3 (T_{ci}T_{cj})^{1/2} \tag{13}$$

$$Z_{cm} = 0.2905 - 0.085\omega_m \tag{14}$$

Then several weighting factors, ϕ_i, have been defined with various mixing rules which have been summarized by Hong (1982) and they include:

molar average,

$$\phi_i = x_i \tag{15}$$

surface fraction,

$$\phi_i = \frac{x_i V_{ci}^{2/3}}{\sum_{i}^{m} x_i V_{ci}^{2/3}} \tag{16}$$

weight fraction average,

$$\phi_i = \frac{x_i MW_i}{\sum_i^m x_i MW_i} \qquad (17)$$

and the mixing rules for T_{cm} includes a P_c weighting factor,

$$T_{cm} = \sum_i^m \sum_j^m \phi_i \phi_j (T_{ci} T_{cj})^{1/2} (1 - k_{ij}) \qquad (18)$$

where

$$\phi_i = \frac{x_i P_{ci}}{\sum_i^m x_i P_{ci}} \qquad (19)$$

This is just to mention a few of a score of proposed mixing and combining rules for evaluating pseudocomponent properties. Statistical mechanical considerations can be used to derive other mixing rules for a specific equation of state. For example the pseudocomponent mixing rules for the Peng-Robinson equation of state (Peng and Robinson 1976) one can obtain the following expressions for properties of pseudocomponents:

$$T_{cm} = \frac{\sum_i^m \sum_j^m x_i x_j (T_{ci} T_{cj})^{1/2} \left({}^{T_{ci}}\!/\!_{P_{ci}} + {}^{T_{cj}}\!/\!_{P_{cj}} \right)}{2 \sum_i^m x_i \, {}^{T_{ci}}\!/\!_{P_{ci}}} \qquad (20)$$

$$P_{cm} = \frac{T_{cm}}{\sum_i^m x_i \, {}^{T_{ci}}\!/\!_{p_{ci}}} \qquad (21)$$

To derive these expressions the dimensions of parameters a and b for the Peng-Robinson equation of state with pressure and temperature are taken into account. It is observed that the contribution of more complex mixing rules over the simple ones, Equations 1-5, in defining pseudocomponents is insignificant. There is no physical significance behind the mixing rules for the pseudocomponent binary unlike parameters. In this report a pseudobinary interaction parameter between any two different pseudocomponents is evaluated with the regression program in order to match the calculation with the the exact compositional description of the mixture.

DESCRIPTION OF THE ALGORITHM

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

$$Z = Z(v, T, a_m, b_m) \tag{22}$$

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

$$a_m = a_m(x_i, x_j, a_{ij}); \qquad i, j = 1,2,\ldots, c \tag{23}$$

$$b_m = b_m(x_i, x_j, b_{ij}); \qquad i, j = 1,2,\ldots, c \tag{24}$$

with the following combining rules:

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

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

where k_{ij} and l_{ij} are generally non-zero parameters when $i \neq j$ and $k_{ij}=l_{ij}=0$ for $i=j$.

Provided one knows the exact number of components of the multicomponent 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) pseudocomponents (for example s=3 when one wants to represent the data in a ternary diagram). Then the equation of state of the multicomponent mixture can be shown in the following form:

$$Z = Z(v, T, a_m, b_m) \tag{27}$$

where

$$a_m = a_m\left(\xi_i, \xi_j, A_{ij}^{ps}\right); \qquad i, j = 1,2,\ldots, s \tag{28}$$

$$b_m = b_m\left(\xi_i, \xi_j, B_{ij}^{ps}\right); \qquad i, j = 1,2,\ldots, s \tag{29}$$

with the following combining rules:

$$A_{ij}^{ps} = \left(1-\kappa_{ij}\right)\left(A_{ii}^{ps}A_{jj}^{ps}\right)^{1/2} \tag{30}$$

$$B_{ij}^{ps} = \left(1-\lambda_{ij}\right)\frac{\left(B_{ii}^{ps} + B_{jj}^{ps}\right)}{2} \qquad (31)$$

It should be pointed out that contrary to the case of Eqs. 25 and 26 parameters κ_{ij} and λ_{ij} will be in general non-zero parameters for both cases of $i \neq j$ and $i=j$. When $i=j$ parameters κ_{ii} and λ_{ii} will be called "Lumping Parameters" and when $i \neq j$ parameters κ_{ij} and λ_{ij} will be called "Pseudobinary Interaction Parameters". In Eqs. 28 and 29 ξ_i and ξ_j are "Group Mole Fractions" and A^{ps}_{ii}, A^{ps}_{jj}, B^{ps}_{ii}, B^{ps}_{jj} are pseudocomponent parameters associated with each group.

At this stage we have to address three questions: (i) How to define the pseudocomponent parameters? (ii) How to calculate the lumping parameters? (iii) How to calculate the pseudobinary interaction parameters?

(i) Definition of Pseudocomponent Parameters
The existing techniques available for calculation of pseudocomponent parameters have already been reviewed in the previous section. In the present technique one can use any of the available techniques without loss of generality. So long as the same pseudocomponent calculation technique is used for defining pseudocomponents the present technique will predict the same phase behavior for the multicomponent system under consideration. However, in all the calculations which follow one must not switch from one pseudocomponent calculation technique to another.

(ii) Calculation of Lumping Parameters
These parameters are calculated by assuming that a pseudocompound 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 pseudocompound with the mixture properties of the group of compounds which are lumped together. This technique of calculation makes the numerical value of lumping parameters dependent on the kind of mixing rules used for evaluating the pseudocomponent parameters, temperature, and composition of the compounds in the pseudocomponent.

(iii) Calculation of Pseudobinary Interaction Parameters
After the pseudocomponent parameters are defined and the lumping parameters are calculated pseudobinary interaction parameters can be calculated by matching the properties of every pseudobinary mixture with a true multicomponent mixture consisting of all the compounds appearing in the pseudobinary mixture. This technique of calculation makes the numerical value of pseudobinary interaction parameters dependent on temperature and composition of the compounds in the pseudobinary mixture. In some cases the temperature at which the system fluid is studied is higher than the critical temperature of the heavier pseudocomponent in the pseudobinary representation. Under such condition the regression analysis cannot be performed unless the pseudocritical properties obtained from mixing rules are adjusted or the grouping configuration is modified.

APPLICATIONS

As an example the Peng-Robinson equation of state which has received a wide acceptance in process engineering calculations is chosen with the computational methods described in this paper. The experimental data of the mixtures studied in this investigation are not reported since the objective of this research is not to evaluate the performance of the equation of state but to test the proposed pseudoization technique vis a vis the computation performed with the original mixture characterization.

First Application

A synthetic oil (Metcalfe and Yarborough 1979) of 10 components (the binary interaction parameters and the composition are given in Table 1 and 2, respectively) is selected to test the proposed technique.

Table 1. Binary Interaction Parameters Used with the Peng-Robinson Equation of State.

	CO2	C1	C2	C3	C4	C5	C6	C7	C8	C10	C14
CO2	-										
C1	.092	-									
C2	.132	.000	-								
C3	.124	.014	.000	-							
C4	.133	.013	.010	.000	-						
C5	.122	.023	.010	.000	.000	-					
C6	.110	.042	.010	.000	.000	.000	-				
C7	.100	.035	.010	.000	.000	.000	.000	-			
C8	.114	.049	.010	.000	.000	.000	.000	.000	-		
C10	.150	.047	.010	.000	.000	.000	.000	.000	.000	-	
C14	.150	.045	.010	.000	.000	.000	.000	.000	.000	.000	-

Table 2. Synthetic Oil Composition Used for the First Application.

Components	Molar fraction (%)
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

When the heavy-end fractions are described by the molecular weight, the specific gravity, and the boiling point, empirical correlations (Cavett 1962; Standing 1982) 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 pseudocomponents, consisting of [C_1] (methane), [C_2-C_6]

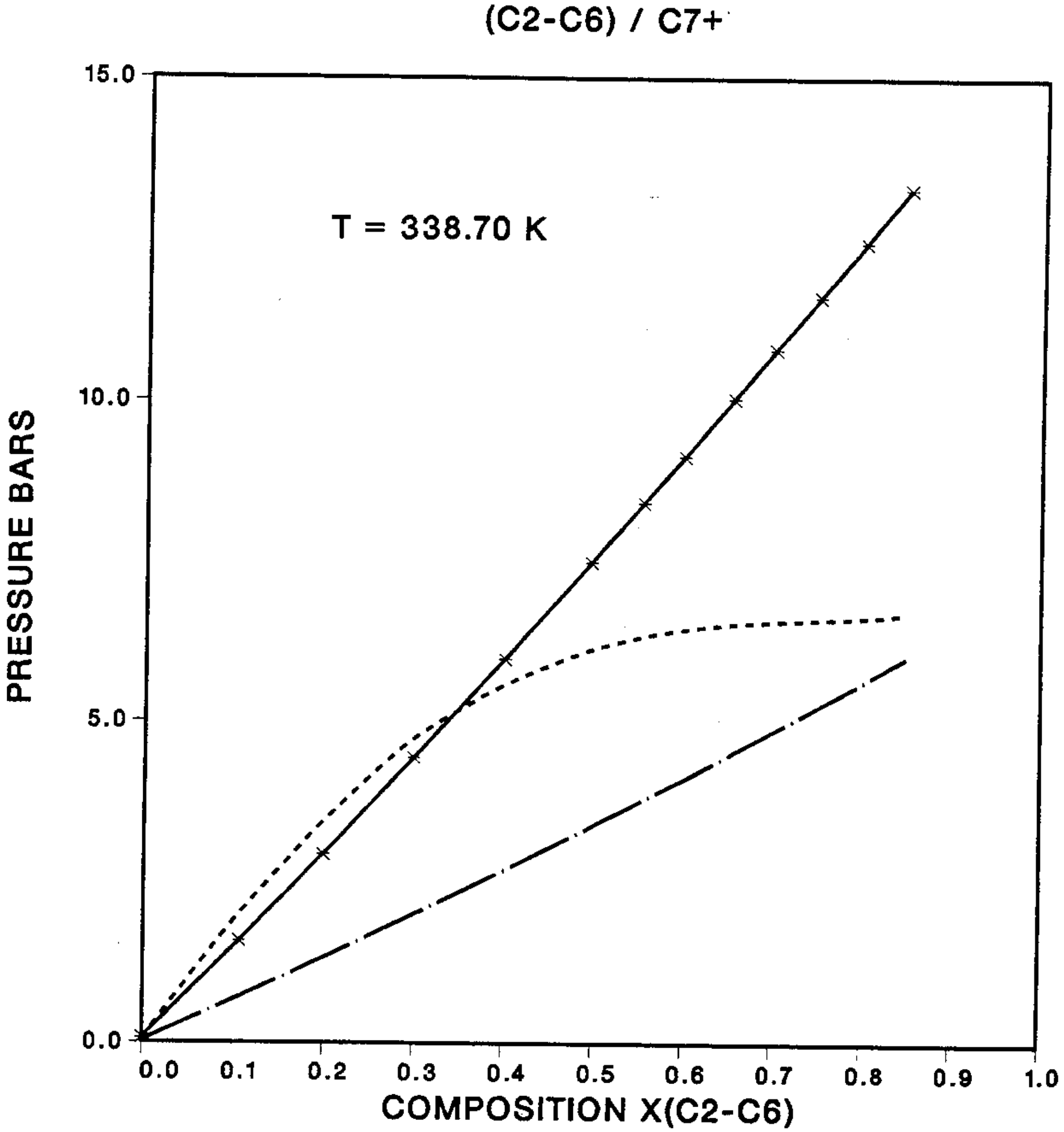

Figure 1. P-X diagram for the [C2-C6]/[C7+] pseudobinary system at 338.70K. Chain-dotted line: calculation without the lumping and pseudobinary interaction parameters; dots: calculation with the pseudobinary parameters but without the lumping parameter; solid line: calculation with the lumping and pseudobinary interaction parameters; symbols: exact multicomponent calculation

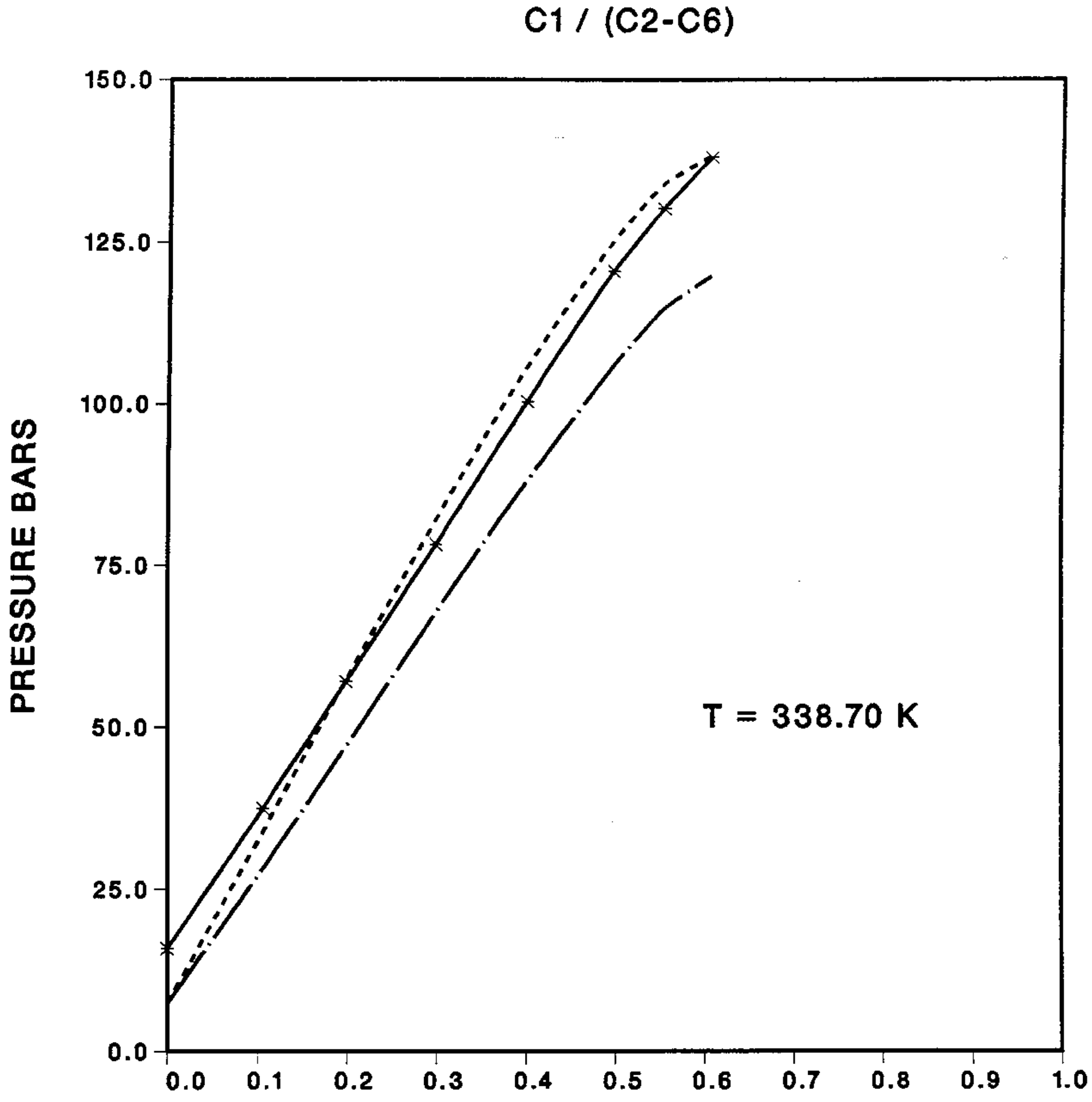

Figure 2. P-X diagram for the [C1]/[C2-C6] pseudobinary system at 338.70K. Chain-dotted line: calculation without the lumping and pseudobinary interaction parameters; dots: calculation with the pseudobinary parameters but without the lumping parameter; solid line: calculation with the lumping and pseudobinary interaction parameters; symbols: exact multicomponent calculation

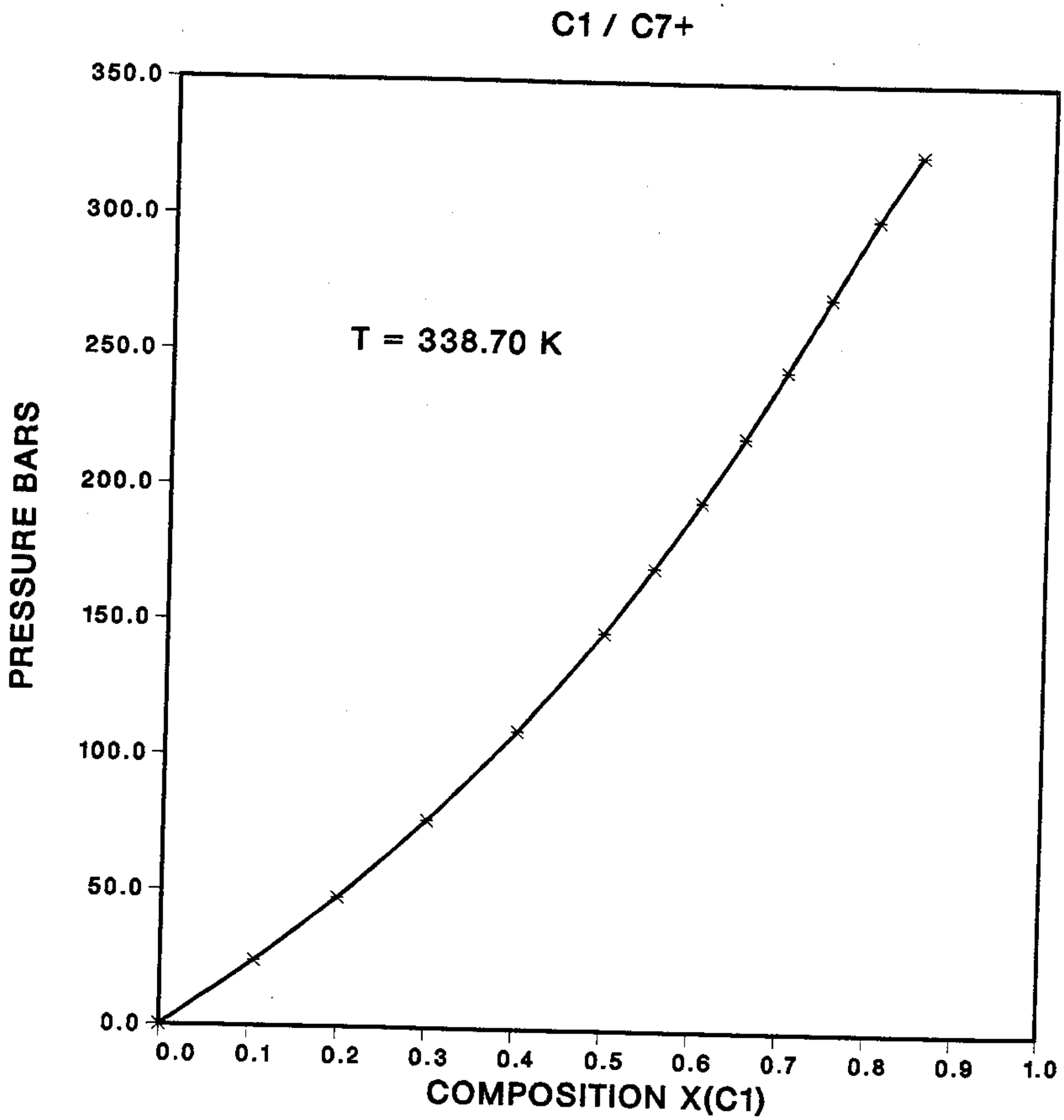

Figure 3. P-X diagram for the [C1]/[C7+] pseudobinary system at 338.70K. Solid line: calculation with the lumping and pseudobinary interaction parameters; symbols: exact multicomponent calculation.

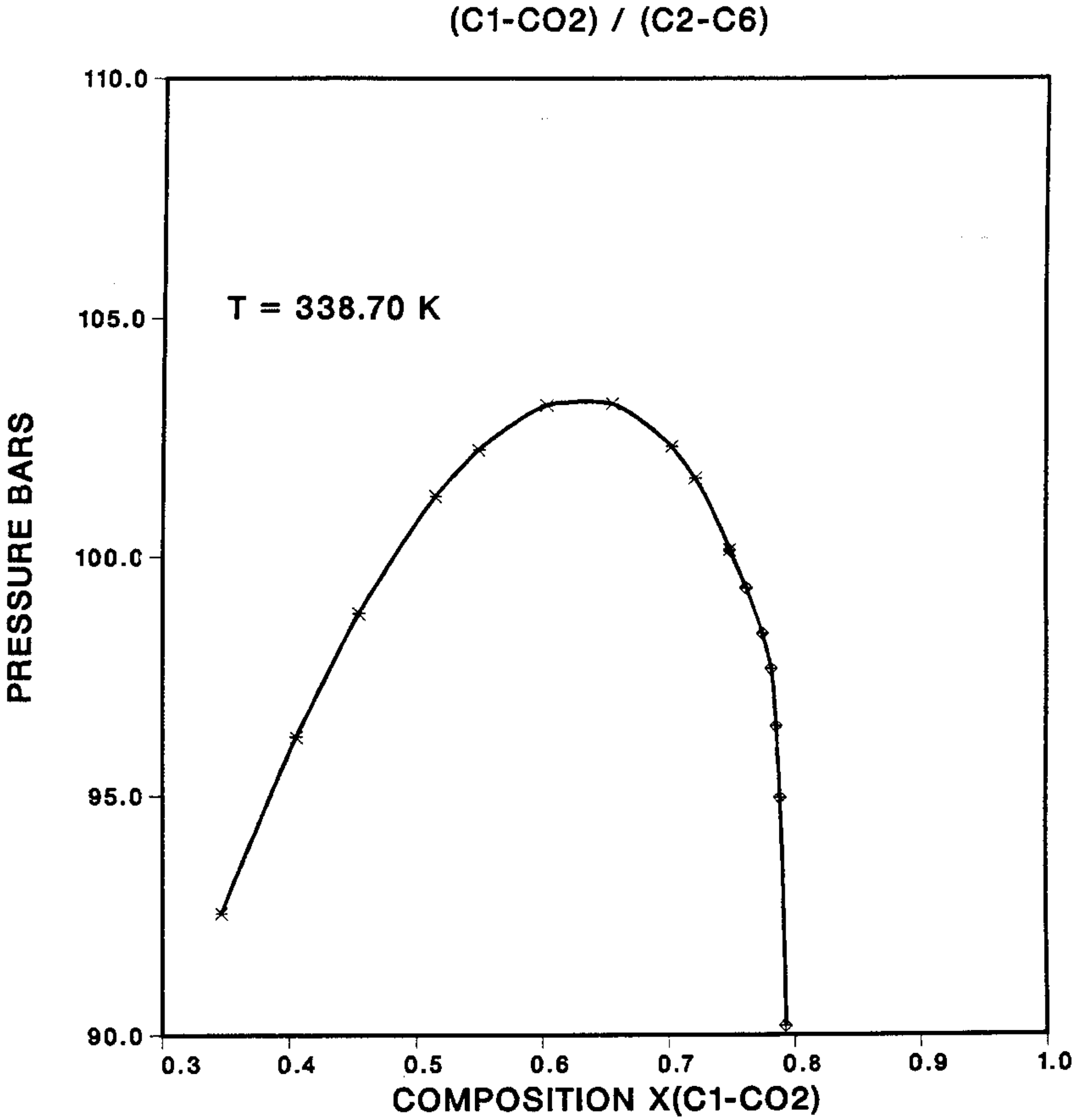

Figure 4. P-X diagram for the [C1-CO2]/[C2-C6] system at 338.70K. Solid line: calculation with pseudoization technique; symbols: exact multicomponent calculation.

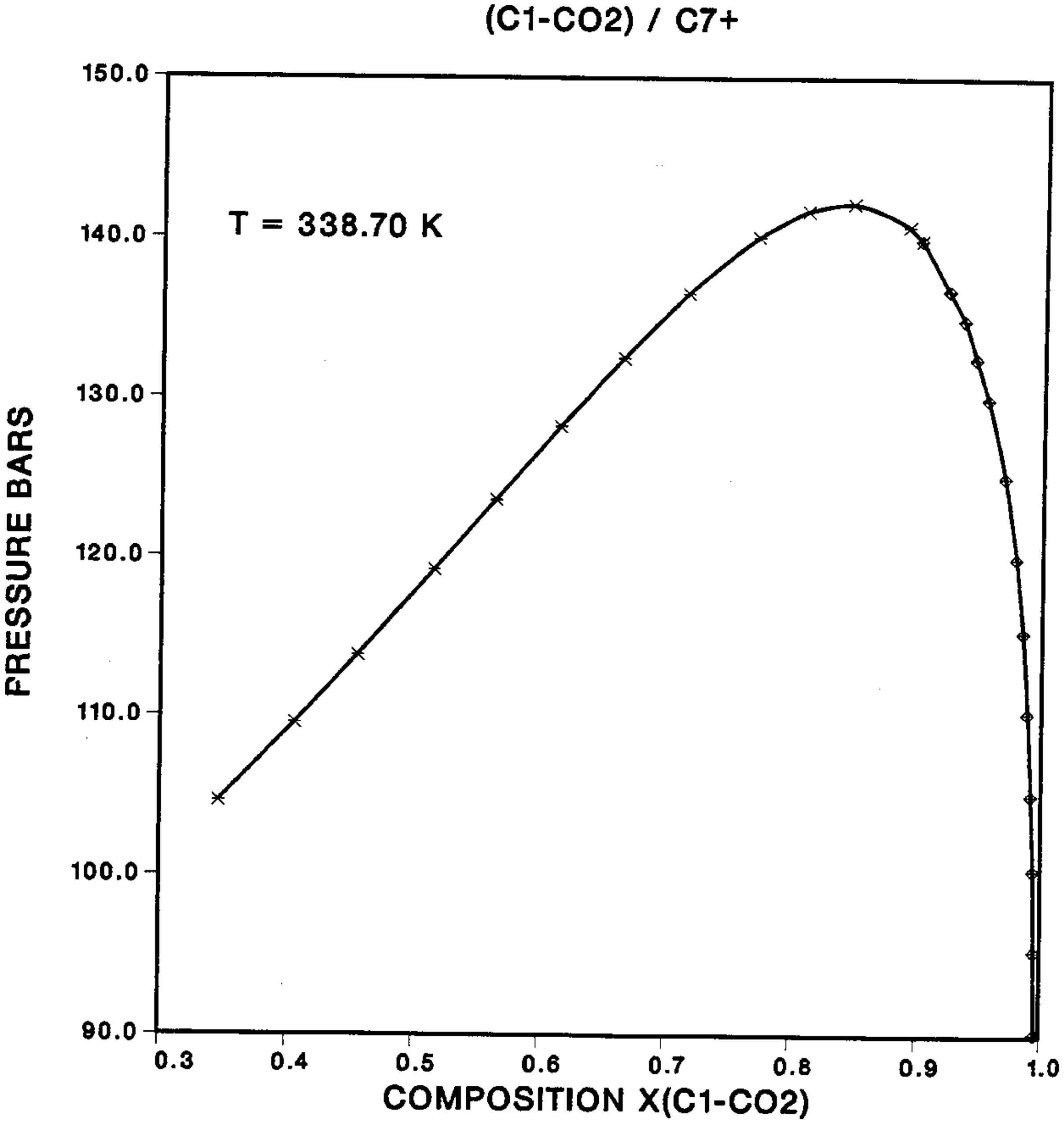

Figure 5. P-X diagram for the [C1-CO2]/[C7+] system at 338.70K. Solid line: calculation with pseudoization technique; symbols: exact multicomponent calculation.

CO2 / SYNTHETIC OIL

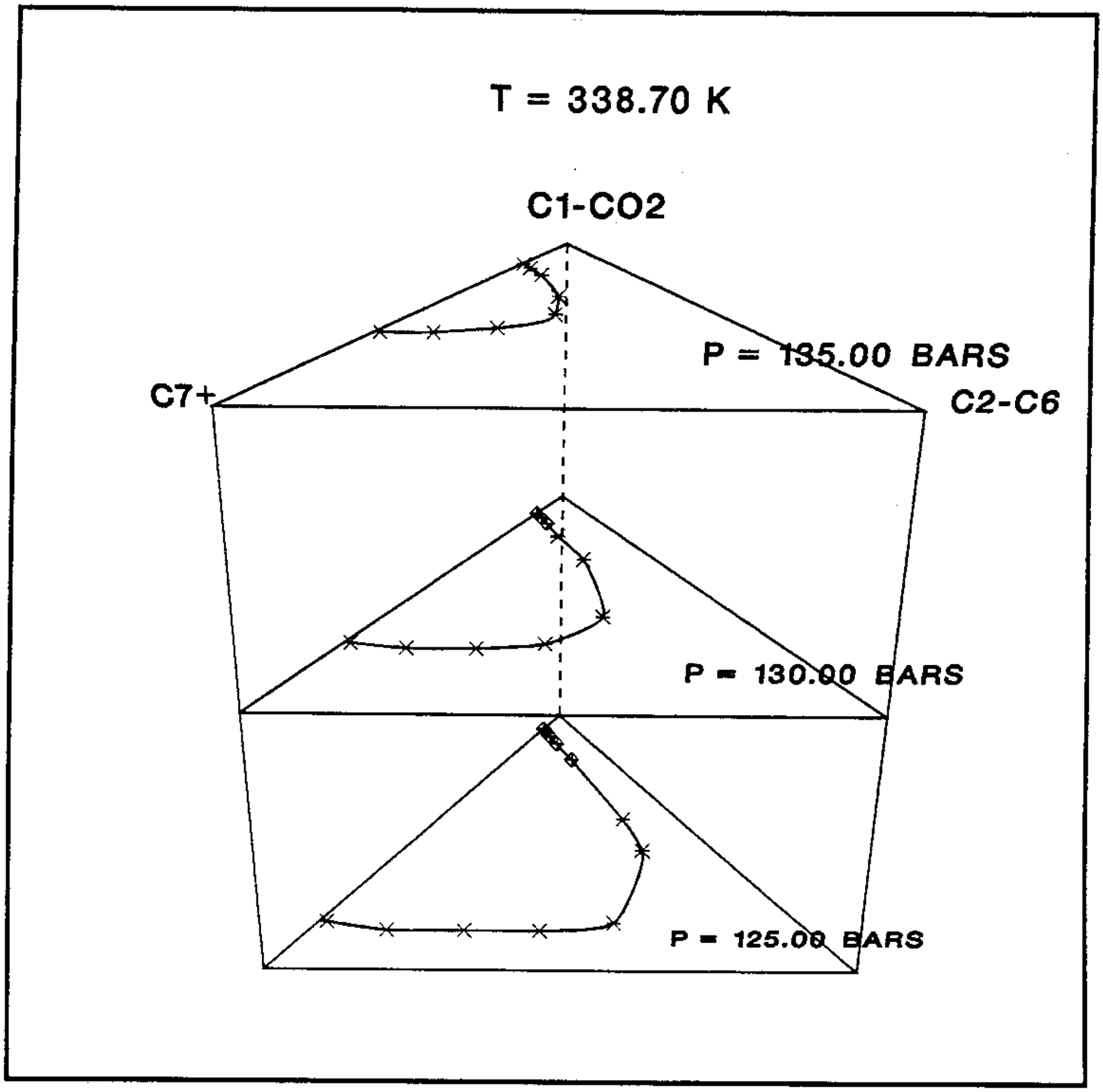

Figure 6. Pseudoternary diagram for CO_2/synthetic oil at 338.70K. Solid line: calculation with pseudoization technique; symbols: exact multicomponent calculation.

(ethane to hexane), and [C_7+] (heptane and heavier fractions). The computer program based on the proposed technique performs a specified number of bubble-point-pressure calculations which will be used in the objective function of the regression analysis. Figure 1 shows the P-X diagram of the [C_2-C_6]+[C_7^+] pseudobinary 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 pseudocomponents but without the pseudobinary interaction parameters and lumping parameters. The dashed line is the result with two pseudocomponents and the pseudobinary interaction parameter, but, without the lumping parameters. The solid line is obtained with two pseudocomponents, the pseudobinary interaction parameter and the lumping parameters. Figure 2 illustrates the same calculations as in Figure 1 for the [C_1]+[C_2-C_6] pseudobinary system. In Figure 3 the P-X diagram of the [C_1]+[C_7^+] pseudobinary system is reported where only the pseudobinary 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 [C_2-C_6] group and a second lumping parameter for the [C_7+] group.

Figures 4-6 are for prediction of the phase behavior of a vaporizing gas drive process with CO_2 as the injected gas and the synthetic oil as the reservoir oil. 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 4 and 5 are used to evaluate the binary interaction parameters between CO_2 and the pseudocomponents of the synthetic mixture. The predicted pseudoternary diagram for this system is shown in Figure 6 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 condensate (Wu and Batycky 1986) system (high in methane and low in heavy hydrocarbons) with the composition as in Table 3 is constructed and it is reported by Figure 7. In this calculation 4 pseudocomponents are chosen which are [CH_4], [N_2], [CO_2,C_2-C_5], and [C_6+].

Table 3. Gas Condensate Composition Used for the Second Application.

Components	Molar fraction (%)
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

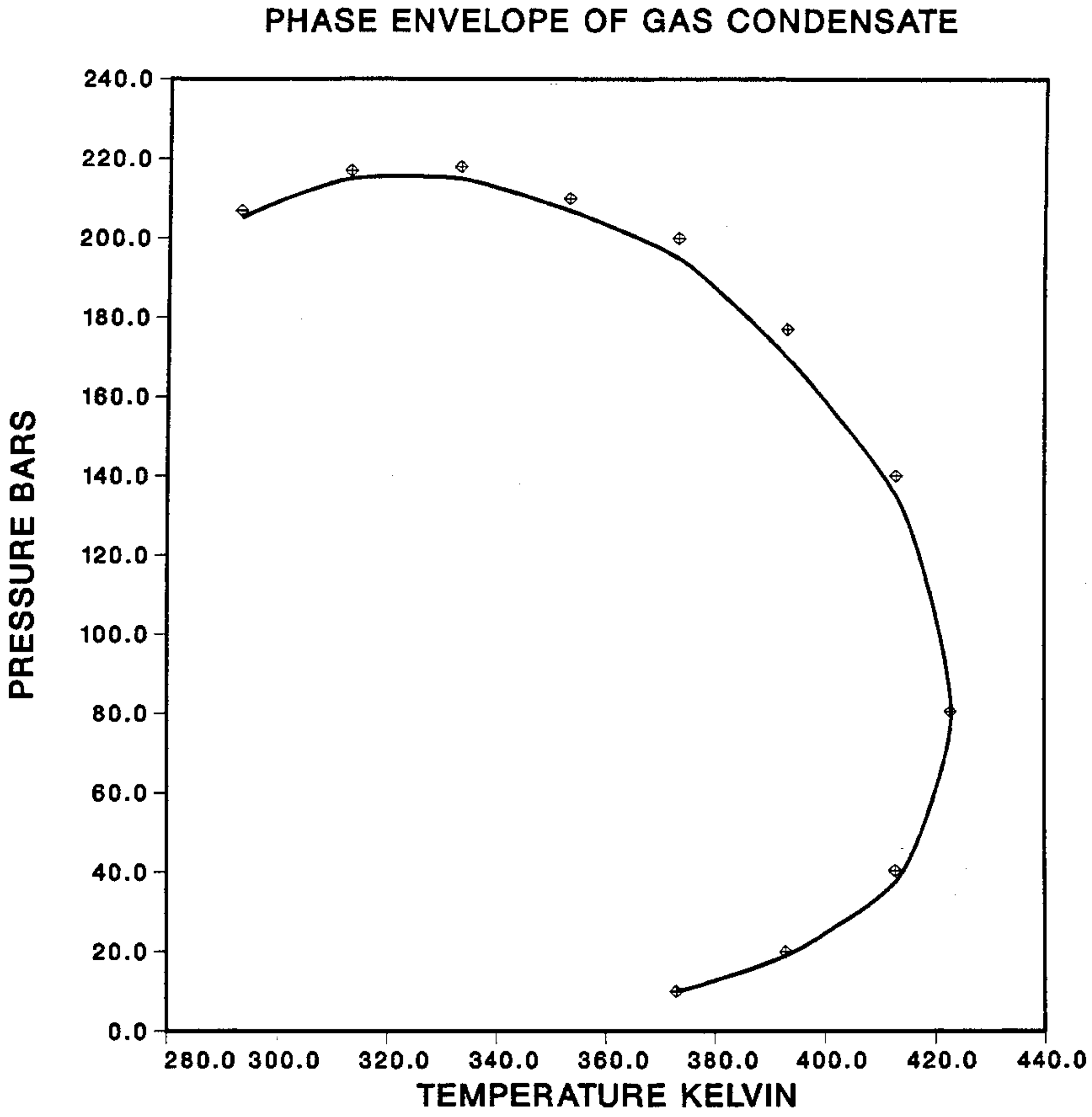

Figure 7. Phase envelope of gas condensate at 338.70K. Solid line: calculation with pseudoization technique; symbols: exact multicomponent calculation.

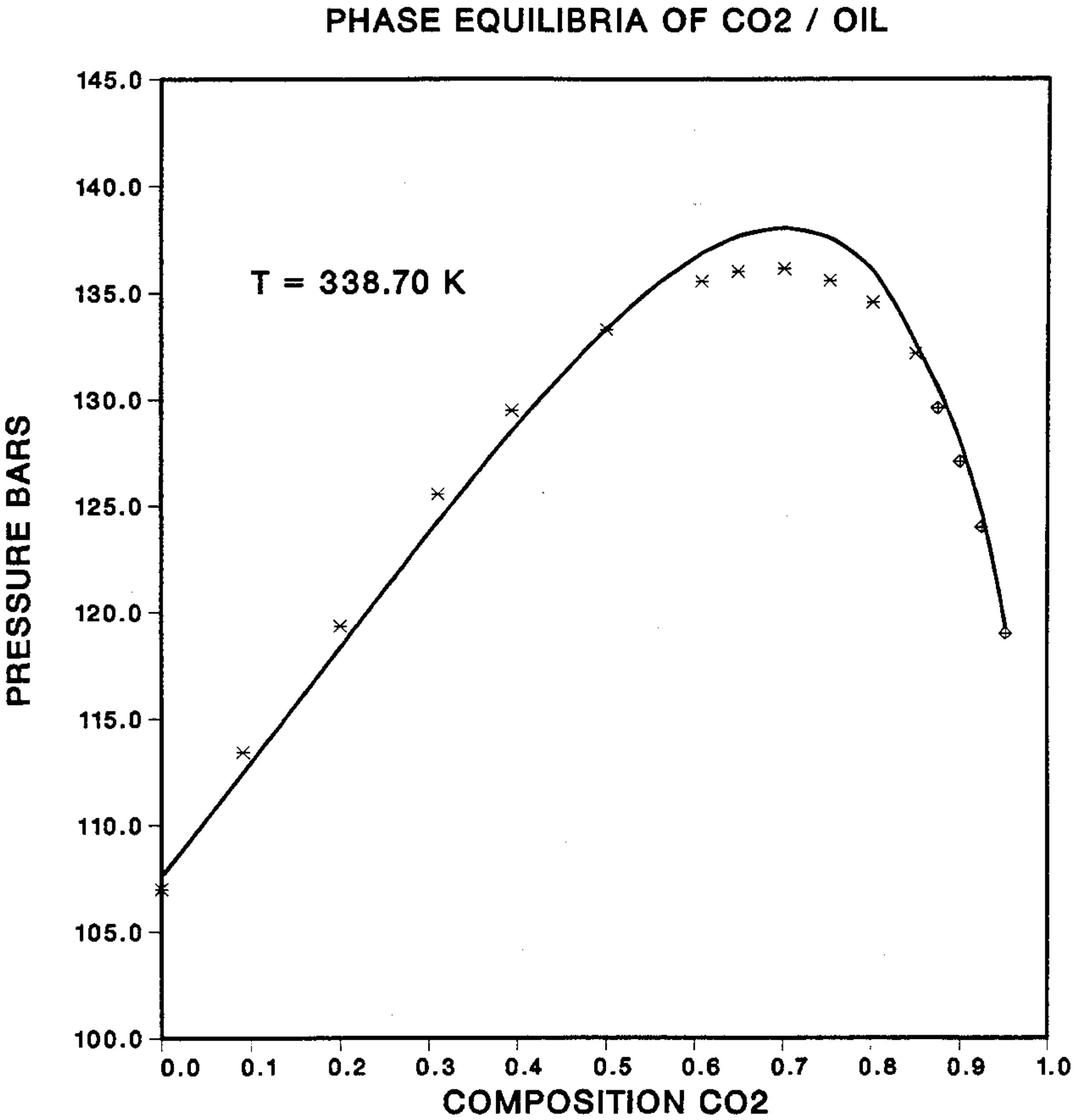

Figure 8. P-X diagram for CO2/reservoir oil at 338.70K. Solid line: calculation with pseudoization technique; symbols: exact multicomponent calculation.

Also, a P-X diagram of carbon dioxide-reservoir oil system (Wu and Batycky 1986) with the composition as in Table 4 is constructed using the same 4 pseudocomponents and it is reported by Figure 8. In both of these cases the results of calculations obtained with the present approach are in very good agreement with the exact multicomponent calculations.

Table 4. Reservoir Oil Composition used for the Second Application.

Components	Molar fraction (%)
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

Third Application

The final application is to establish a relationship between the cricondenbar locus of P-X diagram of a multicomponent mixture and the phase separation regions of the pseudoternary diagram of the same mixture. This kind of relationship is of significant importance in application of pseudoization techniques in high pressure processes such as supercritical fluid extraction of heavy compounds from mixtures and miscible flood enhanced oil recovery.

For every multicomponent mixture at a given composition one can plot a P-T diagram. For the same mixture, provided the temperature and relative composition of c-1 components are kept constant, one can plot a P-X diagram (pressure versus composition of one component). In the present computation we characterize our mixture by three pseudocomponents [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 9 and 10. Also reported in Figures 9 and 10 are the pseudoternary diagrams related to the same mixtures at different pressures.

The major difference between Figures 9 and 10 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 multicomponent mixture.

Figure 9 shows the cases when a multicomponent mixture may exhibit an open phase-envelope ($P<P_d$), a closed phase-envelope ($P_d \leq P<P_b$), or no phase-envelope ($P \geq P_b$) in a pseudoternary diagram representation. In no case one can observe two

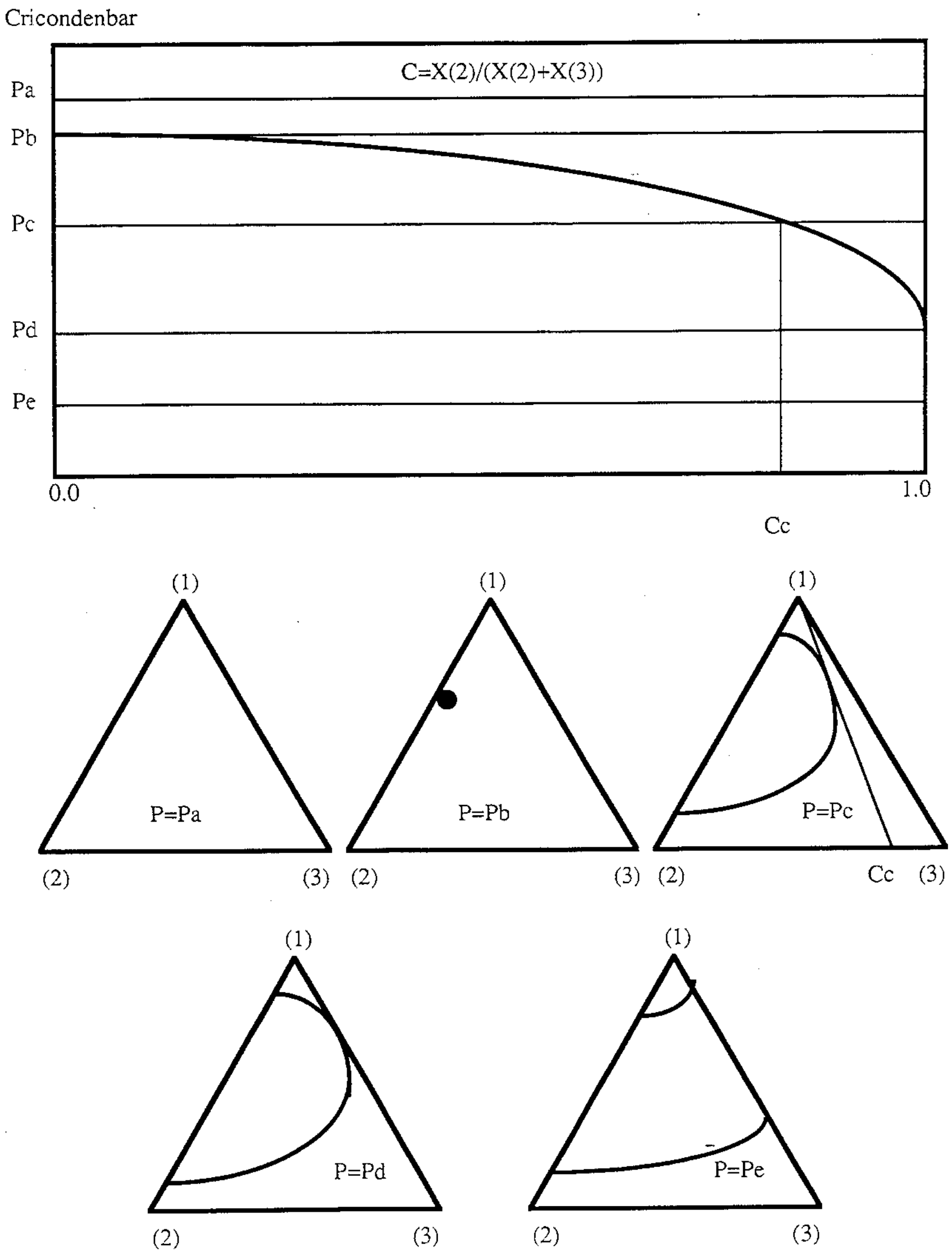

Figure 9. Relationship between cricondenbar locus of P-X diagram and phase separation regions in pseudoternary diagram

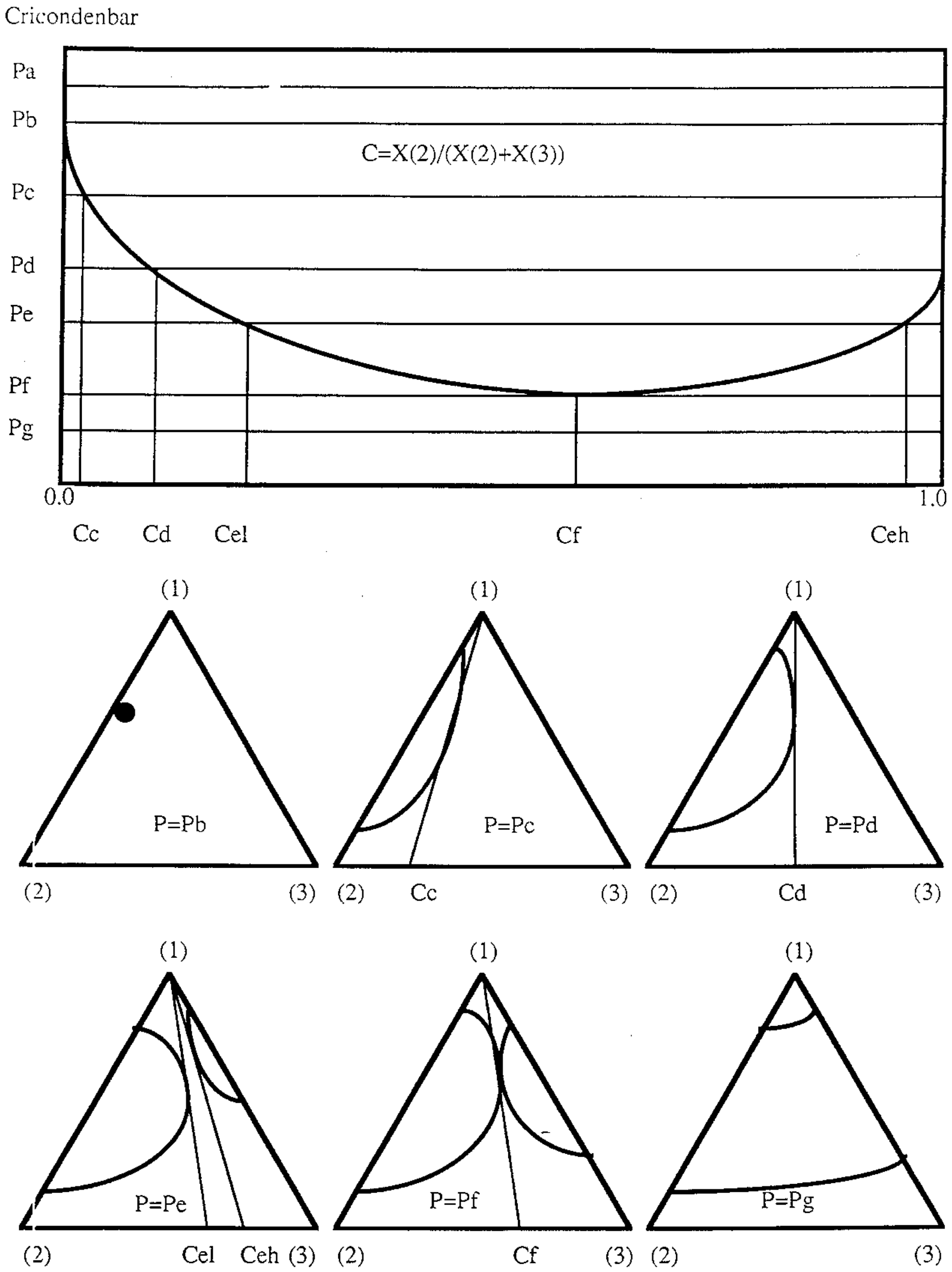

Figure 10. Relationship between cricondenbar locus of P-X diagram and phase separation regions in pseudoternary diagram

closed phase-envelopes when the cricondenbar locus is monotonic with respect to C as it is the case of Figure 9.

Figure 10 shows the cases when a multicomponent mixture may exhibit an open phase-envelope ($P<P_f$), Two closed phase-envelopes ($P_f \leq P<P_d$), one closed phase-envelope ($P_d \leq P<P_b$), or no phase-envelope ($P \geq P_b$) in a pseudoternary diagram representation. The reason for observing two closed phase-envelopes in this case is because the cricondenbar locus has a minimum with respect to C=X(2)/[X(2)+X(3)].

CONCLUSION

The technique proposed here enables one to use a reduced compositional fluid representation in phase behavior simulation without any loss in modeling accuracy. The non-linear regression-based phase behavior algorithm described in this report can have several applications in the simulation processes involving equations of state. These include adjustment of equation of state parameters to match laboratory PVT data, characterization of heavy end fractions, and most importantly large-scale simulation of petroleum field reservoirs. The algorithm is versatile and can be used with any generalized equation of state.

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