

# Phase behavior prediction of petroleum fluids with minimum characterization data

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## Abstract

A new accurate and efficient computational method is presented for property calculation and phase equilibrium prediction of petroleum fluids using a minimum amount of input characterization data. This method is based on the combination of the discrete thermodynamic framework of the light components and a continuous thermodynamic characterization of the plus-fraction in petroleum fluids. The key features of the proposed method are the facts that: (i) the light fraction is specified by a definite number of discrete components with known characterization parameters; (ii) the plus-fraction is characterized by a generalized continuous distribution function in which three average plus-fraction properties, namely, the average molecular weight, the average normal boiling point and the average specific gravity, appear as the input data; (iii) there is no need for this method to characterize various families of hydrocarbons which may be present in the petroleum fluid plus-fraction; (iv) the model is applicable to any equation of state (EOS) and any set of mixing rules and combining rules; (v) the conventional multi-component phase behavior packages as well as continuous (or semi-continuous) phase equilibrium algorithms can be used with this model to predict the equilibrium ratio, gas/oil ratio, and other petroleum fluid properties; (vi) this model has the potential for application in phase behavior predictions with solid deposition which is the case with waxy and asphaltenic condensates and other crude oils. The proposed model is applied for vapor–liquid equilibrium calculation and bulk, liquid and vapor, phases property prediction of several reservoir fluid mixtures for which experimental data are available with success. This method is accurate because it predicts the properties of petroleum reservoir fluids as precisely as any other existing method. It is efficient because it removes the guess work for the characterization of the plus-fraction which has been the major barrier in the efficient calculation of bulk and phase equilibrium properties of petroleum reservoir fluids. © 1999 Published by Elsevier Science B.V. All rights reserved.

*Keywords:* Phase behavior prediction; Petroleum; Minimum characterization data; Light fraction; Plus-fraction

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## 1. Introduction

Petroleum fluids, which include gas condensates, absorber oils, petroleum crude and heavy oil, are in the category of complex mixtures. A complex mixture is defined as one in which various families of compounds

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with diverse molecular properties are present. Knowledge about the phase behavior of these mixtures are of interest in the natural gas and oil production, transportation, processing and refining industries. In petroleum fluid mixtures there could exist various families of hydrocarbons (paraffins, aromatics, naphthenes, etc.), various heavy non-hydrocarbon organic compounds (diamondoids, organometallics, resins, asphaltenes, etc.) and other impurities (such as carbon dioxide, hydrogen sulfide and other sulfur compounds, water, salts, etc.). Due to their complexity and multi-family nature such mixtures would go through various phase transitions which includes, but not limited to, liquid–liquid, liquid–vapor, liquid–solid, solid–solid, etc. Some of these phase transitions are reversible and some of them are irreversible, resulting in dissociated compounds or aggregates. There is a great deal of interest in the petroleum and natural gas industries to develop computational packages to predict the behavior of such mixtures.

The model presented here is an initial attempt to predict the behavior of such mixtures with the least amount of input data necessary. The model developed here is presently limited to hydrocarbon mixtures and their light impurities in liquid and vapor phases in the absence of any dissociation, aggregation, or irreversibility appearing in the system. In this context, we consider a mixture ‘complex’ when its discrete light-component impurities and hydrocarbons (up to a certain carbon number) can be individually identified and characterization of its heavy hydrocarbons called ‘plus-fraction’ are specified.

The major obstacle in the efficient design of processes dealing with hydrocarbon mixtures is the difficulty in the accurate and efficient prediction of their phase behavior and other properties. This is because for many naturally occurring hydrocarbon mixtures complete compositional analysis is not available. As a result, one cannot utilize the existing industrial packages in which identification of all the real and pseudo-components are necessary. Also, in cases where the complete compositional analysis is available, the computational schemes become quite lengthy and inefficient due to the lack of the related pure components characterization parameters and properties. To overcome this difficulty there exist at least two approaches in the literature.

(i) In the first approach which is usually called ‘the pseudo-component approach’ a mixture is divided into known light components and several plus-fractions, with arbitrary parts, consisting of several neighboring species (Chorn and Mansoori, 1989). By using the pseudo-component method for petroleum fluids, the lighter components (for example  $C_1$  to  $C_6$ ) are analytically identified and the heavier parts (in this case  $C_{7+}$  fractions) are empirically split into a number of fractions that each is characterized by one or more average properties. On the other hand, some highly complex petroleum fluids contain various families of compounds such as paraffinic, olefinic, naphthenic and aromatic hydrocarbons for which application of the pseudo-component method would require specification of a very large number of pseudo-components. Thus, accurate phase equilibrium calculation of such complex mixtures by using this approach would demand a great deal of computer time. In addition, the method of selecting the pseudo-components and calculation of their compositions and properties is quite sensitive on the results of the calculations (Chorn and Mansoori, 1989).

(ii) In the second approach which is called ‘continuous mixture approach’, composition of the chemical species are usually described by some continuous distribution functions either in analytical or numerical form, with respect to one or more measurable variables, for example, the molecular weight or boiling point (Du and Mansoori, 1987; Heynes and Matthews, 1991). This method could significantly reduce the computational complexities mentioned above provided the mixture under consideration consists of only one well-defined family of compounds. When the number of the families of compounds exceeds unity this method becomes inefficient and cumbersome. Most of the continuous mixture methods in the literature involve consideration of only one family of hydrocarbons (Du and Mansoori, 1986), or using an averaging technique in taking into account the contribution of several families of hydrocarbons (Radosz et al., 1987).

In order to develop an accurate and efficient phase equilibrium calculation for multi-family petroleum fluid mixtures a new method is introduced here. This method is based on the combination of the discrete thermodynamic framework of the light components and a continuous thermodynamic characterization of the plus-fraction representing the heavy components in petroleum fluids. This method is versatile enough to be applied to a petroleum fluid mixture consisting of any number of families of hydrocarbons. The plus-fraction

equation of state (EOS) parameters generated by this method are functions of a number of average measurable macroscopic properties of the plus-fraction. As a result, they are independent of the number and kind of the families of hydrocarbons present in the mixture which are usually difficult to characterize. This method can be applied to any EOS. But in the present report computations using the Peng–Robinson (PR)-EOS are reported for the sake of comparisons with the existing literature calculations based on this equation.

In what follows we first present the model and the method of characterization used for the construction of the distribution function and property calculation of the plus-fraction. Then, the EOS for the petroleum fluid is formulated and the method of phase equilibrium calculation of such a complex mixtures is presented. Finally, comparisons between the proposed method, previous calculations and the experimental data are reported. These comparisons indicate a quite satisfactory agreement between the experimental data and predictions by the present method.

## 2. Characterization of petroleum fluids

In order to calculate the bulk and phase equilibrium properties of petroleum fluids we need to develop analytical expressions for their thermodynamic functions including the compressibility factor and chemical potentials of components and fractions. Derivation of such expressions requires detailed information about the petroleum fluid constituents and properties known as the ‘characterization’ of petroleum fluids (Chorn and Mansoori, 1989).

Let us consider a petroleum fluid in which many families of hydrocarbons and a number of defined impurities are present. We assume such a complex mixture can be characterized by its light discrete components and impurities compositions ( $x_i$ ) and a continuous plus-fraction with an over-all mole fraction of  $x_{C+}$  and a composition distribution function  $F(I)$ , where  $I$  is an independent variable such as the molecular weight. This assumption is shown to be valid for various petroleum fluids regardless of the nature of their hydrocarbon plus-fractions and the number of families of hydrocarbons present (Riazi, 1989). Considering that the plus-fraction is assumed to be a continuous mixture, functionality of the thermodynamic properties including the compressibility factor and the chemical potential(s) are dependent on the composition of the discrete light components and the plus-fraction distribution function. The probability density function (distribution function) of molecular weight for the plus-fraction of petroleum fluids, regardless of the number of families of hydrocarbons present in them, can be expressed by an expression in the following form.

$$F(I) = \frac{B_{Mw}^2}{I_{C+} A_{Mw}} \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw} - 1} \exp \left[ - \frac{B_{Mw}}{A_{Mw}} \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw}} \right]. \quad (1)$$

In this equation  $I_{C+}$  is the initial value of molecular weight ( $I$ ) for the plus-fraction (molecular weight of component C in the discrete section of a petroleum fluid) and  $A_{Mw}$  and  $B_{Mw}$  are parameters of the distribution function. Eq. (1) is derived from a generalized model for properties of petroleum fluids plus-fraction which is based on a data bank on various properties of a large number of petroleum fluids (crude oils and gas condensates) in the following form (Riazi, 1989).

$$\frac{I - I_{C+}}{I_{C+}} = \left[ \frac{A_{Mw}}{B_{Mw}} \ln \left( \frac{1}{1 - \mathfrak{N}_{Mw}(I)} \right) \right]^{\frac{1}{B_{Mw}}} \quad (2)$$

where  $\mathfrak{N}_m(I) = \int_{I_0}^I \xi_m(J) dJ$  is the cumulative mole fraction of the cuts of the plus-fraction up to the  $i$ th fraction. Knowledge about the molecular weight distribution function of the plus-fraction allows us to calculate the

composition of a pseudo-component,  $\xi_m(I)$ , within the plus-fraction, with a molecular weight in the range of  $I_i$  to  $I_{i+1}$ , using the following expression:

$$\xi_m(I) = \int_{I_i}^{I_{i+1}} F(I) dI. \quad (3)$$

It should be pointed out that a pseudo-component with the composition  $\xi_m(I)$  within the plus-fraction will have a composition of  $[x_{C+} \cdot \xi_m(I)]$  within the whole petroleum fluid. Parameters  $A_{Mw}$ ,  $B_{Mw}$  and  $I_{C+}$ , appearing in Eq. (2), can be determined by fitting Eq. (2) to the experimental molecular weight vs. cumulative mole fraction data of the plus-fraction. For instance, the best estimation for  $I_{C+}$  for heptane-plus fractions, is found to be the average molecular weight of the  $C_6$  hydrocarbons. Furthermore, it is shown that for most of the petroleum fluids, parameter  $B_{Mw}$  can be set equal to unity. In the latter case, with known values for  $I_{C+}$  and  $B_{Mw} = 1$ , parameter  $A_{Mw}$  will be equal to  $\bar{I}$  which is the average molecular weight of the plus-fraction.

Generally, the average value of the molecular weight,  $\bar{I}$ , can be calculated from the first moment of Eq. (1) with respect to  $I$ :

$$\bar{I} = \int_I I F(I) dI. \quad (4)$$

Calculation of the first moment of Eq. (1) will give:

$$\frac{\bar{I} - I_{C+}}{I_{C+}} = \left( \frac{A_{Mw}}{B_{Mw}} \right)^{1/B_{Mw}} \Gamma \left( 1 + \frac{1}{B_{Mw}} \right) \quad (5)$$

where  $\Gamma$  represents the gamma function. When  $B_{Mw}$  is approximated to be unity, which is shown to be valid for most of the petroleum fluids studied, we obtain the following simple expression for the average molecular weight,  $\bar{I}$ :

$$\frac{\bar{I} - I_{C+}}{I_{C+}} = A_{Mw} \quad \text{when } B_{Mw} = 1. \quad (6)$$

Then this equation can be used to estimate the numerical value of parameter  $A_{Mw}$  of the distribution function from the knowledge of the initial,  $I_{C+}$ , and average,  $\bar{I}$ , molecular weights of the plus-fraction.

In order to perform bulk property and phase equilibrium calculation for a petroleum fluid at various conditions of temperature and pressure, we need to use equations of state. Parameters of majority of equations of state for a fluid mixture are expressed with respect to the critical properties, acentric factor, unlike interaction parameters, and compositions of components of the mixture under consideration. For the plus-fraction of a petroleum fluid mixture, narrow range fractions can be assumed as discrete pseudo-components. Then, the following equations for the critical temperature, critical pressure and acentric factor of narrow range petroleum fractions may be used (American Petroleum Institute, 1988):

$$T_c(I) = 10.6443 \left[ \exp \left( -5.1747 \times 10^{-4} T_b(I) - 0.5444 S_g(I) + 3.5995 \times 10^{-4} T_b(I) S_g(I) \right) \right] \\ \times T_b(I)^{0.81067} S_g(I)^{0.53691} \quad \text{when: } 70 \leq I \leq 295 \quad (7)$$

$$P_c(I) = 6.162 \times 10^6 \left[ \exp \left( -4.725 \times 10^{-3} T_b(I) - 4.801 S_g(I) + 3.1939 \times 10^{-3} T_b(I) S_g(I) \right) \right] \\ \times T_b(I)^{-0.4844} S_g(I)^{4.0846} \quad \text{when } 70 \leq I \leq 295. \quad (8)$$

and

$$\omega(I) = -\log [P^s(I)/P_c(I)] - 1.0 @ T_r = 0.7 \quad (9)$$

where:

$$\log(P^s(I)) = \frac{3000.538E(I) - 6.76156}{43E(I) - 0.987672} \quad \text{when } E(I) > 0.0022, \quad (10)$$

$$\log(P^s(I)) = \frac{2663.129E(I) - 5.994296}{95.76E(I) - 0.972546} \quad \text{when } 0.0022 \geq E(I) \geq 0.0013, \quad (11)$$

$$\log(P^s(I)) = \frac{2770.085E(I) - 6.41263}{36E(I) - 0.989679} \quad \text{when } E(I) < 0.0013 \quad (12)$$

and

$$E(I) = \frac{T_b(I)/0.7T_c(I) - 0.0002867T_b(I)}{748.1 - 0.2145T_b(I)}. \quad (13)$$

In the above expressions  $T_b(I)$  is the true boiling point,  $S_g(I)$  is the specific gravity, and  $P^s(I)$  is the vapor pressure of the  $i$ th cut of the plus-fraction. According to these equations the critical temperature and pressure are calculated as functions of the true boiling point and specific gravity of petroleum cuts, the acentric factor is calculated as a function of the petroleum cut critical temperature and vapor pressure. Vapor pressure of petroleum cut is also expressed with respect to its true boiling point and critical temperature.

Knowing the values of the true boiling point and specific gravity for narrow range cuts, one can calculate parameters of an EOS for the plus-fraction of a petroleum fluid. In the limiting case when we could consider a very large number of narrow cuts in the plus-fraction, values of  $T_b(I)$  and  $S_g(I)$  can then be expressed as continuous functions. For the purpose of calculating these functions, one could use a continuous model for distributions of specific gravity and true boiling point of petroleum plus-fraction cuts. The following correlation is proposed (Riazi, 1989) for the true boiling of a hydrocarbon-plus-fraction with a known cumulative weight fraction,  $\xi_w(J)$ ,

$$\mathbf{x}_w(I) = \int_{I_0}^I \xi_w(J) dJ:$$

$$T_b^* = \frac{T_b - T_{b_0}}{T_{b_0}} = \left[ \frac{A_{T_b}}{B_{T_b}} \ln \left( \frac{1}{1 - \mathbf{x}_w(I)} \right) \right]^{1/B_{T_b}} \quad (14)$$

where  $A_{T_b}$ ,  $B_{T_b}$  and  $T_{b_0}$  are constants for a given petroleum fluid and  $\xi_w(J)$  is the weight fraction of the  $j$ th part (cut) of a hydrocarbon-plus-fraction. A similar correlation was also proposed (Riazi, 1989) for the specific gravity of a hydrocarbon-plus fraction with known cumulative volume fraction,  $\mathbf{x}_v(I) = \int_{I_0}^I \xi_v(J) dJ$ :

$$S_g^* = \frac{S_g - S_{g_0}}{S_{g_0}} = \left[ \frac{A_{S_g}}{B_{S_g}} \ln \left( \frac{1}{1 - \mathbf{x}_v(I)} \right) \right]^{1/B_{S_g}} \quad (15)$$

where  $A_{S_g}$ ,  $B_{S_g}$ , and  $S_{g_0}$  are constants for a given petroleum fluid and  $\xi_v(J)$  is the volume fraction of the  $j$ th part (cut) of the plus-fraction. In general, parameters of the above two correlations may be determined by fitting them to the experimental data. However, the following expressions can be derived for the average specific gravity and average true boiling point.

$$\bar{T}_b = \int_{I_0}^{\infty} \xi_w(I) T_b(I) dI = T_{b_0} \left[ 1 + \left( \frac{A_{T_b}}{B_{T_b}} \right)^{1/B_{T_b}} \Gamma \left( 1 + \frac{1}{B_{T_b}} \right) \right] \quad (16)$$

$$\bar{S}_g = \int_{I_0}^{\infty} \xi_v(I) S_g(I) dI = S_{g_0} \left[ 1 + \left( \frac{A_{S_g}}{B_{S_g}} \right)^{1/B_{S_g}} \Gamma \left( 1 + \frac{1}{B_{S_g}} \right) \right] \quad (17)$$

The expressions for  $\xi_w$  and  $\xi_v$  appearing in the above equations represent the distributions of specific gravity and the true boiling point, respectively. They are expressed with respect to  $F(I)$  by the following equations.

$$\xi_w(I) = \frac{I}{\int_I F(I) I dI} F(I) \quad (18)$$

$$\xi_v(I) = \frac{I/S_{g_i}}{\int_I F(I) I/S_{g_i} dI} F(I) \quad (19)$$

Furthermore, it is recommended (Riazi, 1989) to use the fixed values of  $B_{T_b} = 1.5$  and  $B_{S_g} = 3$  for most of the petroleum fluids in the absence of available data. In this case Eqs. (16) and (17) can be solved to calculate parameters  $A_{T_b}$  and  $A_{S_g}$  from the average and initial true boiling point and average and initial specific gravity in the following forms.

$$A_{T_b} = 1.7485 \left( \frac{\bar{T}_b}{T_{b_0}} - 1 \right)^{3/2} \quad \text{when } B_{T_b} = 1.5 \quad (20)$$

$$A_{S_g} = 4.2163 \left( \frac{\bar{S}_g}{S_{g_0}} - 1 \right)^3 \quad \text{when } B_{S_g} = 3.0 \quad (21)$$

It should be noted that  $T_{b_0}$  and  $S_{g_0}$  are the average true boiling point and the average specific gravity, respectively, of the lightest (or first) component of the plus-fraction. In practice, for heptane—plus-fractions, a good estimate for  $T_{b_0}$  and  $S_{g_0}$  are the average true boiling point and specific gravity of the  $C_6$  hydrocarbons, respectively.

In order to calculate critical properties and acentric factor as functions of molecular weight, it is necessary to express  $T_b$  and  $S_g$  with respect to the molecular weight ( $I$ ). To do this we need to express  $\mathfrak{K}_w(I)$  and  $\mathfrak{K}_v(I)$  as functions of molecular weight. From Eq. (2) we can express cumulative mole fraction  $\mathfrak{K}_m(I)$  with respect to  $I$  in the following form.

$$\mathfrak{K}_m(I) = 1 - \frac{1}{\exp \left[ \frac{B_{Mw}}{A_{Mw}} \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw}} \right]}. \quad (22)$$

Considering the relation between the cumulative mole fraction,  $\mathfrak{K}_m(I)$ , and the distribution function  $F(I)$ :

$$d\mathfrak{K}_m(I) = F(I) dI \quad (23)$$

and the relations between the weight fraction,  $\xi_w(I)$ , and volume fraction,  $\xi_v(I)$ , with respect to the molecular weight distribution function  $F(I)$ , Eqs. (18) and (19), we will derive the following expressions for  $\mathfrak{N}_w(I)$  and  $\mathfrak{N}_v(I)$  as functions of  $I$ .

$$\mathfrak{N}_w(I) = \frac{\int_{I_{C+}}^I \frac{B_{Mw}^2}{A_{Mw}} I \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw}-1} \left[ \exp \left( \frac{-B_{Mw}}{A_{Mw}} \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw}} \right) \right] dI}{\int_{I_{C+}}^{\infty} \frac{B_{Mw}^2}{A_{Mw}} I \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw}-1} \left[ \exp \left( \frac{-B_{Mw}}{A_{Mw}} \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw}} \right) \right] dI} \quad (24)$$

$$\mathfrak{N}_v(I) = \frac{\int_{I_{C+}}^I \frac{B_{Mw}^2}{A_{Mw}} I \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw}-1} \left( \exp \left( \frac{-B_{Mw}}{A_{Mw}} \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw}} \right) \right) / S_g(I) dI}{\int_{I_{C+}}^{\infty} \frac{B_{Mw}^2}{A_{Mw}} I \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw}-1} \left( \exp \left( \frac{-B_{Mw}}{A_{Mw}} \left( \frac{I - I_{C+}}{I_{C+}} \right)^{B_{Mw}} \right) \right) / S_g(I) dI} \quad (25)$$

After integration of the integrals appearing in Eq. (25) and substitution of the result for  $\mathfrak{N}_w(I)$  in Eq. (14), we will derive the following expression for the true boiling point distribution with respect to the molecular weight of the plus-fraction:

$$\left[ \frac{T_b(I) - T_{b0}}{T_{b0}} \right]^{3/2} = 1.16566 \left[ \frac{\bar{T}_b - T_{b0}}{T_{b0}} \right]^{3/2} \left[ \frac{I - I_{C+}}{\bar{I} - I_{C+}} - \ln \left( \frac{I + \bar{I} - I_{C+}}{\bar{I}} \right) \right]. \quad (26)$$

Similarly, one can derive the following expression for the specific gravity distribution with respect to the molecular weight of the plus-fraction by integrating the integrals in Eq. (26) and substitution of the result for  $\mathfrak{N}_v(I)$  in Eq. (15):

$$\left[ \frac{S_g(I) - S_{g0}}{S_{g0}} \right]^3 = 1.411 \left[ \frac{\bar{S}_g - S_{g0}}{S_{g0}} \right]^3 \left[ \frac{\bar{S}_g}{\bar{I}} \sum_{J=I_0}^I \frac{J}{S_g(J)} \exp \left( \frac{I_{C+} - J}{\bar{I} - I_{C+}} \right) \Delta J \right] \quad (27)$$

where:  $\Delta J = I_j - I_{j-1}$

Since the specific gravity,  $S_g(I)$ , appears in both the right and the left sides of Eq. (28), this equation is an implicit function of  $S_g(I)$ . Because of this calculation of specific gravity as a function of molecular weight must be performed by a trial and error method.

Substitution of Eqs. (26) and (27) in Eqs. (7)–(12) will give the distribution of critical properties and acentric factor of the plus-fraction as functions of its molecular weight.

### 3. Formulation of the equation of state for petroleum fluids

In this section we illustrate the application of the present method in formulating equations of state for petroleum fluids. This method is equally applicable to all the equations of state in which parameters are expressed with respect to the critical properties. The PR-EOS is one such equation for which the phase equilibrium computational results with some other model calculations are available. The usual form of the PR-EOS which is reported in the literature is

$$p = \frac{RT}{(v-b)} - \frac{a(T)}{v^2 + 2bv - b^2}. \quad (28)$$

When this EOS is applied for mixtures, its parameters  $a$  and  $b$  are expressed with respect to the mole fractions by the following mixing rules.

$$a = \sum_i \sum_j x_i x_j a_{ij} \text{ and } b = \sum_i x_i b_i \quad (29)$$

It should be pointed out that there are other possibilities for choosing mixing rules for parameters  $a$  and  $b$  (Mansoori, 1993), but for the sake of comparisons with previous calculations based on the PR-EOS we use the above set of mixing rules. For  $a_{ij}$ , the cross-energy parameter, we use the following conventional combining rule as well,

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - k_{ij}) \quad (30)$$

where  $k_{ij}$  is the adjustable unlike-interaction (coupling) parameter. Parameters  $a_{ii}$  and  $b_i$  of the PR-EOS are expressed with respect to the critical properties and acentric factor of component  $i$  by the following expressions:

$$a_{ii} = \frac{0.45724 R^2 T_{c_i}^2 \left[ 1 + m_i \left( 1 - \sqrt{T/T_{c_i}} \right) \right]^2}{P_{c_i}}, \quad (31)$$

$$b_i = 0.0778 R T_{c_i} / P_{c_i} \quad (32)$$

and parameter  $m_i$  is expressed with respect to the acentric factor,  $\omega_i$  the following expression:

$$m_i = 0.37464 + 1.54226 \cdot \omega_i - 0.26992 \cdot \omega_i^2. \quad (33)$$

In order to extend application of the above equations to a complex mixture consisting of several light discrete components and one continuous plus-fraction, the mixing rules for  $a$  and  $b$ , Eq. (29), are written, in the following forms:

$$a = \sum_{i=1}^C \sum_{j=1}^C x_i x_j a_{ij} + 2 x_{C+} \sum_{j=1}^C x_j \int_I F(I) a_j(I) dI + x_{C+}^2 \int_I \int_J F(I) a(I, J) \cdot dI dJ \quad (34)$$

$$b = \sum_{i=1}^C x_i b_i + x_{C+} \int_I b(I) F(I) \cdot dI \quad (35)$$

where  $C$  is the number of discrete components and  $x_{C+}$  is the mole fraction of the total plus-fraction in the petroleum fluid. The other variables and parameters appearing in these equations are already defined. In these equations the light discrete components are shown by small-letter indices ( $i$  and  $j$ ) and the continuous plus-fraction components are represented by capital-letter indices ( $I$  and  $J$ ). Considering this, the expressions for the  $a_j(I)$ , resulting from the interaction between the discrete  $j$ th component and the continuous  $I$ th cut will be:

$$a_j(I) = (a_j)^{0.5} [a(I)]^{0.5} [1 - k_j(I)]. \quad (36)$$

Similarly, the expressions for the  $a(I, J)$ , resulting from the interaction between the continuous  $J$ th component and continuous  $I$ th cut will be:

$$a(I, J) = [a(J)]^{0.5} [a(I)]^{0.5} [1 - k(I, J)]. \quad (37)$$

For the light discrete components the critical properties and acentric factor data are available in the literature (American Petroleum Institute, 1988). Thus, the summation parts of Eqs. (34) and (35) can be calculated by substitution of the critical properties of the light discrete components in Eqs. (32)–(34) and using their molar composition in the mixture.



For cuts of the plus-fraction of the oil we use expressions  $T_c(I)$ ,  $P_c(I)$  and  $\omega(I)$  given by Eqs. (7)–(13) which are expressed as functions of the molecular weight ( $I$ ). By substituting  $T_c(I)$ ,  $P_c(I)$  and  $\omega(I)$ , given by Eqs. (7)–(9), in Eqs. (31)–(33) one can calculate parameters  $a(I)$  and  $b(I)$  as functions of the molecular weight and temperature.

At this stage we write parameter  $a_{ii}$  in the following form in order to separate constants from the variable, which in this case is the temperature:

$$a_{ii} = (a_{1i} - a_{2i}\sqrt{T})^2. \quad (38)$$

Considering the definition of  $a_{ii}$  given by Eq. (32) we will have the following expressions for  $a_{1i}$  and  $a_{2i}$ .

$$a_{1i} = (1 + m_i) \sqrt{0.457235 R^2 T_{c_i}^2 / P_{c_i}} \quad (39)$$

$$a_{2i} = m_i \sqrt{0.457235 R^2 T_{c_i} / P_{c_i}} \quad (40)$$

Let us also consider the assumption that only methane/plus-fraction-cuts unlike-interaction parameters are

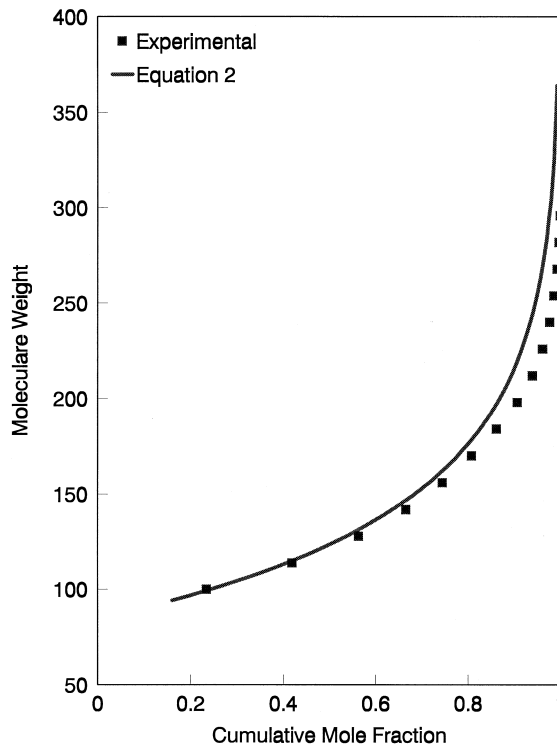


Fig. 1. Prediction of the molecular weight of the plus-fraction vs. cumulative mole fraction for a gas condensate using Eq. (2) and comparison with the experimental data of Hoffman et al. (1953).

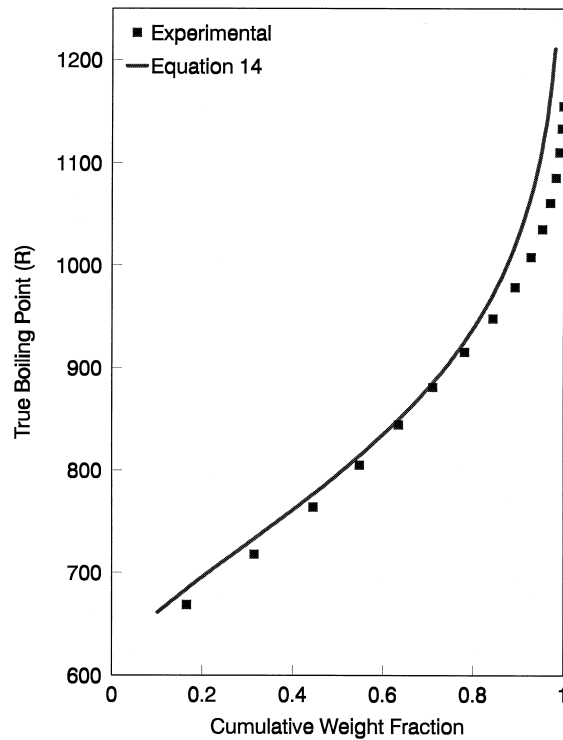


Fig. 2. Prediction of the true boiling point of the plus-fraction vs. cumulative weight fraction for a gas condensate using Eq. (14) and comparison with the experimental data of Hoffman et al. (1953).

significant to be included in the EOS calculation of petroleum fluids. As a result, the following correlation for  $k_{ij}$  is used in the present calculations (Angelos et al., 1992; Du and Mansoori, 1986):

$$\left. \begin{array}{l} k_1(I) = 0.14S_g(I) - 0.0668 \quad \text{for all values of } I \\ k_j(I) = 0 \quad \text{for all values of } I \text{ \& for } j \neq 1 \\ k_{ij} = 0 \quad \text{for all values of } i \text{ \& } j \end{array} \right\} \quad (41)$$

In the above equation  $k_j(I)$  is the unlike-interaction parameter between methane and the plus-fraction cut ( $I$ ). Then, by replacing the unlike-interaction parameters, Eq. (41), in Eqs. (34), (36) and (37) we will derive the following expression for parameter  $a$ .

$$a = \left[ \sum_{i=1}^C x_i a_i^{0.5} \right]^2 + 2 \sum_{j=1}^C x_j x_{C+} \int_I F(I) a(I)^{0.5} a_j^{0.5} [1 - k_j(I)] dI + \left[ x_{C+} \int_I F(I) a(I)^{0.5} dI \right]^2 \quad (42)$$

In the above equation  $a(I) = [a_1(I) - a_2(I)\sqrt{T}]^2$ . Replacing  $a_{1i}$  and  $a_{2i}$  and defining  $a_{C+}$  and  $a_{S_g C+}$ , Eq. (42) changes to the following form:

$$\begin{aligned} a = & \left[ \sum_{i=1}^C x_i a_{1i} - \sqrt{T} \sum_{i=1}^C x_i a_{2i} \right]^2 + 2x_{C+} x_1 [a_{11} - \sqrt{T} a_{21}] (1.0668 a_{C+} + 0.14 a_{S_g C+}) \\ & + 2x_{C+} a_{C+} \left[ \sum_{j=2}^C x_j a_{1j} - \sqrt{T} \sum_{j=2}^C x_j a_{2j} \right] + x_{C+}^2 a_{C+}^2 \end{aligned} \quad (43)$$

and the following definitions are used for  $a_{C+}$  and  $a_{S_g C+}$ :

$$a_{C+} = \int_I F(I) a_1(I) dI - \sqrt{T} \int_I F(I) a_2(I) dI = a_{1C+} - \sqrt{T} a_{2C+} \tag{44}$$

$$a_{S_g C+} = \left[ \int_I F(I) a_1(I) S_g(I) dI - \sqrt{T} \int_I F(I) a_2(I) S_g(I) dI \right] = a_{1S_g C+} - \sqrt{T} a_{2S_g C+}. \tag{45}$$

Also the expression for  $b$  can be written in the following form:

$$b = \sum_{i=1}^C x_i b_i + x_{C+} b_{C+} \tag{46}$$

where  $b_{C+}$ , the parameter of the plus-fraction, is defined by the following expression:

$$b_{C+} = \int_I b(I) F(I) \cdot dI. \tag{47}$$

Using the distribution function of the plus-fraction,  $F(I)$ , and functionalities of the critical properties, acentric factor and specific gravity vs. molecular weight, one can calculate  $a_{C+}$ ,  $a_{S_g C+}$  and  $b_{C+}$ , numerically.

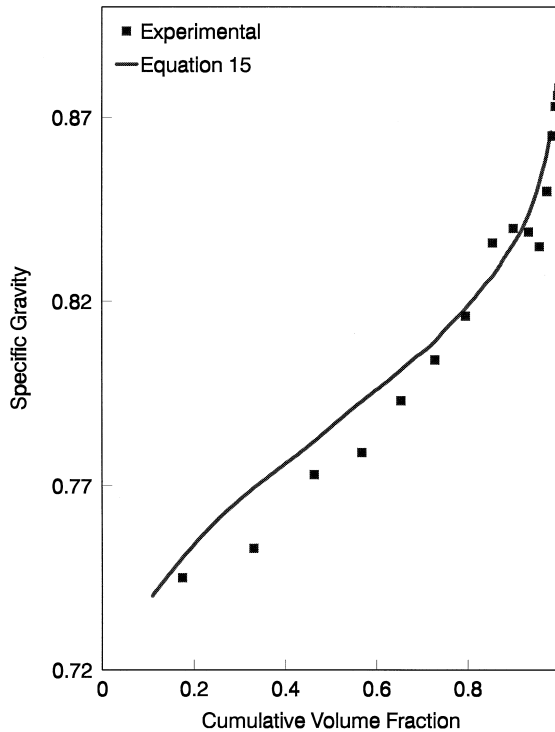


Fig. 3. Prediction of the specific gravity of the plus-fraction vs. cumulative volume fraction for a gas condensate using Eq. (15) and comparison with the experimental data of Hoffman et al. (1953).

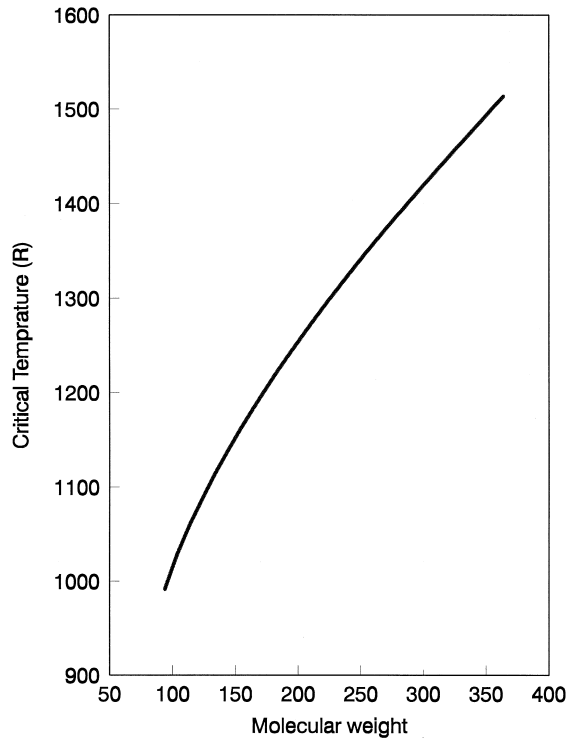


Fig. 4. Prediction of the critical temperature of the plus-fraction vs. mole fraction for the Hoffman et al. (1953) gas condensate using the present method.

In order to produce analytic solutions for these we suggest to correlate the data for  $a_1(I)$ ,  $a_2(I)$  and  $b(I)$  to the following third-order polynomials with respect to the molecular weight of the plus-fractions.

$$a_1(I) = g_{11} + g_{12}I + g_{13}I^2 + g_{14}I^3 \quad (48)$$

$$a_2(I) = g_{21} + g_{22}I + g_{23}I^2 + g_{24}I^3 \quad (49)$$

$$a_1(I)S_g(I) = g_{31} + g_{32}I + g_{33}I^2 + g_{34}I^3 \quad (50)$$

$$a_2(I)S_g(I) = g_{41} + g_{42}I + g_{43}I^2 + g_{44}I^3 \quad (51)$$

$$b(I) = g_{51} + g_{52}I + g_{53}I^2 + g_{54}I^3 \quad (52)$$

These third-order polynomials were shown to fit well all the available plus-fraction petroleum fluid data for parameters  $a_1(I)$ ,  $a_2(I)$ ,  $a_1(I)S_g(I)$ ,  $a_2(I)S_g(I)$  and  $b(I)$ . By substituting Eqs. (48)–(52) into Eqs. (44), (46) and (47) and integration in the range of  $I_{C+}$  (representing the initial molecular weight of the plus-fraction) to  $I_f$  (representing the highest molecular weight of the plus-fraction which in some cases may be taken as infinity), we can produce analytic expressions for parameters  $a_{1C+}$ ,  $a_{2C+}$ ,  $a_{1S_gC+}$ ,  $a_{2S_gC+}$  and  $b_{C+}$ , appearing in Eqs. (44)–(47), in the following forms:

$$a_{1C+} = \alpha_{11} - \alpha_{12} \cdot \exp\left(\frac{-1}{A_{Mw}} \cdot \frac{I_f - I_{C+}}{I_{C+}}\right), \quad (53)$$

$$a_{2C+} = \alpha_{21} - \alpha_{22} \cdot \exp\left(\frac{-1}{A_{Mw}} \cdot \frac{I_f - I_{C+}}{I_{C+}}\right), \quad (54)$$

$$a_{1S_g C+} = \alpha_{31} - \alpha_{32} \cdot \exp\left(\frac{-1}{A_{Mw}} \cdot \frac{I_f - I_{C+}}{I_{C+}}\right), \quad (55)$$

$$a_{2S_g C+} = \alpha_{41} - \alpha_{42} \cdot \exp\left(\frac{-1}{A_{Mw}} \cdot \frac{I_f - I_{C+}}{I_{C+}}\right), \quad (56)$$

and

$$b_{C+} = \alpha_{51} \alpha_{52} \cdot \exp\left(\frac{-1}{A_{Mw}} \cdot \frac{I_f - I_{C+}}{I_{C+}}\right) \quad (57)$$

where parameters  $\alpha_{q1}$  and  $\alpha_{q2}$ , ( $q = 1, 2, 3, 4, 5$ ), appearing in the above expressions will have the following general forms:

$$\alpha_{q1} = g_{q1} + g_{q2} I_{C+} (1 + A_{Mw}) + g_{q3} I_{C+}^2 (1 + 2 A_{Mw} + 2 A_{Mw}^2) + g_{q4} I_{C+}^3 (1 + 3 A_{Mw} + 6 A_{Mw}^2 + 6 A_{Mw}^3)$$

and

$$\alpha_{q2} = \alpha_{q1} + [g_{q2} + 2 g_{q3} I_{C+} (1 + A_{Mw}) + 3 g_{q4} I_{C+}^2 (1 + 2 A_{Mw} + 2 A_{Mw}^2)] (I_f - I_{C+}) + [g_{q3} + 3 g_{q4} I_{C+} (1 + A_{Mw})] (I_f - I_{C+})^2 + g_{q4} I_{C+}^3 A_{Mw}^3 (I_f - I_{C+})^3.$$

It should be pointed out that all the constants appearing in the right-hand sides of the above two equations are already defined. In case when for the integrals appearing in Eqs. (44)–(47) integrations are performed in the range of  $I_{C+}$  to  $I_f = \infty$  and since  $A_{Mw}$  is a positive value, the second term in Eqs. (53)–(57) becomes zero.

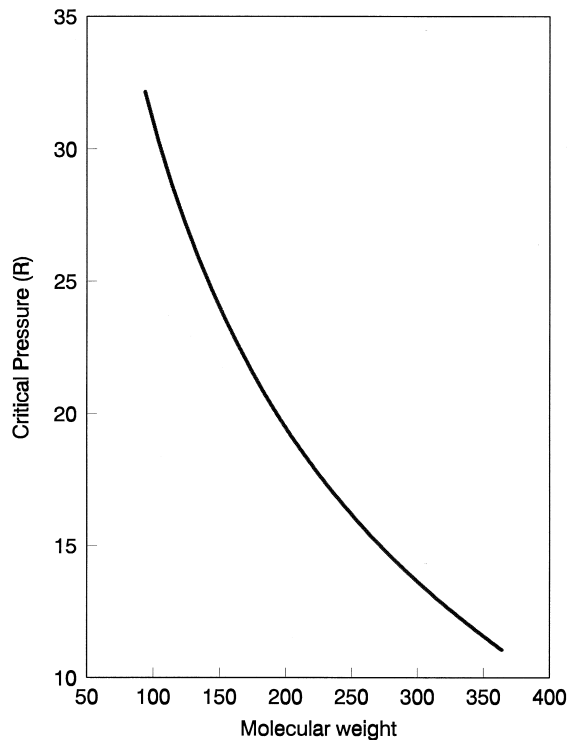


Fig. 5. Prediction of the critical pressure of the plus-fraction vs. mole fraction for the Hoffman et al. (1953) gas condensate using the present method.

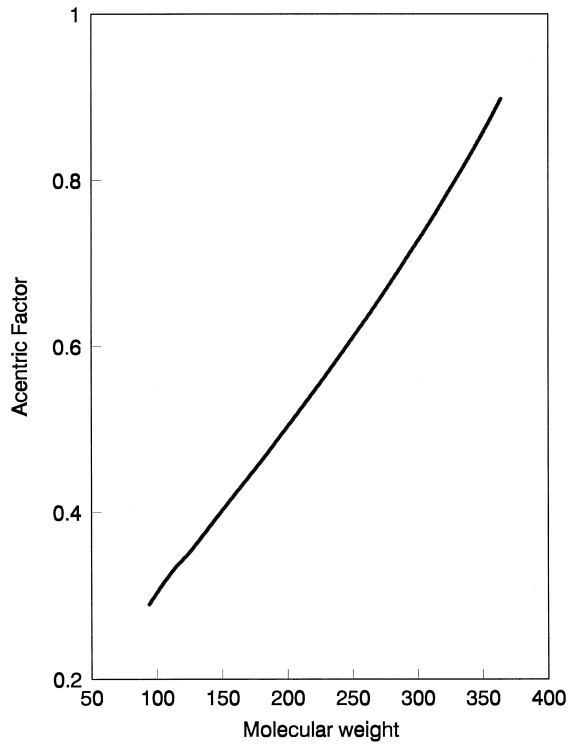


Fig. 6. Prediction of the acentric factor of the plus-fraction vs. mole fraction for the Hoffman et al. (1953) gas condensate using the present method.

In order to perform phase equilibrium calculations, the equality of chemical potentials of discrete components and continuous plus-fraction of oil are utilized. The general expression of chemical potential for the discrete components is as follows.

$$\mu_i - \mu_i^o = \int_V^{\infty} \left( \frac{\partial P}{\partial n_i} - \frac{RT}{V} \right) dV - RT \cdot \ln \left( \frac{V}{RTn_i} \right) + RT. \quad (58)$$

By inserting the expression for pressure in this equation and after integrations, we get the following expression for the chemical potentials of the light discrete components of oil:

$$\mu_i - \mu_i^o = -d_1 + \frac{(n^2 a)'}{n} d_2 + (nb)' d_3 - d_4 + RT \quad \text{where } i = l \rightarrow C \quad (59)$$

where  $n$  is the total number of moles of the mixture and variable  $d_1$  to  $d_4$  are defined as follows:

$$d_1 = RT \cdot \ln(v - b),$$

$$d_2 = \frac{1}{2\sqrt{2}b} \cdot \ln \left( \frac{v + (1 - \sqrt{2})b}{v + (1 + \sqrt{2})b} \right),$$

$$d_3 = \frac{RT}{v - 1b} - \frac{(1 + \sqrt{2})a}{2\sqrt{2}b} \left( \frac{1}{v - (1 + \sqrt{2})b} + d_2 \right) + \frac{(1 - \sqrt{2})a}{2\sqrt{2}b} \left( \frac{1}{v - (1 - \sqrt{2})b} + d_2 \right),$$

$$d_4 = RT \cdot \ln \left( \frac{1}{RTx_i} \right)$$

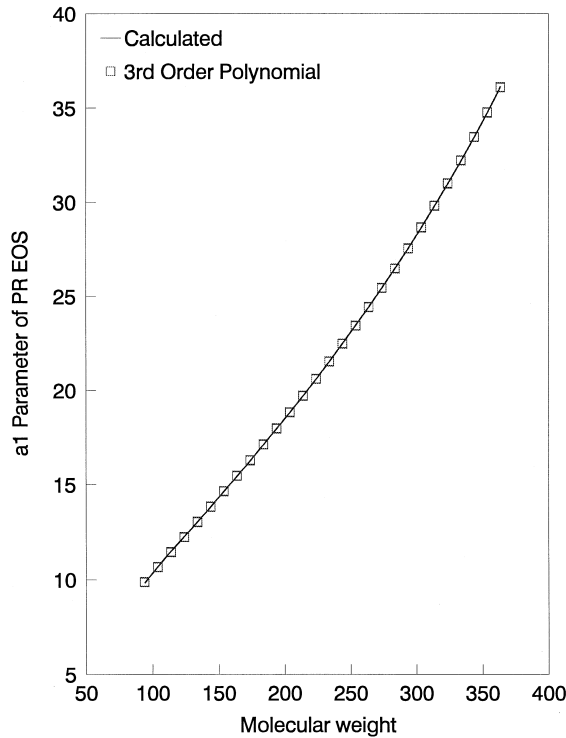


Fig. 7. A typical prediction of the  $a_1$  parameter of the PR-EOS vs. molecular weight using the third-order polynomial, Eq. (48), and comparison with the data of Hoffman et al. (1953) gas condensate.

and

$$\begin{aligned}
 (n^2 a)' &= \frac{\partial(n^2 a)}{\partial n_i} \\
 &= 2n(a_{1i} - a_{2i}\sqrt{T}) \left[ \sum_{i=1}^C x_i a_{1i} - \sqrt{T} \sum_{i=1}^C x_i a_{2i} + x_{C+} \int_I F(I) a(I)^{0.5} (1 - k_i(I)) dI \right], \quad (60)
 \end{aligned}$$

$$(nb)' = \frac{\partial(nb)}{\partial n_i} = b_i \quad (61)$$

Substituting derivatives of EOS parameters with respect to  $I$  (Eqs. (35) and (42)), in Eq. (59), will produce the chemical potential expression for the plus-fraction of the petroleum fluid. As a result, the plus-fraction chemical potential will take the following form:

$$\mu(I) - \mu^o(I) = D_1 + D_2 I + D_3 I^2 + D_4 I^3 + RT \cdot \ln[F(I)]. \quad (62)$$

Parameters  $D_i$  appearing in this equation are defined by the following expressions:

$$\begin{aligned}
 D_1 &= h_i d_2 + b_1 d_3 - d_1 + RT[1 + \ln(RT)], & D_2 &= h_2 d_2 + b_2 d_3, \\
 D_3 &= h_3 d_2 + b_3 d_3, & D_4 &= h_4 d_2 + b_4 d_3,
 \end{aligned}$$

$$\ln[F(I)] = -\ln\left(\frac{A_{Mw} I_{C+}}{x_{C+}}\right) + \frac{1}{A_{Mw}} - \frac{I}{A_{Mw} I_{C+}}$$

and

$$h_1 = 2nx_{C+}(a_{11} - a_{12}\sqrt{T}) \left[ x_{C+}\sqrt{a_{C+}} + \sum_{i=1}^C x_i a_i^{0.5} (1 - k_i(I)) \right],$$

$$h_2 = 2nx_{C+}(a_{21} - a_{22}\sqrt{T}) \left[ x_{C+}\sqrt{a_{C+}} + \sum_{i=1}^C x_i a_i^{0.5} (1 - k_i(I)) \right],$$

$$h_3 = 2nx_{C+}(a_{31} - a_{32}\sqrt{T}) \left[ x_{C+}\sqrt{a_{C+}} + \sum_{i=1}^C x_i a_i^{0.5} (1 - k_i(I)) \right],$$

$$h_4 = 2nx_{C+}(a_{41} - a_{42}\sqrt{T}) \left[ x_{C+}\sqrt{a_{C+}} + \sum_{i=1}^C x_i a_i^{0.5} (1 - k_i(I)) \right].$$

According to the above equations, by knowing the composition of the light discrete components of a petroleum fluid and up to three average plus-fraction properties (average molecular weight, average specific gravity and average true boiling point), we can calculate thermodynamic properties of a petroleum fluid at any given pressure and temperature. The expressions for the chemical potentials given above can be directly applied for phase equilibrium calculations of petroleum fluid mixtures provided those same compositions and average properties for one of the phases under consideration are known.

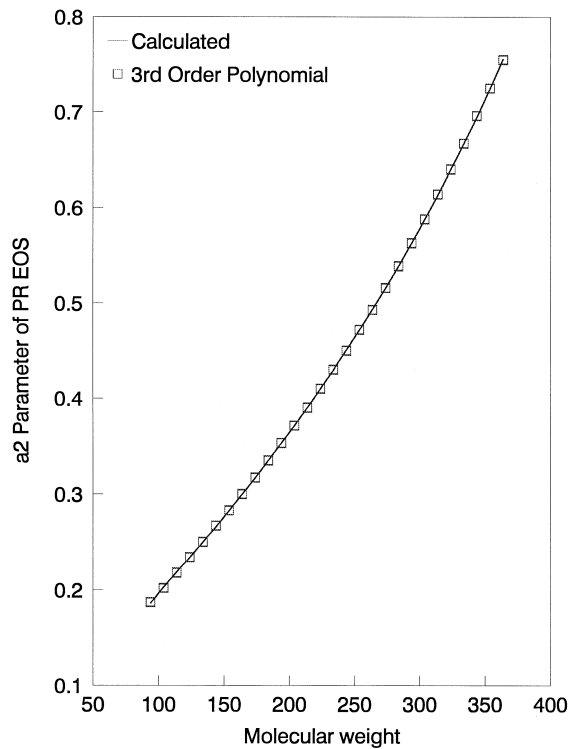


Fig. 8. A typical prediction of the  $a_2$  parameter of the PR-EOS vs. molecular weight using the third-order polynomial, Eq. (49), and comparison with the data of Hoffman et al. (1953) gas condensate.



#### 4. Phase equilibrium calculation

Phase equilibrium calculation for a petroleum fluid using the present model requires a scheme to predict fluid properties and phase behavior. This scheme must include the mass balance equations for the whole mixture taking into account masses of both the light discrete components and the whole plus-fraction. In addition, the scheme must include all the necessary criteria for the thermal, mechanical and chemical equilibrium between phases. Satisfaction of such criteria provides the necessary equations to solve for the unknown variables that characterize the phases in equilibrium.

According to the classical thermodynamics for a heterogeneous closed system at thermal, mechanical and chemical equilibria the total internal energy of the system must be minimal with respect to all the possible changes at constant volume and entropy. In this situation, differential variations with respect to independent variables can occur in the system at constant volume and entropy without producing any change in the total internal energy. Therefore, a general criterion for a system at equilibrium is:

$$(\delta U)_{s,v} \geq 0 \quad (63)$$

where  $\delta$  represents a virtual displacement.

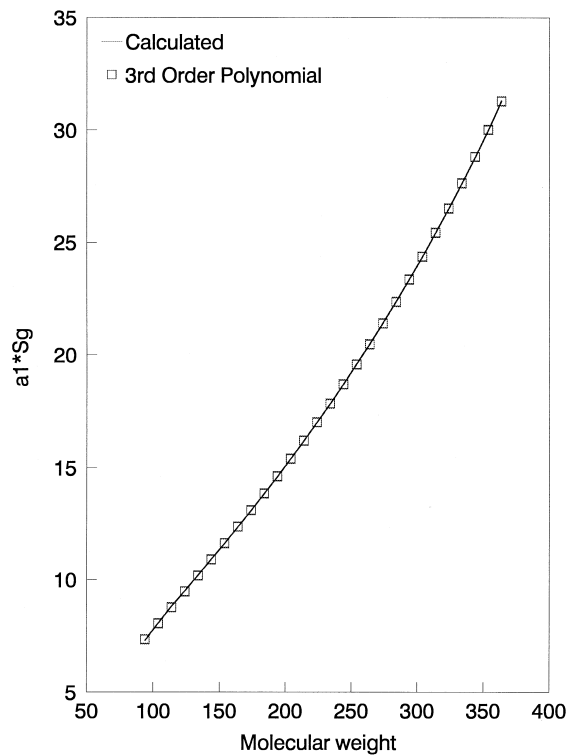


Fig. 9. A typical prediction of the  $S_g \cdot a_1$  parameter of the PR-EOS vs. molecular weight using the third-order polynomial, Eq. (50), and comparison with the data of Hoffman et al. (1953) gas condensate.

Generally, the total differential of internal energy of an open system is related to its other thermodynamic properties by the Gibbs equation:

$$dU = TdS - PdV + \sum_i \mu_i dn_i. \quad (64)$$

Considering a non-reacting vapor–liquid equilibrium closed system (meaning the total number of moles of the system is conserved) and the fact that the equilibrium state of such a system is defined by conservation of its total volume and total entropy, then we may write:

$$dU = (T^V - T^L)dS^L - (P^V - P^L)dV^L + \sum_i (\mu_i^V - \mu_i^L)dn_i^L. \quad (65)$$

Since the above equation must hold for all the possible variations of  $S$ ,  $V$  and  $n_i^L$  then the following conditions must be satisfied:

$$T = T^L = T^V, \quad (66)$$

$$P = P^L = P^V, \quad (67)$$

$$\mu_i^L = \mu_i^V \quad i = 1, 2, \dots, c \quad (68)$$

where  $c$  is the total number of components. These equations are the general phase equilibrium conditions in a vapor–liquid equilibrium system.

For a petroleum fluid, consisting of a finite number ( $C$ ) of discrete light components and a large (continuous) plus-fraction as defined earlier in this report, Eqs. (66) and (67), which represent the thermal and mechanical

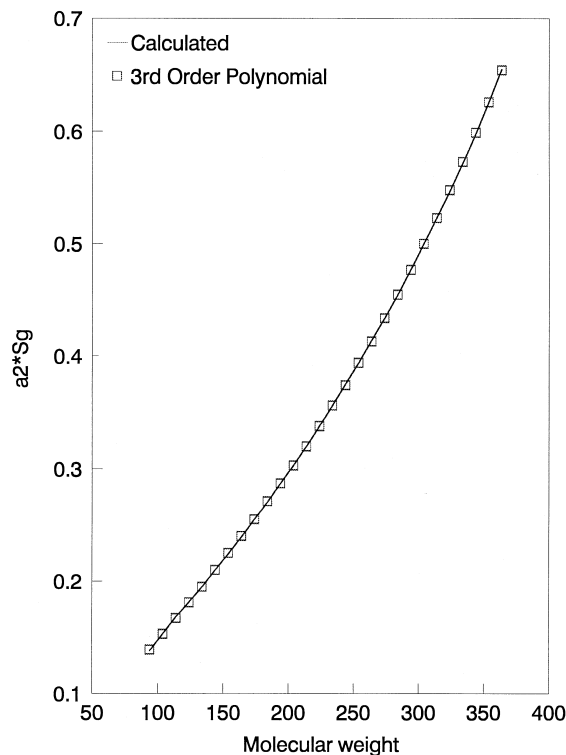


Fig. 10. A typical prediction of the  $S_g \cdot a_2$  parameter of the PR-EOS vs. molecular weight using the third-order polynomial, Eq. (51), and comparison with the data of Hoffman et al. (1953) gas condensate.

equilibria in the system, will remain the same. However, the equality of chemical potential, Eq. (68), may be re-written in the form of two sets of equations.

For the discrete components of the petroleum fluid mixture equality of chemical potentials equations will be,

$$\mu_i^L = \mu_i^V \quad i = (1 \rightarrow C). \quad (69)$$

For the continuous plus-fractions, which are defined by a mole fraction distribution function, Eq. (1), the chemical potential equalities may be expressed in the following form, as a function of the molecular weight,  $I$ , of the plus-fraction cuts

$$\mu^L(I) = \mu^V(I) \quad I = (I_{C+} \rightarrow \infty) \quad (70)$$

which is an indication of the fact that the plus-fraction has a continuous distribution function.

In performing the phase equilibrium calculation for a reservoir fluid we utilize a mix of discrete and continuous phase equilibrium algorithms (Du and Mansoori, 1986, 1987). The pc-based computer packages produced for this calculation are available for distribution by the corresponding author (GAM). In the following section we report the result of such calculations using the present model.

## 5. Calculations and results

The present model is tested for vapor–liquid equilibrium calculation of a variety of petroleum fluids with very satisfactory results. In the calculations reported here the phase equilibrium properties of a number of petroleum fluids for which characterization and experimental data are published in the open literature are

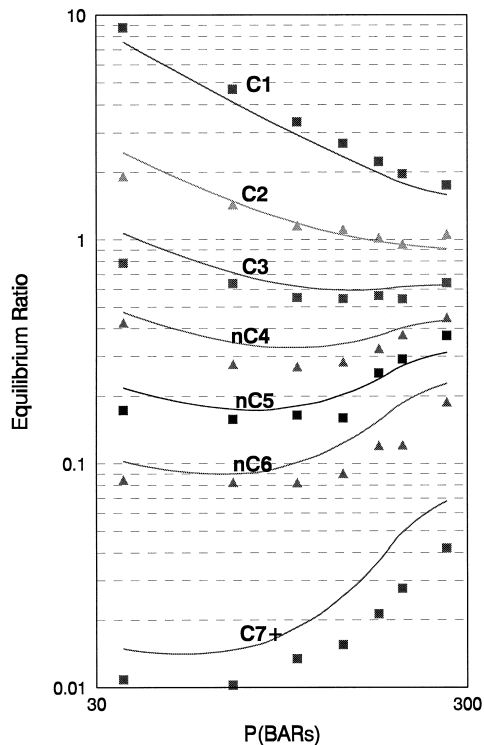


Fig. 11. Comparison of the predicted equilibrium ( $K$ -value) ratio by the present method assuming  $k_{ij} = 0$  with the experimental data of Hoffman et al. (1953).

calculated by the present model and the results are compared with those of other methods. There exist two sets of published reliable oil data for which all the investigators the vapor–liquid calculations are performed: the data of Hoffman et al. (1953) and Roland (1942).

### 5.1. Lean gas condensate and crude oil data of Hoffman et al. (1953)

In the data by Hoffman et al. (1953), hydrocarbons starting with methane and ending with hexanes were identified as the discrete light components and the plus-fraction (starting with  $C_7$ ) was divided arbitrarily into 28 cuts defined so that the mid-boiling point of each cut was taken roughly equivalent to that of the respective normal paraffin hydrocarbon. They presented experimental results of dew point at 201°F (367 K) and flash yields at different pressures and 201°F.

In performing the phase equilibrium calculation by the present method, we consider the first eight hydrocarbons (methane, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, *n*-pentane, *n*-hexane) as the discrete components and the hydrocarbon fractions heavier than hexane as a continuous plus-fraction identified by its molecular weight distribution function, its average molecular weight, its average specific gravity, and its average true boiling point as described in the previous sections.

In the Hoffman data, in addition to the discrete components mole fractions the mole fractions and properties (specific gravity, molecular weight, true boiling point) of each cut of the plus-fraction are reported. In what follows we describe the procedure used here in order to extract the necessary information from this data in order to be able to perform the phase equilibrium calculation. For this data the parameter  $B_{Mw}$  of the distribution function is assumed to be equal to unity, and as a result, parameter  $A_{Mw}$  is calculated from the average

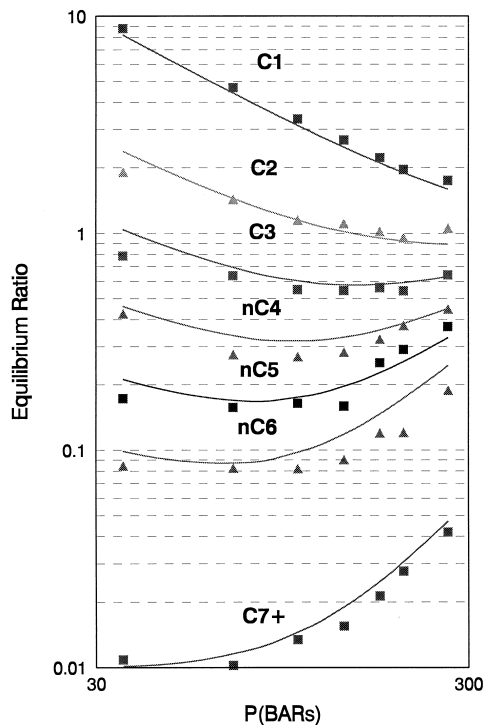


Fig. 12. Comparison of the predicted equilibrium ( $K$ -value) ratio by the present method assuming  $k_{ij} \neq 0$  with the experimental data of Hoffman et al. (1953).

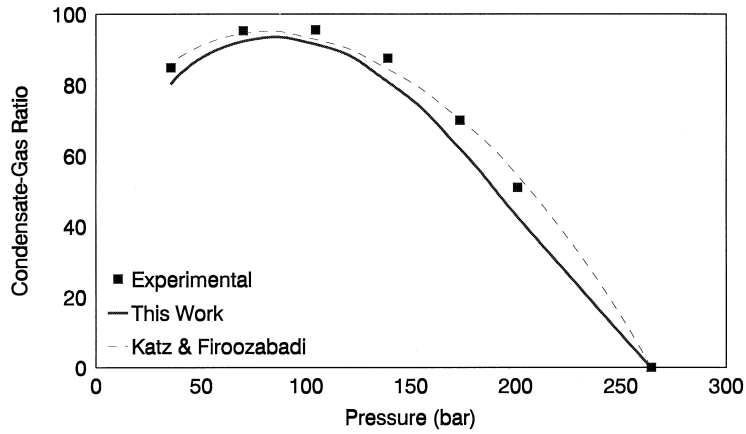


Fig. 13. Comparison of the predicted condensate/gas ratio vs. pressure by the present method assuming  $k_{ij} \neq 0$  with the experimental data of Hoffman et al. (1953).

molecular weight,  $\bar{I}$ , through Eq. (6). The average molecular weight of the plus-fraction is calculated by the following equation:

$$\bar{I} = \frac{\sum_{j=9}^{37} (I_j \xi_j)}{\sum_{j=9}^{37} \xi_j} \quad (71)$$

where  $I_j$  and  $\xi_j$  are the molecular weight and the mole fraction of the  $j$ th cut of the plus-fraction, respectively. It should be pointed out that the over-all mole fraction of the  $j$ th cut in the oil is equal to  $(x_{C+} = \xi_j)$ .

By plotting the molecular weight ( $I$ ) vs. cumulative mole fraction ( $\aleph_i = \sum_{j=0}^i \xi_j$ ) for the plus-fraction and extrapolation to  $\aleph_i = 0$  the initial molecular weight of the plus-fraction is calculated. The initial molecular weight may be also estimated by using the average molecular weight of the  $C_6$  hydrocarbons taken equal to  $I_{C+} = 84$ . In order to determine the average true boiling point and the average specific gravity, we need to know wt.% and vol.% of each cut of the plus-fraction. These values are calculated from their relations with mole fractions (Eqs. (18) and (19)). Knowing the weight fractions, the average true boiling point of the plus-fraction is calculated as follows:

$$\bar{T}_b = \frac{\sum_{j=9}^{37} (T_{b_j} \xi_w(J))}{\sum_{j=9}^{37} \xi_w(J)} \quad (72)$$

and, similarly, the average specific gravity is calculated as follows:

$$\bar{S}_g = \frac{\sum_{j=9}^{37} (S_{g_j} \xi_v(J))}{\sum_{j=9}^{37} \xi_v(J)} \quad (73)$$

Generally, the initial values of  $T_b$  and  $S_g$  can be found by plotting them vs. the cumulative weight and volume fractions, respectively, and extrapolating them to the case of zero cumulative fractions. However, for the present data the average true boiling point and specific gravity of the  $C_6$  hydrocarbons (i.e.,  $T_{b_0} = 607 R$  and  $S_{g_0} = 0.685$ ) are used for the initial values.

Having the averages and initial values of these properties known, parameters  $A_{Mw}$ ,  $A_{T_b}$ ,  $A_{S_g}$  appearing in Eqs. (6), (16) and (17) can be calculated. For parameters  $B_{Mw}$ ,  $B_{T_b}$ , and  $B_{S_g}$ , the recommended values of  $B_{Mw} = 1$ ,  $B_{T_b} = 1.5$ , and  $B_{S_g} = 3$  are used in the present calculations for the sake of simplicity.

In Figs. 1–3 we report the  $M_w = I$ ,  $T_b(I)$ , and  $S_g(I)$  vs. the cumulative mole fraction, the cumulative weight fraction and the cumulative volume fraction, respectively, as calculated by Eqs. (2), (14) and (15) and compared with the experimental data, for both liquid and vapor phases. According to Figs. 1–3 the trends of the data are well represented by the theory, the predictions are in good agreement with the experimental data.

In Figs. 4–6 we report the variation of  $T_c(I)$ ,  $P_c(I)$ ,  $\omega(I)$  vs.  $I$ , of the plus-fraction, as calculated by Eqs. (7)–(9). According to these figures, while  $T_c$  and  $\omega$  increase with the increase of the molecular weight of the plus-fraction cuts,  $P_c$  decreases for the same variation of molecular weight. Data of  $T_c$ ,  $P_c$  and  $\omega$  vs. the molecular weight of the plus-fraction are used to calculate the PR-EOS parameters  $a_1(I)$ ,  $a_2(I)$ ,  $b(I)$  and  $a_1(I)S_g(I)$ ,  $a_2(I)S_g(I)$  using Eqs. (27), (39) and (40) and the  $T_c$ ,  $P_c$  and  $\omega$  data. Calculated values of  $a_1(I)$ ,  $a_2(I)$ ,  $a_1(I)S_g(I)$  and  $a_2(I)S_g(I)$  by the third-order polynomials, Eqs. (48)–(51), are also reported on Figs. 7–10. According to these graphs the third-order polynomials for these parameters vs. molecular weight are in very good agreement with the data.

In order to test the accuracy of the present method for phase equilibrium calculation the experimental data and the predicted equilibrium ( $K$ -value) ratios from flash calculations, with the  $k_{ij} = 0$ , are shown in Fig. 11.

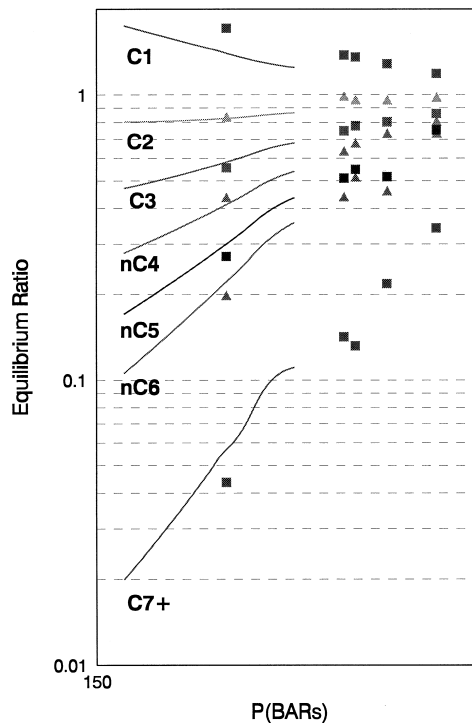


Fig. 14. Comparison of the predicted equilibrium ( $K$ -value) ratio by the present method assuming  $k_{ij} = 0$  with the experimental data of Roland (1942) crude oil at 120°F.

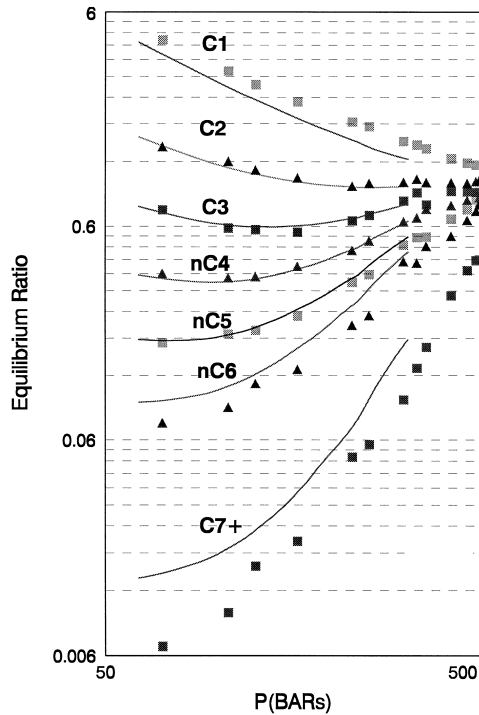


Fig. 15. Comparison of the predicted equilibrium ( $K$ -value) ratio by the present method assuming  $k_{ij} = 0$  with the experimental data of Roland (1942) crude oil at 200°F.

According to this figure the calculations considering  $k_{ij} = 0$  are fairly in good agreement with the experimental data. In Fig. 12 we report the same kind of calculation but including the and  $k_{ij}$  values of Eq. (41). According to Fig. 12 consideration of the unlike interaction parameter in the calculations improves the phase equilibrium predictions, especially for the heavier hydrocarbons and the plus-fraction.

The experimental data and the predicted values of the condensate/gas ratio as a function of pressure are presented in Fig. 13 considering the values reported by Eq. (41). According to this figure the predictions are in good agreement with the experimental data.

### 5.2. Natural gas and crude oil data of Roland (1942)

Roland (1942) reported a set of equilibrium data which were obtained for a mixture of League City natural gas and Billings crude oil for pressure in the range of 1000 to 10000 psia (68.96–689.65 bars) and at two different temperatures of 120 and 200°F (48.88–120.49°C). In the report of Roland the average molecular weight and the average specific gravity of the plus-fraction are given for various temperatures and pressures, but no data for the average true boiling point of the plus-fraction is given. In order to determine parameters of the EOS, the true boiling point of the plus-fraction cuts are necessary.

In order to calculate the true boiling point for the plus-fraction cuts we use the procedure 2B2.1 of API Technical Data Book which expresses the molecular weight as a function of the specific gravity and the true boiling point of a cut in an oil.

$$I = 20.486 \left[ \exp \left( 1.165 \times 10^{-4} T_b(I) - 7.78712 S_g(I) + 1.1582 \times 10^3 T_b(I) S_g(I) \right) \right] \times T_b(I)^{1.26007} \times S_g(I)^{4.98308} \quad \text{for: } 70 \leq I \leq 700 \quad (74)$$

By using Eq. (74) and knowing the molecular weight and the specific gravity of each cut, we can calculate the true boiling point of each cut of the plus-fraction and, consequently, the critical properties and EOS parameters can be estimated. It should be pointed out that this estimation procedure for the true boiling point of cuts may not be as accurate as the prediction from the average true boiling point, using Eq. (14). However, due to the lack of average boiling point data we need to use this method.

For calculation of the initial values for the Hoffman data we used the properties of the cuts. Since the cuts properties (molecular weight, specific gravity, and true boiling point) in the Roland data are not reported, one cannot estimate the initial properties. As a result, the initial values for the Roland data are assumed to be equal to the average  $C_6$  hydrocarbons properties. In addition, the recommended numerical values of parameters  $B_{Mw}$ ,  $B_{T_b}$  and  $B_{S_g}$  are used for this data.

In Figs. 14 and 15, the experimental data and predicted equilibrium ( $K$ -value) ratios at two different temperatures of 120 and 200°F and considering  $k_{ij} = 0$  are reported. According to these Figs. 14 and 15 the predictions by the present method are in fair agreement with the experimental data in case of ignoring the unlike-interaction parameters.

In Figs. 16 and 17, the experimental data for the equilibrium ( $K$ -value) ratios at the same two different temperatures of 120 and 200°F as in Figs. 14 and 15, are compared with the predicted values considering the  $k_{ij}$  values reported by Eq. (4). According to these figures the predictions by the present method are in good agreement with the experimental data in case of considering the unlike-interaction parameters in the calculations.

The computational results reported here indicate that the present method is an accurate technique for predicting the phase behavior of petroleum fluids. The accuracy of this method seems to be as good as the other

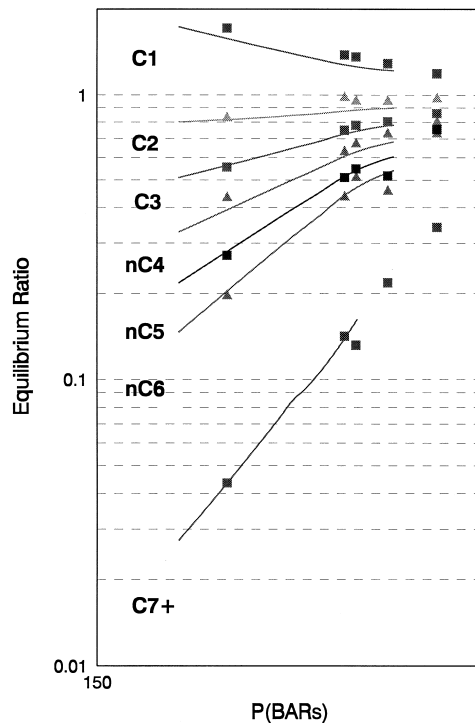


Fig. 16. Comparison of the predicted equilibrium ( $K$ -value) ratio by the present method assuming  $k_{ij} \neq 0$  with the experimental data of Roland (1942) crude oil data at 120°F.



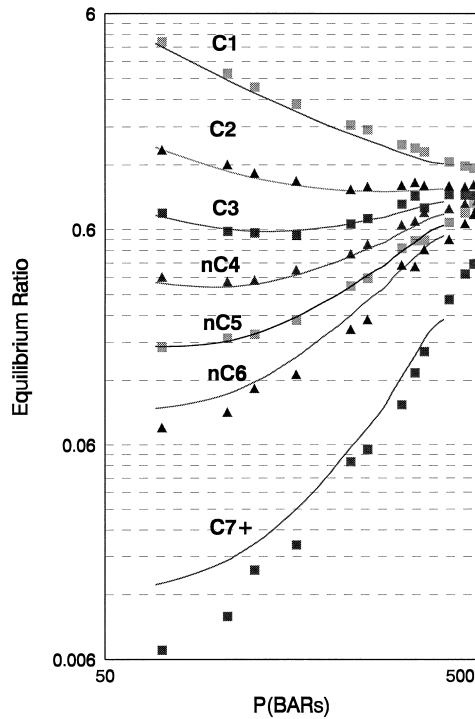


Fig. 17. Comparison of the predicted equilibrium ( $K$ -value) ratio by the present method assuming  $k_{ij} \neq 0$  with the experimental data of Roland (1942) crude oil data at 200°F.

existing methods previously proposed (Du and Mansoori, 1986, 1987; Chorn and Mansoori, 1989). The advantage of this method over the other existing methods is the fact that it requires the least amount of characterization data for the heavy end (plus-fraction). The heavy end (plus-fraction) characterization data (average molecular weight, average specific gravity and average true boiling point) needed in this method are the most common and easy characterization data which are routinely produced for petroleum fluids.

## 6. Nomenclature

$A$	A parameter in Eqs. (2), (14) and (15)
$a$	EOS parameter
$B$	A parameter in Eqs. (2), (14) and (15)
$b$	EOS parameter
$C$	Number of desecrate components
$F$	Probability density distribution function
$I, J$	Molecular weight of cuts in the plus-fraction
$k$	Unlike-interaction coefficient
$n$	Number of moles
$N$	Number of components
$P$	Pressure
$R$	Universal gas constant
$S$	Entropy

$S_g$	Specific gravity
$T$	Absolute temperature
$T_b$	True boiling point
$U$	Internal energy
$V$	Total volume
$v$	Molar volume
$x$	Mole fraction of discrete components
<i>Greek letters</i>	
$\Gamma$	Gamma function
$\omega$	Acentric factor
$\mu$	Chemical potential
$\aleph$	Cumulative mole fraction in the plus-fraction cuts
$\xi$	Mole fraction in the plus-fraction cuts
<i>Subscripts</i>	
0	Initial value of specific gravity and true boiling point
c	Critical point property
$C +$	Initial value of molecular weight of the plus-fraction at $\aleph = 0$
$f$	Final value
$i, j$	Discrete Component identifiers
Mw	Molecular weight
pc	Pseudo-component
r	Reduced property
$S_g$	Specific gravity
$T_b$	True boiling point
v	Volumetric property
w	Weight property
<i>Superscripts</i>	
*	Dimensionless property
	Average value
L	Liquid phase
V	Vapor phase
o	Reference state
s	Saturated property

## 7. Further reading

The reader is referred to the following references for further reading: Benmekki and Mansoori, 1986; Benmekki and Mansoori, 1989; Kawanaka et al., 1991; Kincaid et al.; Magoulas and Tassios, 1990; Mansoori et al., 1989; Obut et al., 1986; Park and Mansoori, 1988; Peng et al. 1987; Peters et al., 1988; Riazi and Mansoori, 1993; Thiele et al., 1983; Twu, 1984; William and Teja, 1986; Wu and Batycky, 1986; Ying et al., 1989.

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## References

- American Petroleum Institute (API), 1988. Daubert, T.E., Danner, R.P. (Eds.), Technical Data Book Petroleum Refining, Chaps. 1, 2 and 4. American Petroleum Institute, Washington, DC.
- Angelos, C.P., Bhagwat, S., Matteews, M.A., 1992. Measurement and modeling of phase equilibria with synthetic multi-component mixtures. *Fluid Phase Equilibria* 72, 189–209.
- Benmekki, E.H., Mansoori, G.A., 1986. Accurate vaporizing gas-drive minimum miscibility pressure prediction. SPE Paper #15677. Society of Petroleum Engineers.
- Benmekki, H., Mansoori, G.A., 1989. Pseudization techniques and heavy fraction characterization with equation of state models. C7+ Fraction Characterization. *Advances In Thermodynamics*, Vol. 1. Taylor & Francis Press, New York, NY, pp. 57–77.
- Chorn, L.G., Mansoori, G.A. 1989. Multi-component fractions characterization: principles and theories. C7+ fraction characterization. *Advances In Thermodynamics* Vol. 1. Taylor & Francis Press, New York, NY, pp: 1–10.
- Du, P.C., Mansoori, G.A., 1986. Phase equilibrium computational algorithms of continuous mixtures. *Fluid Phase Equilibria* 30, 57–64.
- Du, P.C., Mansoori, G.A., 1987. Phase equilibrium of multi-component mixtures: continuous mixture Gibbs free energy minimization and phase rule. *Chem. Eng. Commun.* 54, 139–148.
- Heynes, H.W. Jr., Matthews, M.A., 1991. Continuous mixture vapor–liquid equilibria computations based on true boiling point distillations. *Ind. Eng. Chem. Res.* 30, 1911–1915.
- Hoffman, A.E., Crump, J.S., Hocott, C.R., 1953. Equilibrium constants for a gas–condensate system. *Trans. AIME* 198, 1–10.
- Kawanaka, S., Park, S.J., Mansoori, G.A., 1991. Organic deposition from reservoir fluids. *SPE Reservoir Engineering Journal*, May, pp. 185–192.
- Kincaid, J.M., Azadi, A., Fescos, G., Pellizzi, L., Shon, K.B. Phase equilibria in a special class of polydisperse fluid models.
- Magoulas, K., Tassios, D., 1990. Thermophysical properties of *n*-alkanes from C<sub>1</sub>–C<sub>20</sub> and their prediction to higher ones. *Fluid Phase Equilibria* 56, 119–140.
- Mansoori, G.A., 1993. Radial distribution functions and their role in modeling of mixture behavior. *Fluid Phase Equilibria* 87, 1–22.
- Mansoori, G.A., Du, P.C., Antoniadis, E., 1989. Equilibrium in multi-phase polydisperse fluids. *Int. J. Thermophysics* 10 (6), 1181–1204.
- Obut, S.T., Ertekin, T., Geisbrecht, R.A., 1986. A versatile phase equilibrium package for compositional simulation. *Soc. Pet. Eng. AIME Paper #15083*. 56th Annual California Regional Meeting of the Soc. Pet. Eng., Oakland, CA, April 2–4.
- Park, S.J., Mansoori, G.A., 1988. Aggregation and deposition of heavy organics in petroleum crudes. *Int. J. Energy Sources* 10, 109–125.
- Peng, D.Y., Wu, R.S., Batcky, J.P., Application of continuous thermodynamics to oil reservoir fluid systems using an equation of state. *AOSTRA J. Res.* 3, 113–122.
- Peters, C.J., de Swaan-Arons, J., Levelt Sengers, J.M.H., Gallagher, J., 1988. Global phase behaviour of mixtures of short and long *n*-alkanes. *AIChE J.* 34, 834–841.
- Radosz et al., 1987.
- Riazi, M.R., 1989. Distribution model for properties of hydrocarbon-plus-fractions. *Ind. Eng. Chem. Res.* 28, 1731–1735.
- Riazi, M.R., Mansoori, G.A., 1993. Simple equation of state accurately predicts hydrocarbon densities. *Oil and Gas J.*, July 12, 108–111.
- Roland, C.H., 1942. Vapor–liquid equilibria for natural gas–crude oil mixtures. *Ind. Eng. Chem.* 37 (10), 930–936.
- Thiele, K.J., Lake, L.W., Sepehrnoori, K.A., 1983. A comparison of three equation of state compositional simulator. *Proceeding of the 7th SPE Symposium on Reservoir Simulation*, San Francisco, CA, Nov. 16–18.
- Twu, C.H., 1984. An internally consistent correlation for predicting the critical properties and molecular weights of petroleum and coal-tar liquids. *Fluid Phase Equilibria* 16, 137–150.
- William, B.T., Teja, S.A., 1986. Continuous thermodynamics of phase equilibria using a multi-variate distribution function and an equation of state. *AIChE J.* 32, 2067–2078.
- Wu, R.S., Batycky, J.P., 1986. Pseudo-components characterization for hydrocarbon miscible displacement. *Soc. Pet. Eng. AIME Paper #15404*. 61th Annual Technical Conference and Exhibition of the Soc. Pet. Eng., New Orleans, LA, Oct. 5–8.
- Ying, X., Ruqing, Y., Hu, Y., 1989. Phase equilibria for complex mixtures: continuous thermodynamics method based on spline fit. *Fluid Phase Equilibrium* 53, 407–414.