Effect of C_{7+} Properties on Equation-of-State Predictions

Curtis H. Whitson, Rogaland Regional C.*

Abstract

This work studies the effect of heptanes-plus (C_{7+}) characterization on equation-of-state (EOS) predictions. Both the Peng-Robinson EOS (PREOS) and a modified Redlich-Kwong EOS are used. Several characterization schemes found in the literature are used in the study. Six reservoir fluids with extended C_{7+} analysis have been chosen, representing a broad range of compositions and PVT data.

First, the study deals with methods for estimating specific gravities and boiling points of petroleum fractions, two properties usually required by critical property correlations. EOS predictions are made by using critical properties based on specific gravities and boiling points measured experimentally and estimated with correlations.

Next, a review of critical-property correlations is given, including a review of commonly used correlations. Four correlations are chosen to study the effect of critical properties on EOS predictions. Results indicate that relatively small differences in critical properties and acentric factor can result in significant differences in EOS predictions.

Finally, a study is made of the effect that adjustments in C_{7+} critical properties have on EOS predictions; adjustments of EOS constants (Ω_a and Ω_b) and binary interaction coefficients also are studied. The influence of individual and combined adjustments to C_{7+} properties are illustrated graphically. They provide qualitative guidelines that can be used when matching experimental PVT data with an EOS.

Introduction

Recently there has been an increasing interest in EOR methods. One result has been the need to develop numerical models for simulating EOR processes involving complex phase behavior. Most of these models use an EOS to predict vapor/liquid equilibrium (VLE) and volumetric phase behavior.

A typical problem with using an EOS is the difficulty in describing petroleum fractions constituting C_{7+}. These fractions significantly affect EOS predictions, as has been reported in the literature. Usually only limited C_{7+} data are available to describe C_{7+} fractions. Even so, estimates of critical properties—critical pressure, critical temperature, and acentric factor—are required by most EOS's.

Several correlations exist for estimating critical properties of petroleum fractions. Most are empirical equations giving a best fit of graphical correlations based on experi-

mental data. Boiling point and specific gravity usually are required by critical property correlations. Several methods exist for estimating specific gravity and boiling point of petroleum fractions when only C_{7+} properties are known. Four of these have been used in our study.

Several methods have been tried to improve C_{7+} characterization by approximating the chemical makeup of petroleum fractions. The most common approach assumes that petroleum fractions are composed of three hydrocarbon groups: paraffins (P), naphthenes (N), and aromatics (A). Several methods exist for estimating PNA content of petroleum fractions.[1-3]

Three aspects of C_{7+} characterization have been studied: (1) methods for estimating specific gravity and boiling point of petroleum fractions, (2) correlations for estimating critical pressure, critical temperature, and acentric factor, and (3) manual adjustment of critical properties, EOS constants (Ω_a and Ω_b), and binary interaction coefficients (particularly between methane/CO_2 and C_{7+} fractions).

Reservoir fluids used in this study were chosen on the basis of availability of distillation data for C_{7+} fractions and the type of PVT measurements reported. Six fluids have been chosen from the literature, including fluids ranging from a lean gas to a black oil. PVT measurements have been reported at more than one temperature for some of the mixtures, which allows the study of temperature dependence of binary interaction coefficients between methane and C_{7+} fractions.

Two cubic EOS's are used to make PVT predictions. PREOS[4] was chosen because it is widely accepted in the industry and it generally yields better liquid-density estimates than the comparable Soave-Redlich-Kwong[5] (SRK) equation. As a representative of the Redlich-Kwong[6] family, Yarborough's[7] version of the modified Zudkevich-Joffe-Redlich-Kwong[8] (ZJRK) equation was chosen.

Results from this work suggest that C_{7+} characterization has a significant influence on EOS predictions of reservoir fluid behavior. It is difficult to make objective conclusions about which C_{7+} characterization schemes are best. A different approach to characterization is needed. One possible alternative would be to calculate critical properties of petroleum fractions such that measured values of specific gravity and boiling point are force-fit by the EOS.

Physical Property Correlations: A Review

The critical point of a pure compound is defined as the pressure and temperature at which vapor phase has prop-

*Now with Whitson Oil Co. Inc.

erties identical with the equilibrium liquid phase. These conditions also define the endpoint of the vapor pressure curve. Almost all EOS's require critical pressure and critical temperature of individual components in a mixture. Most EOS's also require the acentric factor[9] as a correlating parameter to ensure accurate vapor pressures of pure compounds. Molecular weights are needed to convert molar volumes to densities.

Several correlations exist for estimating critical properties of petroleum fractions. Most of these use specific gravity, γ, and boiling point, T_b, as correlating variables. Some of the more common correlations used by petroleum and chemical engineers are reviewed next.

Roess.
In 1936, Roess[10] presented correlations for critical temperature and pressure. They are developed from flow data on petroleum fractions in a pioneering work previous to most correlation development. The API Technical Data Book[11] retains the original form of Roess' critical temperature equation, although API has modified the original T_c correlation by using recent data from U.S. and North Sea oils.

The main limitation of Roess' T_c correlation is that it should not be used for fractions heavier than C_{20}. It underestimates critical temperatures for heavier fractions and is not, therefore, reliable for reservoir systems with higher-boiling-point fractions.

Edmister.
In 1948, Edmister[12] proposed a simple but accurate equation for estimating acentric factor of pure compounds. It requires normal boiling point, critical pressure, and critical temperature. The equation has been applied successfully to petroleum fractions.

Edmister acentric factors tend to be lower than Kesler-Lee[13] values for fractions heavier than C_{20}. The difference is important for EOS predictions with the ZJRK since acentric factor correlates correction factors for both EOS constants (Ω_a and Ω_b).

If acentric factor is available from another source, the Edmister equation can be rearranged to solve for any of the other three properties (see the discussion of the Robinson-Peng[3] method that follows).

Lydersen.
In 1955, Lydersen[14] presented a method for estimating critical properties of pure compounds. The method employs structural contributions (group contribution theory). The Lydersen correlations are simple but not directly applicable to petroleum fractions since they assume that the compound can be identified by hydrocarbon family and number of carbon atoms. Robinson and Peng use the Lydersen correlation for critical pressure, having first defined the PNA content of a petroleum fraction.

Nokay.
In 1959, Nokay[15] presented seven simple correlations for estimating parachor, boiling point, specific gravity, and critical temperature. The critical temperature correlation is best known because it introduced a simple equation form, later shown to be useful for correlating numerous physical properties (see Riazi-Daubert[16] correlations).

Nokay's original relation for critical temperature has been improved by Spencer and Daubert[17] by fitting the three constants to data for each hydrocarbon family.

Cavett.
In 1962, Cavett[18] proposed correlations for estimating critical pressure and temperature of petroleum fractions. The correlations are built into a program designed to simulate tray-to-tray distillation up to pressures of 7000 kPa [1,000 psia].

Although these correlations have been accepted widely, they are presented without reference to which data are used for their development, and no limitations or comparison with previous correlations are given.

Hariu-Sage.
In 1969, Hariu and Sage presented a method (program) for simulating fractional distillation of crude oils. In their procedure a correlation is given for estimating molecular weight from boiling point and specific gravity (from the Watson characterization factor, K_w). It represents a surface-fit of the Winn nomograph. They claim the correlation gives a reasonable extrapolation to boiling points over 1090 K [1,502°F]. It appears to be more accurate than the Kesler-Lee[13] molecular weight correlation, although the difference may result from using different data to develop the respective equations. The Hariu-Sage correlation can be rearranged to solve directly for specific gravity, but it cannot be solved directly for boiling point.

Bergman.
In 1976, Bergman[1,2] presented a comprehensive study of the retrograde condensation effects on natural gas pipelines. One result from his study was experimental data, which are correlated to give molecular weight and specific gravity as a function of boiling point. Only lean gases and gas condensates with relatively light C_{7+} fractions were used in the Bergman study, thereby limiting the general applicability of property correlations.

A PNA approach is developed to estimate critical properties of the heavy fractions. Only some limitations found in the Robinson-Peng method are shared by the Bergman method. The basic difference between these two methods is that Bergman assumes that all three constituents (PNA) have the same boiling point but different properties otherwise. Robinson and Peng use carbon number as the linking property. The Bergman method for estimating PNA content has less chance of resulting in negative PNA compositions but its general applicability has not been tested for fractions heavier than C_{20}.

Bergman's logic for using the PNA method is that critical property correlations originally were developed for wider boiling point fractions than represented by a single carbon number. This reasoning loses validity when traditional correlations then are suggested by Bergman for fractions heavier than C_{15}. In fact the proposed PNA approach appears to complicate C_{7+} characterization without any practical advantage.

Kesler-Lee.
In 1976, Kesler and Lee[13,19] presented correlations for molecular weight, critical pressure, critical temperature and acentric factor. They are proposed for improving enthalpy predictions. Kesler and Lee claim that critical pressure and temperature correlations give nearly identical results when compared with graphical correlations found in the API Technical Data Book. This claim holds up to a boiling point of about 920 K [1,196°F]. Modifications are introduced to extend the correlations beyond this limit by ensuring that critical pressure approaches atmospheric pressure as boiling point approaches critical temperature.

Two acentric factor correlations are proposed. One is suggested for petroleum fractions with a reduced boiling point (T_b/T_c), less than 0.8, and the other is suggested for heavier fractions. These correlations usually predict acentric factors larger than those by the Edmister equation.

Daubert[20] compares the Kesler-Lee and Edmister equations and shows that for pure compounds (of unspecified type and number) the Edmister[12] correlation performs better. This comparison should not be considered valid for petroleum fractions.

The molecular weight correlation is developed from data with molecular weights ranging from 60 to 650. Less weighting is given to isomers not commonly found in petroleum fractions. There is an unexplained difference between the resulting correlation and values given in the API Technical Data Book.

Katz-Firoozabadi. In 1978, Katz and Firoozabadi[21] presented generalized properties of single-carbon-number (SCN) fractions, including molecular weights, specific gravities, and normal boiling points. They are developed from published data representing relatively paraffinic oils.

Katz and Firoozabadi do not compare EOS predictions based on the generalized properties with those based on measured properties. They suggest using Cavett's critical property correlations. The Edmister correlation for acentric factor probably is used though it is not stated explicitly. A correlation for binary interaction coefficients between methane and petroleum fractions is given for the PREOS.

Robinson-Peng. In 1978, Robinson and Peng[3] proposed a procedure for characterizing petroleum fractions. It is to be used in conjunction with the GPA Peng-Robinson programs, though the method is not restricted to the PREOS.

The proposed property correlations are based on the PNA concept. Equations for PNA properties are provided, including boiling point, specific gravity, molecular weight, critical pressure, critical temperature, and acentric factor. The critical pressure correlation is taken from Lydersen. Critical temperature is back-calculated from acentric factor, boiling point and critical pressure. Acentric factor is assumed a linear function of carbon number.

The characterization scheme is based on the requirement that each petroleum fraction represents a single carbon number. Naphthenes and aromatics have carbon numbers one less than paraffins. No indication of the maximum carbon number is given, although Robinson indicates in a verbal communication that the maximum value is "C_{25}. No, I wouldn't stop there if I had to get an answer. Because I wouldn't know any better way to go if I had C_{30} or C_{40} than to just go ahead with the same scheme. I would recognize that the backup gets shakier and shakier."[22]

Experience with the Robinson-Peng method has led to the following observations.

1. As shown in Fig. 1, SCN specific gravities never exceed 0.875, the aromatic value for C_7. This is physically unacceptable.

2. Distillation data must be converted to boiling-point cuts with paraffin boiling-point intervals.

3. The use of a mass accumulation curve to determine SCN densities (from the tangent to the curve) is highly unreliable.
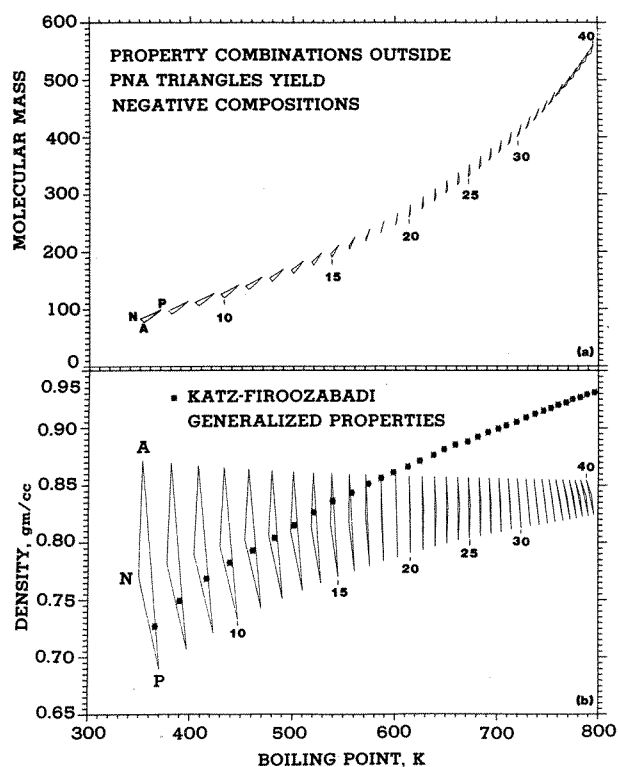

Fig. 1—Peng-Robinson PNA molecular weight and density vs. boiling point.

4. Methods proposed for estimating the PNA content from boiling point, molecular weight, and specific gravity are easily subject to error, resulting in negative compositions. Fig. 1 illustrates the problem by showing the regions that yield non-negative PNA compositions. The problem worsens when we note that boiling points found by using the proposed method almost always will equal the arithmetic average of neighboring paraffin boiling points (exactly if the distillation curve is linear between these two values). This makes the region (or line) in which realistic non-negative PNA compositions can be obtained very small and in some cases nonexistent.

5. Acentric factors for fractions heavier than C_{20} are considerably higher than estimated by either the Edmister or Kesler-Lee equation. They reach a value of 2.0 for C_{45}. It appears that linear extrapolation is not correct for heavier fractions. An indirect result is that critical temperatures are too low.

6. The assumption that naphthene and aromatic fractions have one less carbon number than paraffins is only approximate and loses credibility at higher boiling points.

Because of these limitations, the Robinson-Peng method is not suggested for reservoir fluids containing fractions heavier than C_{20} (about the same limitation as the Bergman method). Unless an accurate estimate of the PNA content is available from mass spectrometry or a reliable correlation, the method probably should not be used.

Rowe. In 1978, Rowe[23] presented equations for estimating boiling point, critical pressure, and critical temperature of paraffin hydrocarbons. He suggests that the correlations be used to characterize C_{7+} fractions

TABLE 1—CONSTANTS FOR PR AND SRK EOS'S

Constant	PR	SRK
Ω_a	0.45724	0.42748
Ω_b	0.07780	0.08664
m_0	0.37464	0.480
m_1	1.54226	1.574
m_2	−0.26992	−0.176

found in reservoir fluids. The correlations are relatively simple to use since carbon number is used as the correlating variable. Rowe suggests carbon number can be calculated from molecular weight, as given by carbon number $=(M-2)/14$.

Yarborough. In 1978, Yarborough[7] presented a method for characterizing petroleum fractions of reservoir fluids. A graphical correlation is given relating specific gravity to carbon number as a function of the aromaticity factor.[24] Whitson[25] fit the curves with a four-constant equation.

The Yarborough method assumes C_{7+} molecular weight and specific gravity are measured. It also assumes that mole fractions are available from chromatographic analysis (paraffin molecular weights are used to convert from weight to mole fractions). The procedure begins by assuming an aromaticity factor. SCN specific gravities are calculated from the specific gravity correlation (a function of carbon number). C_{7+} specific gravity is then calculated using the proper mixing rule and this value is compared with the measured value. The aromaticity factor is adjusted until the measured and calculated C_{7+} specific gravities match.

By using SCN specific gravities and assumed molecular weights, boiling points are estimated from charts or an appropriate correlation. Critical properties are estimated by using boiling points and specific gravities. Acentric factor is estimated from the Edmister equation.

Riazi-Daubert. In 1980, Riazi and Daubert[16] presented simple equations for estimating physical properties of pure compounds and petroleum fractions. The same equation form is used for all properties. It is the same equation form as proposed by Nokay[15] for critical temperature.

The correlations are compared with the Winn nomograph and Mobil nomograph for critical pressure and critical temperature, respectively. The original claim was that the correlations give equivalent results. A later publication by Daubert[20] gives more detailed comparisons with nomographs and other correlations. In the boiling point range of 255 to 590 K [0 to 602°F], the Riazi-Daubert[16] correlations perform better (though only slightly) than other best methods. For systems without components heavier than C_{25}, the Riazi-Daubert correlations are probably the most accurate and easiest to use.

Whitson. In 1980, Whitson[25] proposed a scheme for characterizing C_{7+} fractions found in reservoir fluids. A method is proposed for estimating petroleum fraction specific gravities using molecular weights and a correlation for the Watson[26,27] characterization factor, K_w. The method is similar to the Yarborough[7] scheme except that K_w is related directly to boiling point and it can be solved without trial and error.

The proposed method is based on the assumption that the Watson characterization factor, K_w, which by definition is the cubic root of boiling point (°R) divided by specific gravity: $K_w = \sqrt[3]{T_b(°R)}/\gamma$, is constant for each fraction. A relation between molecular weight, specific gravity, and Watson K_w has been developed from the correlation between molecular weight, specific gravity, and boiling point suggested by Riazi and Daubert:

$$K_w = 4.5579 M^{0.15178} \gamma^{-0.84573}. \quad \ldots \ldots \ldots \ldots \ldots (1)$$

Assuming a constant K_w for each fraction, the specific gravity can be calculated from Eq. 1 as

$$\gamma_i = 6.0108 M_i^{0.17947} K_w^{-1.18241}. \quad \ldots \ldots \ldots \ldots (2)$$

It is necessary to choose K_w such that the mixture specific gravity, γ_{7+}, calculated from

$$\gamma_{7+} = (x_{7+} M_{7+}) \Big/ \sum_{i=1}^{n} x_i M_i / \gamma_i, \quad \ldots \ldots \ldots \ldots (3)$$

equals the measured value. It can be shown that the value of K_w necessary to meet this criterion is given by

$$K_w = [0.16637 \gamma_{7+} S/(x_{7+} M_{7+})]^{-0.84573}, \quad \ldots \ldots (4)$$

where

$$S = \sum_{i=n}^{N} x_i M_i^{0.82053}. \quad \ldots \ldots \ldots \ldots \ldots \ldots (5)$$

The summation is performed for all fractions in the C_{7+} mixture. Having calculated K_w, specific gravity of each fraction is found from Eq. 2. Boiling point, T_{bi}, is merely $(K_w \gamma_i)^3$, found directly from the definition of K_w.

Whitson suggests using the Riazi-Daubert critical property correlations and the Edmister acentric factor correlation. He gives modified critical pressure constants for the Riazi-Daubert correlation at boiling points higher than 730 K [854°F] (SCN greater than 30). The modification results in a discontinuity, which is also reflected by acentric factor.

EOS Constants

Several publications[28,29] suggest that EOS constants a and b (i.e., Ω_a and Ω_b) can be adjusted to match experimental PVT data. It can be shown, however, that this method is essentially the same as the earlier practice of adjusting individual component critical properties.

For the PR[4] and SRK[5] EOS's,

$$a = \mu \ \Omega_a R^2 T_c^2 / p_c \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (6a)$$

and

$$b = \Omega_b RT_c / p_c, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (6b)$$

where

$$\sqrt{\mu} = 1 + m(1 - \sqrt{T_r}) \quad \ldots \ldots \ldots \ldots \ldots \ldots (7a)$$
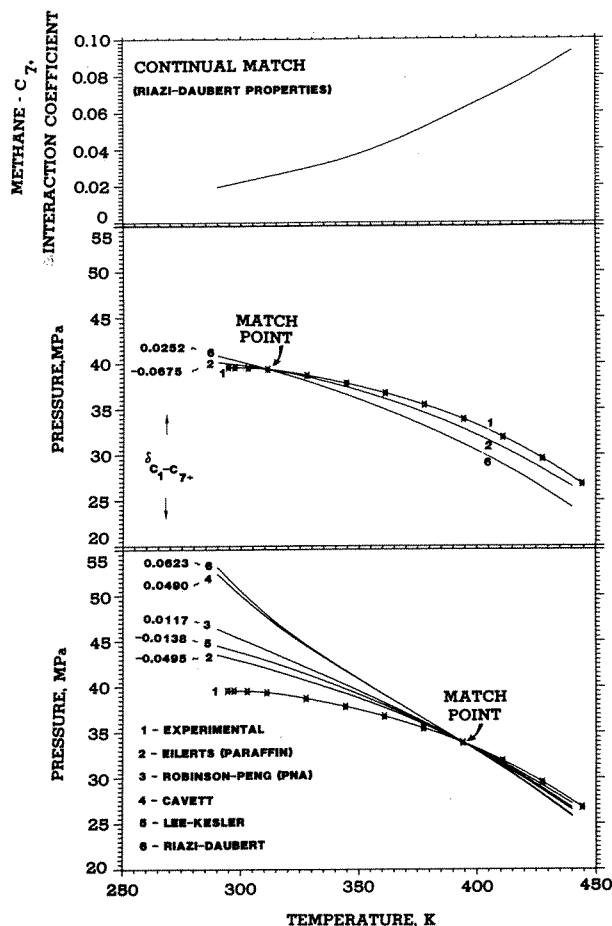
Fig. 2—ZJRK EOS predictions of Eilerts OO-L-544 gas condensate—phase diagram.

and

$$m = m_0 + m_1\omega + m_2\omega^2. \qquad\qquad\qquad (7b)$$

Constants for the PR and SRK EOS's are given in Table 1.

EOS constants Ω_a and Ω_b are determined by forcing the van der Waals critical point criteria to the general form of the EOS; these consist of setting the first and second derivatives, $(\partial p/\partial v) = (\partial^2 p/\partial v^2) = 0$, at T_c and p_c.

The factor μ is a correction factor that is used to force the EOS to predict correct vapor pressures of pure compounds. The correction factor, μ, then is correlated as a function of reduced temperature, T_r. The temperature dependence differs for various compounds and this effect is accounted for by acentric factor.

It might be noted that the correction term μ has no physical meaning at $T_r > 1$ even though it is used. Only methane and the lighter components have $T_r > 1$ at common operating temperatures. Adjustment of Ω_a for methane can be argued on the grounds that the correction term does not extrapolate the physical behavior correctly at supercritical temperatures.

If adjustments are made to Ω_a and Ω_b with factors α and β, respectively, then adjustments to T_c, p_c, and ω give identical EOS results if

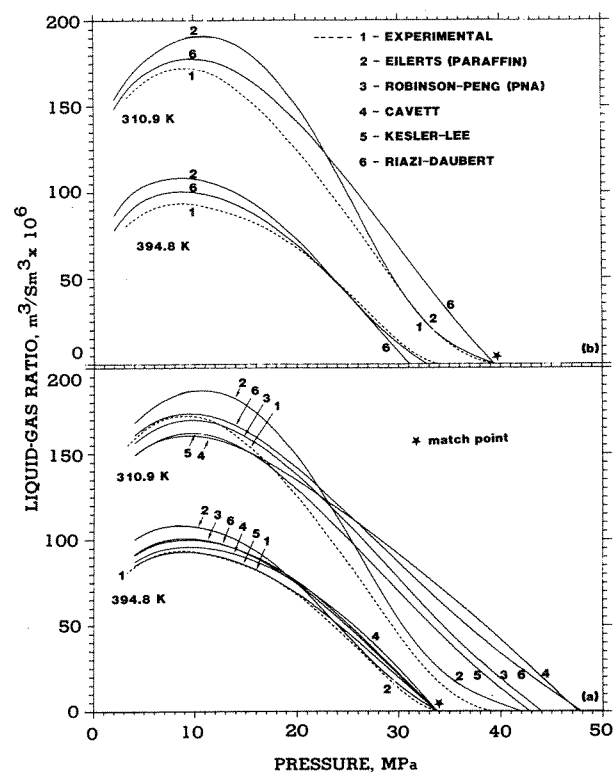$$\tilde{T}_c = (\alpha/\beta)T_c, \qquad\qquad\qquad (8a)$$

Fig. 3—ZJRK EOS predictions of Eilerts OO-L-544 gas condensate—liquid/gas ratio.

$$\tilde{p}_c = (\alpha/\beta^2)p_c, \qquad\qquad\qquad (8b)$$

$$\tilde{\omega} = \frac{-m_1 + \sqrt{m_1^2 - 4m_2(m_0 - \tilde{m})}}{2m_2}, \qquad\qquad (8c)$$

and

$$\tilde{m} = m\frac{1 - \sqrt{T/T_c}}{1 - \sqrt{T/\tilde{T}_c}}. \qquad\qquad\qquad (8d)$$

Eqs. 8a through 8d illustrate that adjustments of a and b can be translated directly to adjustments of T_c, p_c, and ω. If $\alpha/\beta = 1$, only p_c is adjusted. If $\alpha/\beta^2 = 1$, only T_c and ω are adjusted. All other combinations of α and β correspond to an adjustment of all three critical properties.

Constants a and b should not be adjusted more than will result in altered critical properties which are physically meaningful. Eqs. 8a through 8d should help prevent misuse of adjustments to EOS constants.

The saturation pressure of petroleum mixtures often is matched by using binary interaction coefficients. Binaries enter EOS calculations through the mixing rules and affect only EOS constant a for the mixture. Binaries do not have a well-defined physical meaning but are useful for correcting VLE deficiencies of cubic EOS's. Katz and Firoozabadi correlate binaries between methane and petroleum fractions. They indicate good prediction of dewpoints when the correlation is used but poor predictions of bubblepoint. Their suggestion is to match bub-
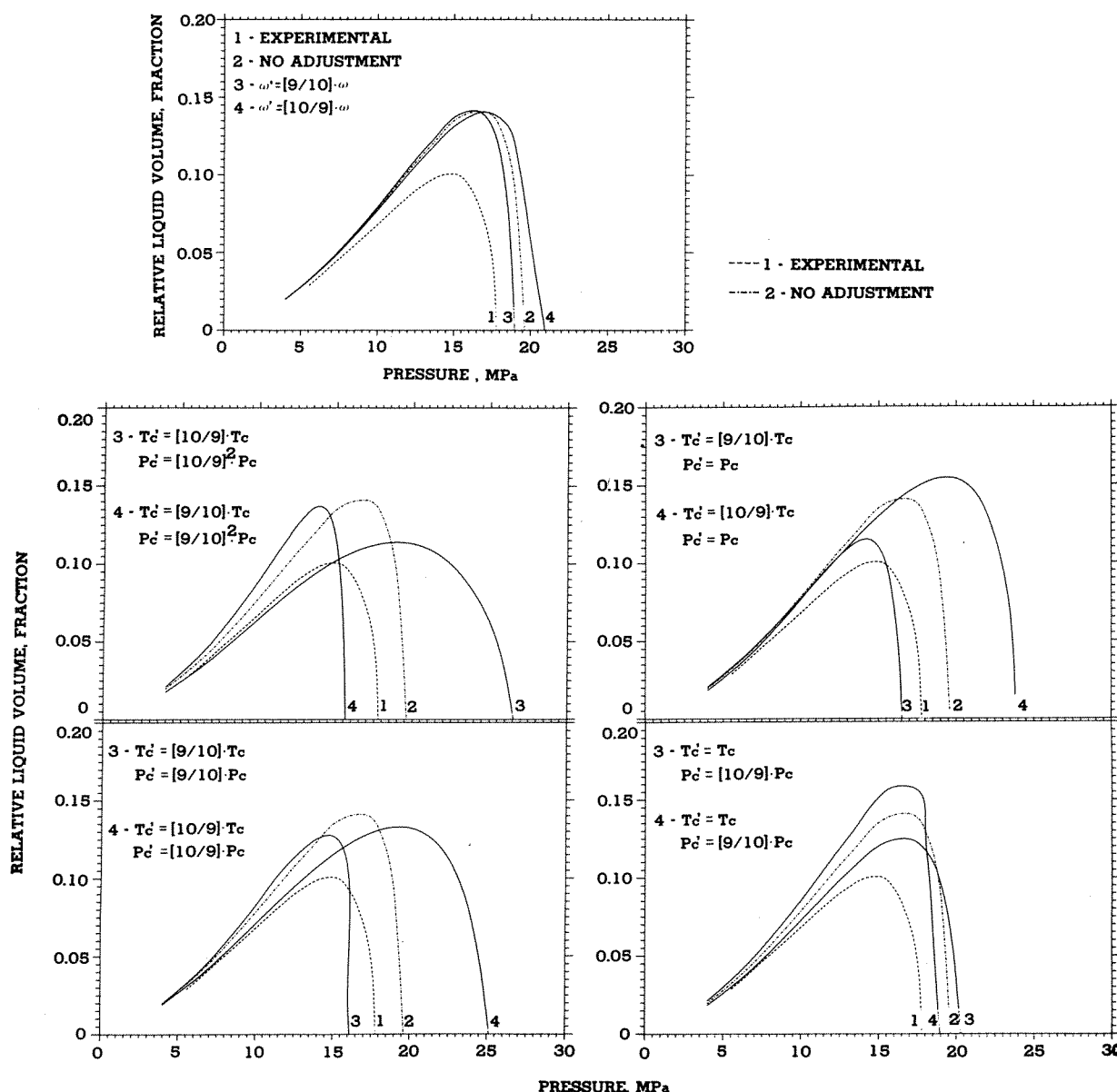
Fig. 4—PREOS predictions of Eilerts CH-P-843 gas condensate—critical properties adjustment.

blepoint with the binary between methane and the heaviest petroleum fraction.

Results

Calculations are performed on six reservoir fluids taken from the literature. Several C_{7+} characterization schemes are used to describe the petroleum fractions. Each example illustrates the effect of C_{7+} properties on EOS predictions. In all cases, the C_{7+} fraction is split into SCN groups. The PR and ZJRK equations are used exclusively for all calculations.

Eilerts OO-L-544 Gas Condensate. The OO-L-544 fluid presented by Eilerts et al.[30,31] is a gas condensate containing 90.162 mol% methane and 1.51 mol% C_{7+}. The C_{7+} fraction has a molecular weight of 167.3 and specific gravity of 0.8051. Fractional distillation data are available up to C_{24}. These data have been converted to

SCN groups according to the Robinson-Peng method (except for density determination). Dewpoint pressure is reported as 33.85 MPa [4,909 psi] at reservoir temperature of 394.8 K [251°F]; the reservoir is initially undersaturated at a pressure of 35.00 MPa [5,076 psi].

Dewpoint pressure is estimated with the ZJRK EOS at 394.8 K [251°F]. Measured specific gravities and boiling points are used to estimate critical properties from five correlations. The first correlation, labeled "Eilerts (paraffin)," is the set of critical properties proposed by Eilerts et al. that represents paraffin values.

Acentric factor is estimated from the Edmister equation except when the Kesler-Lee and Robinson-Peng correlations are used. For all cases, the interaction coefficients between methane and all C_{7+} fractions are adjusted to match the measured dewpoint pressure. Saturation pressures are calculated at temperatures from 290 to 440 K [62 to 332°F] and results are presented in Fig. 2a.
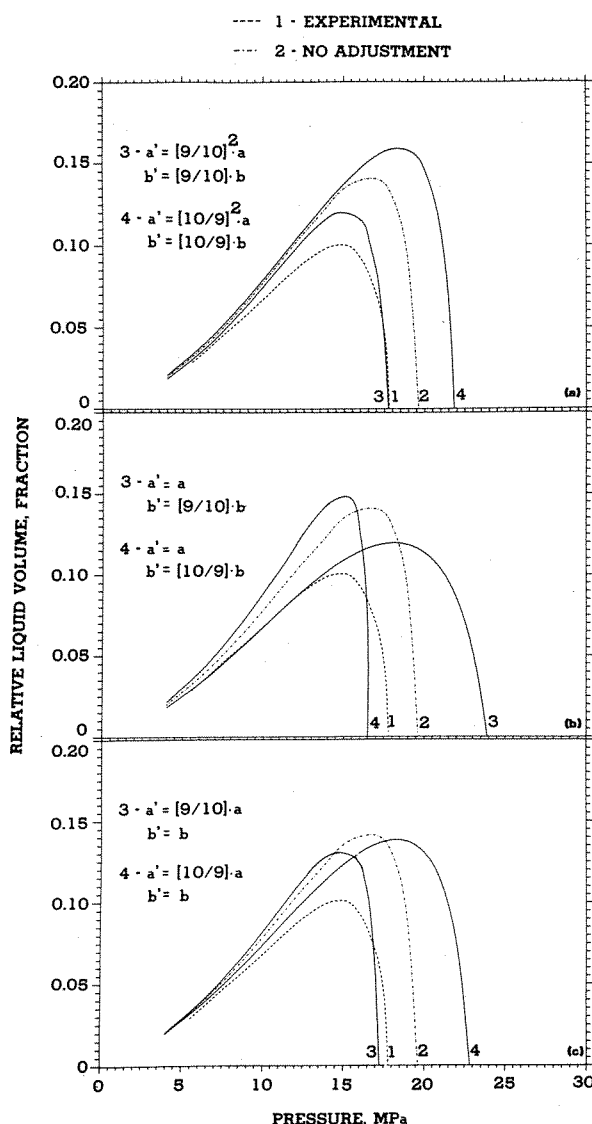
Fig. 5—PREOS predictions of Eilerts CH-P-843 gas condensate—EOS constants adjustment.

Fig. 6—PREOS predictions of Eilerts CH-P-843 gas condensate—phase diagram.

The matching procedure is repeated at 310 K [98°F] using only two of the property correlations. The matched dewpoint is 39.40 MPa [5,714 psi]. Extrapolation in temperature also is performed. Results are given in Fig. 2b.

A continual match of dewpoint pressure is made in the temperature range of 290 to 440 K [62 to 332°F] using the Riazi-Daubert/Edmister correlations. The resulting C_1-C_{7+} interaction coefficients are presented in Fig. 2c.

Liquid/gas ratios (F_{LG}) are calculated as a function of depletion pressure at reservoir temperature by using the five property correlations; the match point is once again 394.8 K [251°F] and 33.85 MPa [4,909 psi]. By using this match, the same calculations are performed at a lower temperature of 310.9 K [100°F]. Results are found in Fig. 3a. F_{LG} is defined as

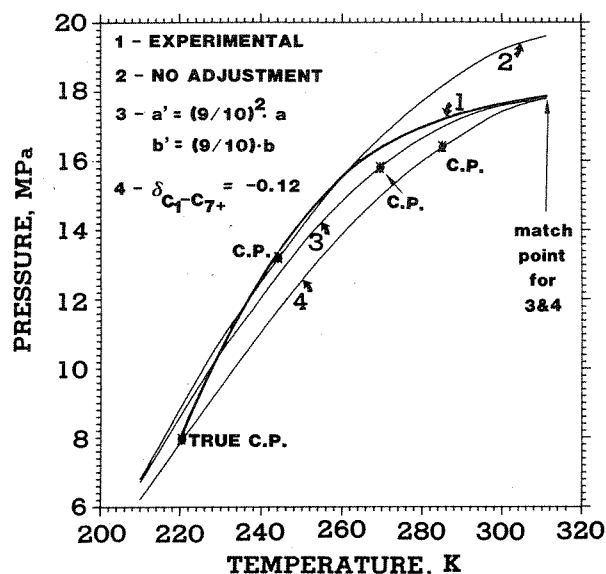$$F_{LG} = 42.26 \frac{M_g V_{rL}}{\rho_g (1 - V_{rL})}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

where ρ_g is gas gravity in g/cm^3, M_g is gas molecular weight, V_{rL} is relative volume of liquid to the total gas-plus-liquid volume, and F_{LG} has units of $m^3/10^6$ std m^3.

The same procedure is repeated, but the match point was reversed. In this case, only two of the property correlations are used. Liquid/gas ratios are plotted vs. pressure in Fig. 3b.

Eilerts CH-P-843. The CH-P-843 fluid is a gas condensate containing 76.432 mol% methane and 2.992 mol% C_{7+}. The C_{7+} molecular weight is 125 with a specific gravity of 0.7385. Fractional distillation data did not indicate hydrocarbons heavier than C_{13}. There are considerably more intermediates in this fluid than in OO-L-544. Numerous experimental data are provided by Eilerts. These include: the p-T phase diagram from 220 to 310 K [−63 to 98°F], critical point, cricondenbar, cricondentherm and two-phase liquid/liquid region. Some liberty has been taken in this work when extrapolating the p-T phase diagram.

The PR EOS is used to predict some of the experimental PVT observations. Paraffin critical properties suggested by Eilerts are used together with Edmister acentric factors.

Figs. 4a through 4e show the effect of adjusting C_{7+} critical properties. Dewpoint pressure and liquid volume, relative to total volume, are estimated at 310.9 K [100°F]. Curves labeled 1 and 2 are the same for all figures. Curve 1 is determined from experimental data, whereas Curve 2 is the PR prediction using unaltered paraffin properties for the C_{7+} fractions.

The effect of simultaneously adjusting critical pressure and temperature is shown in Figs. 4a and 4b. Results of adjusting only critical pressures are shown in Fig. 4d; results of adjusting only critical temperature are shown in Fig. 4c; results of adjusting only acentric factor are shown in Fig. 4e.
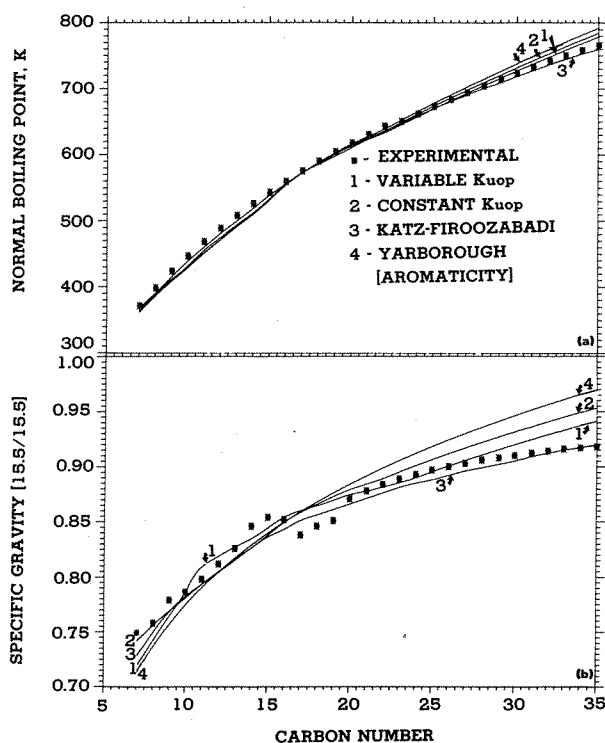
Fig. 7—Experimental vs. estimated boiling points and specific gravities of Hoffman oil.

Figs. 5a through 5c show the effect of adjusting EOS constants a and b. Both constants are adjusted in Fig. 5a. Only constant b is adjusted in Fig. 5b and only constant a in Fig. 5c. Note that Curve 3 in Fig. 5a (decreasing both a and b) results in an excellent prediction of dewpoint pressure and liquid dropout.

The p-T phase diagram is predicted by using three C_{7+} characterization schemes. The first uses unaltered paraffin critical properties without adjusting interaction coefficients. The second is the same as Curve 3 in Fig. 5a. The third alternative uses unaltered paraffin critical properties but matches dewpoint pressure at 310.9 K [100°F] with the methane/C_{7+} interaction coefficient of -0.12. Phase diagrams and critical points are presented in Fig. 6.

Jacoby Synthetic Mixtures. The synthetic mixtures presented by Jacoby[32] are studied using the PR and ZJRK EOS's. Several critical property correlations have been chosen to describe the eight boiling point fractions constituting hexanes-plus.

The p-T phase diagram for mixture S-3 is predicted by matching saturation pressure of 27.4 MPa [3,974 psi] at 370.5 K [207°F] with a methane/C_{6+} interaction coefficient of 0.0536. Experimental data show a dewpoint at this temperature. A bubblepoint is predicted using both PR and ZJRK equations, independent of the property correlation. Extrapolation in temperature is reliable for all
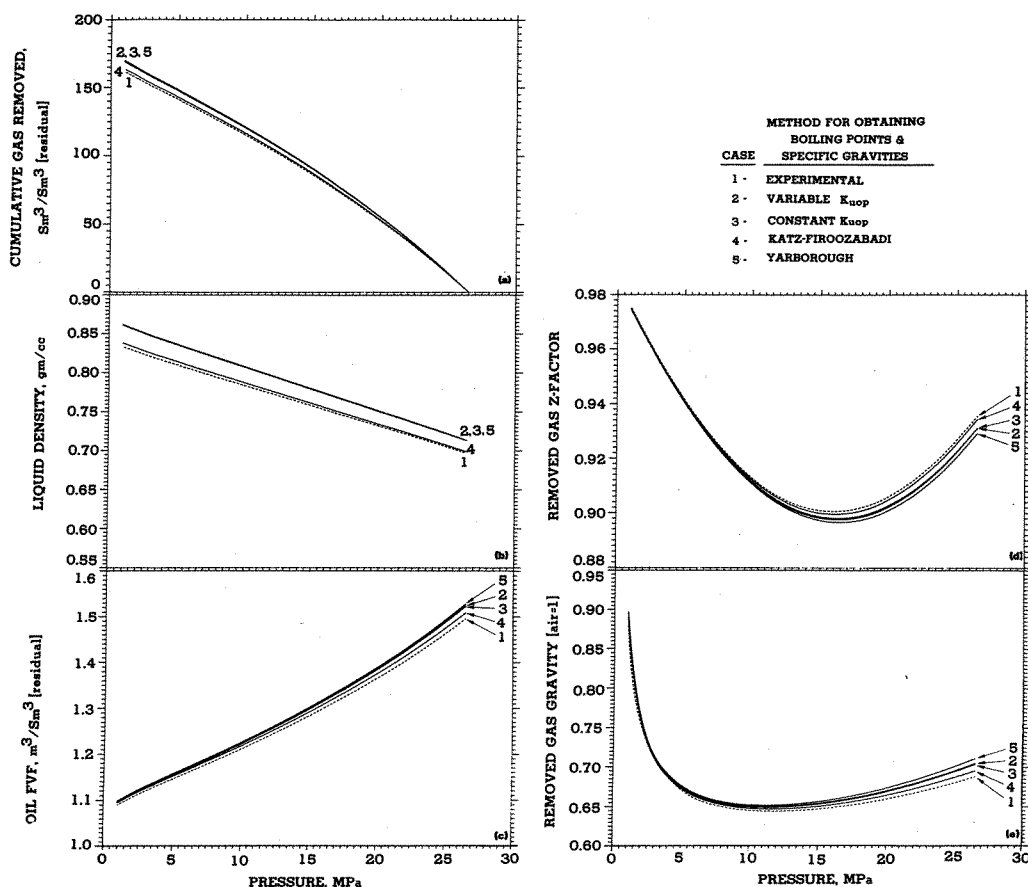

Fig. 8—ZJRK EOS predictions of Hoffman oil—simulated differential liberation test.
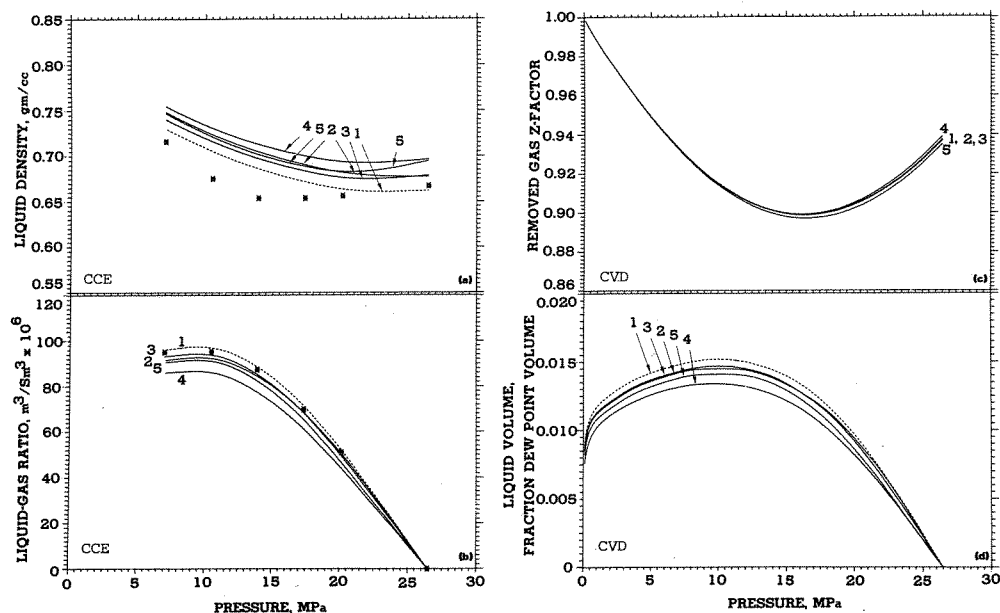
Fig. 9—ZJRK EOS predictions of Hoffman gas—simulated expansion tests.

correlations. However, the estimated critical temperature is always 70 to 100 K [125 to 180°F] high.

Many attempts were made to predict the phase diagram created by recombining separator samples at various gas/oil ratios (GOR's). For all critical property correlations, both EOS's predicted reasonable ($\pm 5\%$) saturation pressures up to the last two GOR's (S-6 and S-7). The estimated critical composition (GOR) was considerably different than measured experimentally. Bubblepoints are predicted until a GOR of between 890 and 1,340 std m^3/std m^3 [38 and 57 kmol] (S-4 and S-5). Experimental data suggest that the last bubblepoint should have been between 620 and 710 std m^3/std m^3 [26 and 30 kmol] (S-2 and S-3).

Hoffman-Crump-Hocott Reservoir Oil. The Hoffman-Crump-Hocott[33] (HCH) reservoir oil is used to study the effect of property correlations on typical PVT behavior. The oil is saturated at initial conditions of 26.4 MPa [3,828 psi] and 367.0 K [201°F]. It contains 52.00 mol% methane and 36.84 mol% heptanes-plus. The C_{7+} molecular weight is 198.7 with a specific gravity of 0.8412. Distillation analysis is available to C_{35}; boiling point cuts approximate SCN groups with paraffin boiling points.

Several aspects of C_{7+} characterizations have been investigated by using the HCH oil. First, a comparison is made between three schemes for estimating specific gravities and boiling points of SCN fractions. Fig. 7 compares experimental and estimated values of γ and T_b. The Kesler-Lee correlations are used to estimate critical properties and acentric factors.

EOS predictions also have been performed by using four different critical property correlations. One case (1') uses variable interaction coefficients between methane and C_{7+} fractions, matching bubblepoint pressure with the C_1-C_{22+} coefficient. Results of simulated differential liberation are found in Figs. 8a through 8e. Prediction of a swelling test indicates a strong compositional influence of the methane binary interaction coefficients with petroleum fractions. That is, the saturation pressure vs. gas injected curve is much lower when using a constant binary between methane and all C_{7+} fractions than when using the Katz and Firoozabadi correlation together with a large binary between methane and the heaviest component.

HCH Reservoir Gas. Hoffman et al.[33] also present numerous data for the gas-cap fluid in equilibrium with the reservoir oil. The gas contains 91.35 mol% methane and 1.54 mol% C_{7+}. The C_{7+} molecular weight is 141 with a specific gravity of 0.7867. Dewpoint pressure equals bubblepoint pressure of the oil (26.4 MPa [3,828 psi]) at reservoir temperature of 367 K [201°F].

The same comparisons made in the previous example are made for this fluid (except the case with varying interaction coefficients). Instead of simulating a differential liberation experiment, constant composition expansion (CCE) and constant volume depletion (CVD) processes are simulated. CCE predictions are compared with experimental data reported by Hoffman et al.

Figs. 9a through 9d present results of the comparisons made between different methods of estimating specific gravities and boiling points. Kesler-Lee properties are
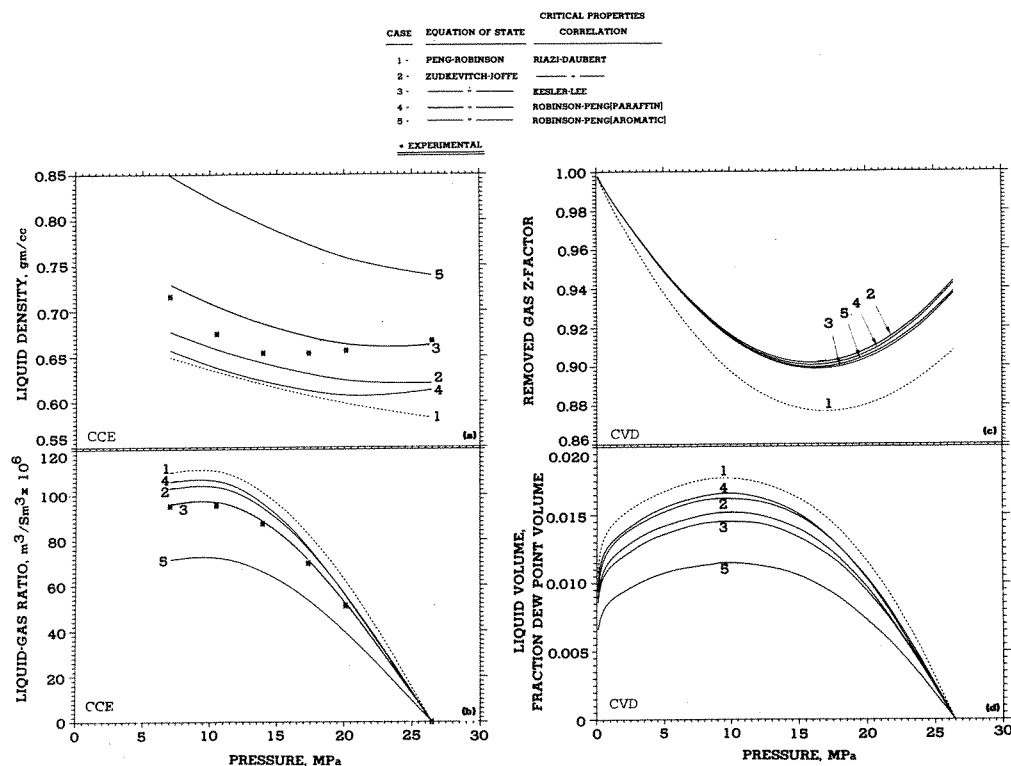
CASE	EQUATION OF STATE	CRITICAL PROPERTIES CORRELATION
1 -	PENG-ROBINSON	RIAZI-DAUBERT
2 -	ZUDKEVITCH-JOFFE	— · —
3 -	——— : ———	KESLER-LEE
4 -	——— : ———	ROBINSON-PENG(PARAFFIN)
5 -	——— : ———	ROBINSON-PENG(AROMATIC)

• EXPERIMENTAL

Fig. 10—ZJRK and PREOS predictions of Hoffman gas— simulated expansion tests.

used in the ZJRK EOS. Figs. 10a through 10d present results of the comparisons made between different property correlations. Both PR and ZJRK equations are used.

Hong Reservoir Oil A/CO_2 System. Hong[34] gives experimental data for a reservoir oil/CO_2 system. The oil contains 31.00 mol% methane and 32.43 mol% C_{7+}. C_{7+} molecular weight is 199. No distillation data or C_{7+} specific gravity are reported. Mole fractions and "tuned" critical properties are given for C_7-C_{12} SCN groups and the remaining C_{13+} fraction. Bubblepoint pressure of the initial oil is 11.4 MPa [1,653 psi] at 327.6 K [130°F].

The Hong oil/CO_2 system has been chosen to illustrate the effect of CO_2/hydrocarbon (CO_2/HC) binary interaction coefficients on predicted phase behavior. The PREOS is used by Hong. Both PR and ZJRK equations are used in this study.

Using the PREOS, four methods are used to describe the CO_2/HC interaction coefficients. The first method uses guidelines provided by Hong. Coefficients are varied from 0.14 to 0.20, decreasing as a function of acentric factor. The second method uses the empirical equation suggested by Kato.[35] The third method uses a constant, molar average of coefficients from the first method. The last method uses a constant CO_2/HC coefficient of 0.145; this value was determined by matching the bubblepoint pressure at 50 mol% CO_2.

Results of the first three cases are shown in Figs. 11a and 11b. For the first case (A), saturation pressures match experimental data up to CO_2 concentrations of 80 mol%. The critical CO_2 concentration is overestimated by 10 mol%. This predicted phase diagram is similar to the one obtained with a constant CO_2 coefficient of 0.145.

Using the Kato coefficients (B), saturation pressures are grossly underestimated. Bubblepoint pressures are

predicted up to a CO_2 concentration of 70 mol%. Using the average CO_2/HC binaries of 0.175 (from A) results in overestimated saturation pressures; at 60 mol% CO_2 no saturation pressure is predicted below 30 MPa [4,351 psi], whereas the experimental critical pressure at this concentration is 17.7 MPa [2,567 psi].

Phase behavior of this system also has been predicted by using the ZJRK EOS. Only a slight change (from 0.137 to 0.147) in CO_2-C_{7+} coefficients is necessary to match the entire phase envelope. The adjusted value is nearly identical with the one found using the PREOS (0.145). As in other cases, critical CO_2 concentration is overestimated.

Discussion

Interaction Coefficients. The effect of increasing binary interaction coefficients between methane and C_{7+} fraction is to increase saturation pressure prediction. This observation appears to be general for both the bubblepoint and retrograde dewpoint regions, and applies for both the PR and ZJRK EOS's.

In general, the PREOS requires larger (usually positive) coefficients to match saturation pressure, where the ZJRK equation often requires negative values. Apparently C_{7+} critical properties influence the value of interaction coefficients needed to match saturation pressure.

It appears that C_1-C_{7+} interaction coefficients have a relatively strong temperature dependence. An important consequence is that saturation pressures may be overestimated if coefficients matched at one temperature are used to estimate saturation pressure at lower temperatures. This problem seems to be less significant if the match at one temperature is extrapolated to higher temperatures.

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Correlations of methane/hydrocarbon binaries indicate that interaction coefficients increase with increasing molecular size. A comparison between using a constant C_1-C_{7+} coefficient and variable (increasing) values had little effect on most EOS predictions. Some properties were influenced, however, including gas compressibility and molecular weight, swelling factor, saturation pressure increase caused by gas injection, and interfacial tension.

Concerning the use of CO_2/HC binary interaction coefficients it appears that there is little advantage in using coefficients that vary as a function of molecular size.

General Observations. The influence of C_{7+} properties on EOS predictions appears to be substantial for reservoir fluids. The choice of critical property correlation usually has more influence on EOS predictions than the method used to estimate specific gravities and boiling points (when these properties are not available).

Several observations not directly related to C_{7+} characterizations are worth noting. The two EOS's used in this study always overestimate mixture critical temperature. The same behavior has been observed for several other systems. This problem can be particularly important if a rich gas condensate (near the critical point) is being studied.

The ZJRK equation gives an overall better performance than the PREOS. The major difference is seen in liquid density (volumetric) predictions. On the other hand, the PREOS has a simple form and can be reproduced readily, which is not the case for most of the ZJRK variants.

Conclusions

1. Different correlations used for estimating critical properties of petroleum fractions can have a large effect on EOS predictions of mixture phase behavior. No single C_{7+} correlation or combination of correlations gives consistently better EOS predictions.

2. The use of binary interaction coefficients between methane and petroleum fractions to match mixture saturation pressure has several drawbacks. First, the binaries appear to have a strong temperature dependence, which may be important in thermal recovery, process design, and multiphase flow in pipe. Second, the compositional dependence of binaries may be important, in which case processes such as revaporization and multicontact miscibility will be affected.

3. Different methods for estimating specific gravities and boiling points of petroleum fractions do not appear to have as strong an effect on EOS predictions as different methods for estimating critical properties. The Watson-K_w method suggested by Whitson is suggested for three reasons: (1) it ensures that measured C_{7+} specific gravity equals the calculated value, (2) specific gravities can be determined directly without trial and error, and (3) boiling points result directly from the match of C_{7+} specific gravity.

4. An alternative method for calculating critical properties for use in a specific EOS would be to force the EOS to fit measured physical properties of individual petroleum fractions (normal boiling point and specific gravity). This method should enhance VLE and liquid density predictions for the C_{7+} fractions in a petroleum mixture.
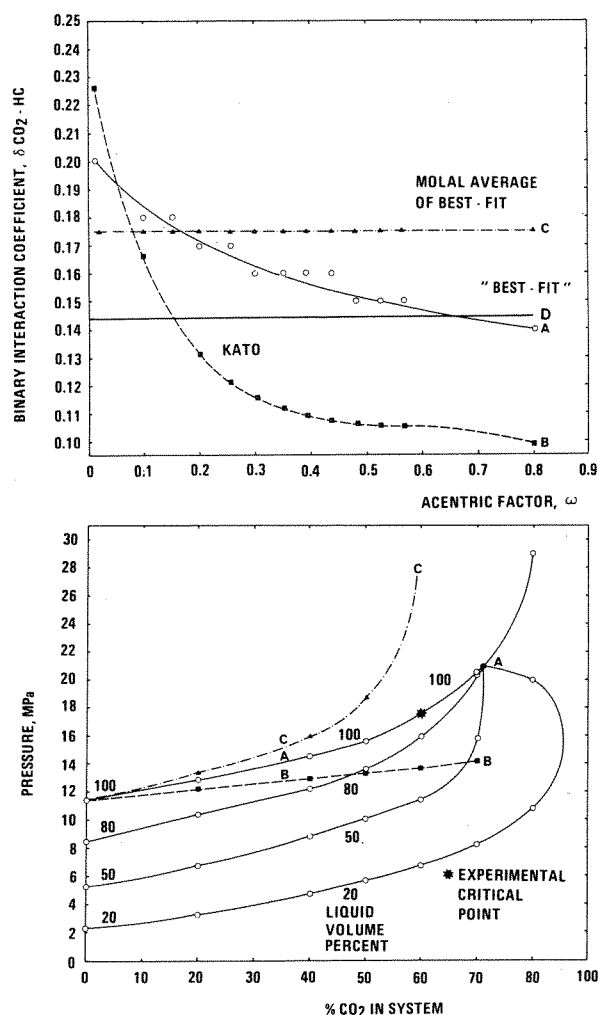
Fig. 11—PREOS predictions of Hong oil—phase diagram and interaction coefficients.

Nomenclature

a = EOS constant
b = EOS constant
F_{LG} = liquid/gas ratio, $m^3/10^6$ std m^3
K_w = Watson characterization factor
M = molecular mass, mass per mole
p_c = critical pressure, kPa [psi]
R = universal gas constant, 8.3143 J/(mol·K) [cal/g mol-°C]
T = absolute temperature, K [°F]
T_b = normal boiling point, K [°F]
T_c = critical temperature, K [°F]
T_r = reduced temperature ($T_r = T/T_c$)
V_{rL} = liquid volume, relative to total volume
α = correction factor for EOS constant a
β = correction factor for EOS constant b
γ = specific gravity, relative to water at 15.5°C [59.9°F]
μ = correction variable in EOS constant a
ρ = density, g/cm^3
ω = acentric factor
Ω_a = EOS constant
Ω_b = EOS constant

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SI Metric Conversion Factors

$$
\begin{array}{llll}
°API & 141.5/(131.5 + °API) & & = \text{g/cm}^3 \\
\text{cu in.} & \times\ 1.638\ 706 & E+01 & = \text{cm}^3 \\
°F & (°F + 459.67)/1.8 & & = K \\
\text{psi} & \times\ 6.894\ 757 & E-03 & = \text{MPa}
\end{array}
$$

SPEJ