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THERMODYNAMIC ASPECTS OF ENHANCED OIL RECOVERY WITH SUPERCRITICAL CO_2

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ABSTRACT

This paper investigates how theories and data on phase equilibria, and volumetric and transport properties of mixtures can be applied to some mechanisms that have been proposed in the literature to aspects of EOR with CO_2.

In this work, the multiple-variable approach for establishing the equation parameters (temperature, fugacity and density dependence) which has been applied by Joffe, Schroeder and Zudkevitch (27) to the Redlich-Kwong (R-K) equation was extended and was also applied to the Peng-Robinson (P-R) equation and to establishing the interaction parameters.

RESUMEN

En este trabajo se investiga como la teoría y datos sobre equilibrio de fase y las propiedades volumétricas y de transporte de mezclas pueden ser aplicadas a algunos mecanismos que han sido propuestos en la literatura sobre aspectos de Recuperación Mejorada de Crudo (EOR) con CO_2.

En este trabajo el método de múltiple variable para establecer los parámetros de la ecuación (temperatura, fugacidad y densidad) aplicados por Joffe, Schroeder y Zudkevitch (27) a la ecuación de Redlich-Kwong (R-K) fue extendido y aplicado también a la ecuación de Peng-Robinson (P-R) estableciéndose los parámetros de interacción.

INTRODUCTION

Enhanced oil recovery (EOR) significantly impacts above-grounds operations such as field separations, treatment and processing at the gas plant.

Theoretical studies and operating data have shown that when oil recovery is enhanced by flooding with CO_2, revamping of gas-plant facilities is warranted not only due to the obvious need to recover the CO_2 and sweeten the products, but also because the quantity and quality of the gas after EOR can be different from those of the pre-EOR feed gas.

In this presentation, theories and data on phase equilibria, and volumetric and transport properties of mixtures will be applied to some mechanisms that have been proposed in the literature to aspects of EOR with CO_2. The aim is to present simplistic interpretations of published observations and "drive-modeling" in terms of chemical and gas engineering thermodynamic terminology. It is recognized that any modeling of an EOR operations is an integral of many approximated rate related phenomena, of which phase behavior is only one. Nevertheless, understanding and, hopefully, simulating the latter aspect may provide lead time for considering whether revamping the gas plant is desired.

MECHANISMS OF EOR AND TERMODYNAMIC ASPECTS

Although enhanced recovery via CO_2 flooding is a relatively new processing technique, the literature is replete with information and proposed explanations for the way by which it works. In essence, the oil, brine and associated gas in the pore are induced by CO_2 to migrate out of the pores and ease their pumping to the above ground separators. This mobility is influenced by the nature of the rock, the phases in the pores, their interfacial tensions, densities, viscosities and other physical properties which in turn are functions of temperature and pressure. Heterogeneity of the reservoir media can cause undesired flow patterns and distributions which are main causes of reduces sweep efficiency. A simulation program should employ reliable models, including predicting of PVT, phase and transport properties.

Since mobilities, dispersions, etc. of fluids are the key variables of the recovery process, development of an understanding and a predictive capability to describe the nature of the fluids at given instances, and/or locations, has been considered an important contribution (4, 11, 14, 20, 21, 22, 23, 24, 35, 36, 37, 39, 41, 43, 44, 50, 53,55). In the authors' opinion, the nature of each phase, its composition, density, viscosity and surface tension enter calculations of the variables influencing the migration (flow) of the fluid mixtures. Although other variables can be more influencial, description of the thermodynamic aspects can provide one needed tool to reservoir engineers. A qualitative assessment of the effect of thermodynamic and transport phenomena on EOR with CO_2 is given in Table 1.

TABLE 1. EFFECT OF THERMODYNAMIC DATA ON EOR WITH CO_2

EFFECT OF CONDITION ON	FLOW MOBILITY	SWELLING	QUALITY RECOVERY	PERMEABILITY
DENSITY/PVT	●	●	●	●
PHASE: V-L-E	●	●	●	I
L-L-E	●	●	●	I
L-L-V-E	●	●	●	I
A-L-L-V-E	●	O	O	O
B-L-L-V-E	●	-	O	●
VISCOSITY	●	-	●	●
DIFFUSIVITY	I	-	O	●
SURFACE TENSION	●	-	●	●
IONIZATION REACTION	O	-	O	I

● VERY IMPORTANT

O LESS IMPORTANT OR NOT PROVEN

I INDIRECT

- NOT APPLICABLE

L = LIQUID, E = EQUILIBRIUM, V = VAPOR, A = ASPHALTENES, B = BRINE

Different models have been proposed in the literature for the mechanism of EOR with injection of CO_2. This is mainly due to the fact that the experimental data that have been gathered of different fluids at different conditions could not be explained by a single model. Hutchinson and Braun(24) suggested a mechanism of "high pressure vaporization" where, following initial contact, the lean gas vaporizes enough light ends out of the rich oil to make the front of the flood miscible in the downstream oil. Rathmell and Stalkup (44) and Holm (21) discussed the common and the different features of CO_2 and propane miscible drives. The pointed out that at some conditions, CO_2 flooding can result in an immiscible drive.

Metcalfe and Yarborough (35) discussed different mechanisms for "cold" wells, those at temperatures below the critical of CO_2, and "hot" reservoirs. They listed the conditions at which miscible and immisible drives with CO_2 can occur. The various aspects of multiple-contact-miscibility (MCM) have been modeled by Metcalfe, Fussel and Shelton (36). The approach proposed by these researchers (35, 36) was to describe mechanisms and drives by simulating extraction processes computations with the use of triangular diagrams. The role played by the light ends and the adverse influence of methane and nitrogen on EOR with CO_2 were highlighted by Holm and Josendal (23), and by Orr, et al (38, 39, 41).

All the models proposed in the last ten years recognize the presence and the effects of multiple-phase formation. Henry and Metcalfe (20) presented data on single and multiple contacts between CO_2 and West Texas crudes and verified that conclusions deduced from single contact experiments are applicable to modeling multiple contact experiments.

Many attempts have been made (14, 22, 35, 37) to relate observed EOR phenomena to the phase behavior and the variations of the oil volume with pressure, i.e. swelling followed by contraction, in the presence of CO_2 as shown on curve 1 of Figure 10. It has been desired to establish a thermodynamic model for experimentally observed minimum miscibility pressure (MMP); the latter is established by "slim-tube" experiments. In the authors' opinion, the relation between this variable and classical thermodynamic considerations is not direct.

The effect of CO_2 flooding and formation of multiphases on the viscosity, surface tension and mobility and the impacts the flow characteristic of the phases, and the efficiency of EOR, have also been discussed in the literature. Some empirical limits have been proposed for the lowered viscosity and interfacial tension of the oily (nonwetting) phases as to their beneficial effects on efficient oil recovery. However, EOR phenomena are different at different conditions. Vaporization, condensation, and extraction prevail at intermedate temperatures, above 88°F and below 135 - 140°F (35 - 48) while condensation/extraction prevail at lower temperatures, their effects on the transport properties and mobility also vary. Vaporization / condensation can be assumed for EOR at temperatures above 140°F and low-miscibility drive may be the rule for EOR of heavy oils. Recent data (6, 11) show that mid-range gravity and some heavy oils also swell and their mixtures with CO_2 exhibit lower viscosities and interfacial tensions.

The above models emphasize the important effects of the miscibility of the light ends, including the gasoline and kerosene in CO_2 on low temperature flooding. In essence, the gasoline/kerosene/CO_2 phase in the front end of the drive can become the solvent for the heavier fractions.

Yarborough (61), Turek et al (53, 55), and Orr et al (30, 31) proposed that the phase behavior of systems encountered in EOR with CO_2 can be described by equations of state (42, 45). With some modifications made to accommodate the multiphase behavior. In the authors' opinion, this in only a partial solution. Coefficients and the interaction parameters of the empirical equations must be so selected that reasonably accurate predictions of both phase behavior and densities can be calculated.

In this work, the multiple-variable approach for establishing the equation parameters (temperature, fugacity and density dependence) which has been applied by Joffe, Schroeder and Zudkevitch(27) to the Redlich-Kwong (R-K) equation was extended and was also applied to the Peng-Robinson (PR) equation and to establishing the interaction parameters.

SOLUBILITY AND OTHER EQUILIBRIA IN CO_2 – HYDROCARBON SYSTEMS

Application of Theorems by Lewis and Poynting and correcting for nonideal mixing yields the simple equation relating the concentration of compound i in the liquid (x_i) and the vapor (y_i) in a system under low-to-moderate pressures.

$$\hat{\phi}_{iv} y_i P = \gamma_i x_i P_i^o \phi_{iL}^o \cdot \exp \int_{P_i^o}^{P} \frac{V_i}{RT} dP \qquad (1)$$

By definition, the phase equilibrium ratio,

$K_i = y_i/x_i$, is obtained from equation 1 through the following equation :

$$K_i = \frac{y_i P_i^o \phi_i^o L \cdot \exp \int_{P_i^o}^{P} \frac{V_i}{RT} dP}{\hat{\phi}_{iv} P} \qquad (2)$$

The variables are : P is the pressure; P_i^o is vapor pressure of i at t; $\phi°$ and ϕ_i are the fugacity coefficients of i under P° and P respectively; γi is the activity coefficient in the liquid phase and the exponential term stems from the need to equate the sides of Equation 1 under the pressure.

When γi, $\hat{\phi}_i$, $\phi_i^°$ and the Poynting effect are assumed each to equal unity, Equation 1 reduces to Raoult's law. Under low pressures the ratio $\phi_i^°/\hat{\phi}_i$ is near unity and, hence the low pressure portion of the K values isotherm vary as straight line function of pressure on a logarithmic scale.

Values of γi^{∞}, for some hydrocarbons at infinite dilution in CO_2, were calculated from literature data on vapor-liquid and liquid-liquid equilibria for binary systems with paraffinic hydrocarbons at temperatures around 80°F (≈300K) and 1000 psia (≈6.8 MPa)

The results are summarized in Table 2 and are illustrated in Figure 1. The representative values of γ^{∞} for CO_2 in Table 2 and the observations of Francis (17), and Dandge et al (8) provide thermodynamic confirmation to the conclusions of those who have studied EOR with CO_2, i.e. at the low temperature range of EOR, around 80°F, CO_2 is readily soluble in light and medium range hydrocarbons. However, it is selective as a solvent for hydrocarbons. Hence, liquid mixtures of CO_2 and paraffins

TABLE 2. INFINITE DILUTION ACTIVITY COEFFICIENT PARAFFINS/CO_2 @ 80°F AND 1000 PSIA

HYDROCARBON		INFINITE DILUTION ACTIVITY COEFFICIENT @80°F = 300K 1000 PSIA = 6.9 MPa		REF.
N	NAME	CO_2 in HC	HC in CO_2	
3	PROPANE	2.	2.	26[a]
7	n-HEPTANE	2.	6.	26[b]
12	n-DODECANE	1.9	22	16
14	n-TETRADECANE	1.73	29	16
15	n-PENTADECANE	1.7	44	16
16	n-HEXADECANE	1.65	58	34,38
20	n-EICOSANE	1.85	390	16
30	SQUALANE	1.7	320	16

a. ANALYSIS OF DATA OF REAMER, H.H., SAGE, B. H. AND LACEY, W. N. IND. ENG. CHEM. 36, 88, (1944)

b. ANALYSIS OF DATA OF KALRA, H., KUBOTA, H., ROBINSON, D. B. AND Ng, H-J., JOURN. CHEM. ENG. DATA, 23, 4, 317, (1978)

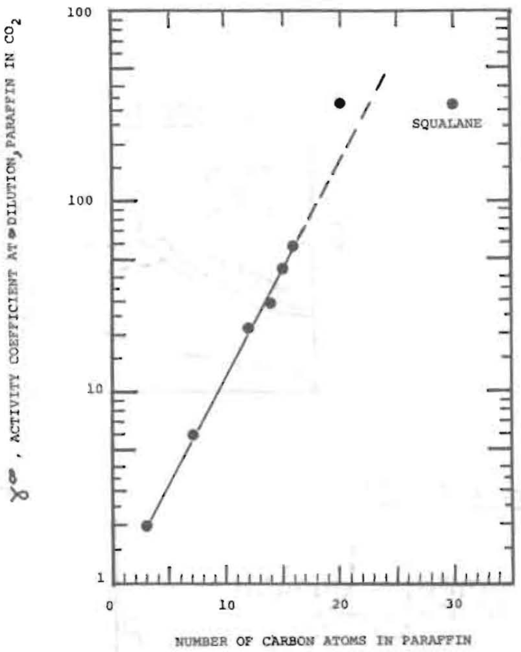

FIGURE 1. ACTIVITY COEFFICIENT AT INFINITE DILUTION PARAFFINS IN CO_2 - RICH LIQUID AT 80°F AND 1000 PSIA (300K and 6.8 MPa)

heavier than hexane exhibit dichotomy (splitting to two liquid phases). The lack of symmetry in the γ^∞ values is a direct indication that when separate liquid phases are present, both phases are rich with CO_2. As the temperatures in question are either near of above the critical of carbon dioxide, these are high pressure systems (above 500 psia).

Light hydrocarbons, except methane, form azeotropic mixtures with CO_2, the loci of some extend to and affect the binary critical loci. This is schematically shown in Figure 2a, where these systems are a subclass of Class I. Riviews of mixtures of CO_2 with branched paraffins and cyclic hydrocarbons (8, 17) indicated that CO_2 tolerates i.e. dissolves compounds of the latter groups much more than it does the normal paraffins.

PHASE EQUILIBRIA AT HIGH PRESSURES AND CRITICAL LOCI

From studies of binary systems under pressure and, also, utilizing the van der Waals equation, Kuenen predicted (in 1907) that the effects of differences of molecular nature, and in boiling and freezing points would cause discontinuities in critical locus surfaces. This was later confirmed by the data of Tsiklis and of Krichevski (around 1941). Systematic studies in the past 30 years have built quite a treasure of data on systems under high pressures. Van Konynenburg and Scott (56) proposed classifying binary mixtures and critical loci according to what affects their transitions between gas-liquid, liquid-liquid, solid-solid and gas-gas phase equilibria. These curves, together with pure-component vapor pressure (and in some cases azeotropes) curves form the principal boundaries, in P-T spaces, of the surfaces representing equilibrium among fluid and solid phases. Using as a basis the P-T proyections of critical and three phase curves resulting from their calculations, Van Konynenburg grouped fluid phase diagrams into five major classes, designated I to V.

The Van Konynenburg's classification in outlined in Figure 2. In each class there are many subclasses. Classes I and II encompass binary systems of compounds whose critical temperatures are close to each other. Hence, the critical loci are continuous. Nonideal mixing (γ effects) can cause

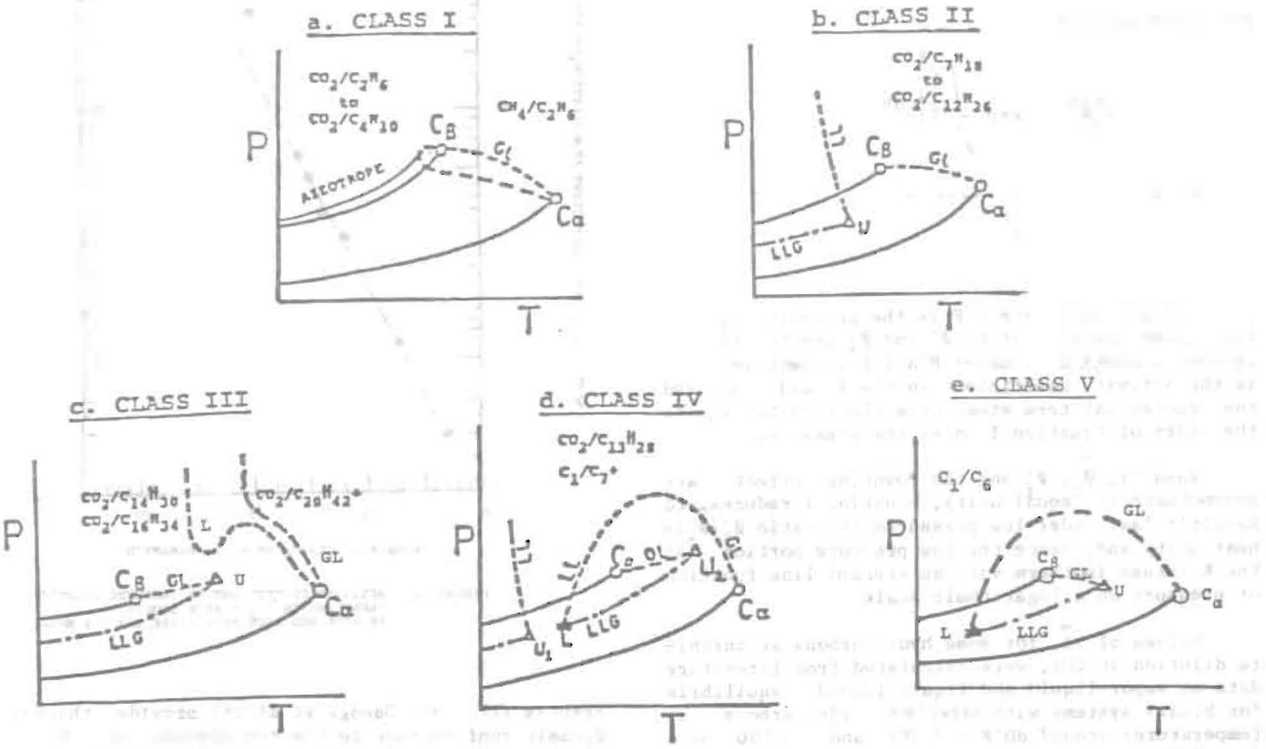

FIGURE 2. CLASSES OF PHASE AND CRITICAL BEHAVIOR (56) FOR MIXTURES ENCOUNTERED IN EOR WITH CO_2

azeotropes and deformation, i.e. deviations from the dome shape, of the critical curve, as shown in Figure 2a for mixtures of light hydrocarbon with CO_2. Stronger repulsive forces (large values) cause separation into two liquid phases, as shown in Figure 2b. The combination of strong repulsion (two liquids) and large differences in critical and freezing temperatures reflect themselves in the behaviors described by the subclasses of Class III.

In Classes III, IV and V, the critical loci are not continuous; they do not connect the criticals of the pure compounds. In each system of these classes, one portion of the critical curve starts from the critical of the light compound, C_B, and extends to the Upper Critical Miscibility point, U_1. The other branch starts at the critical point of the heavy compound, C_α, with the tendency toward C_B, but the curve never reaches C_B. In systems of Classes IV and V, it ends at the lower critical miscibility temperature, L. In Class III, it may or may not merge with the locus of the liquid - liquid critical miscibility points depending on the magnitude of the differences in freezing and critical temperatures of the components. This is illustrated in Figures 3 and 4.

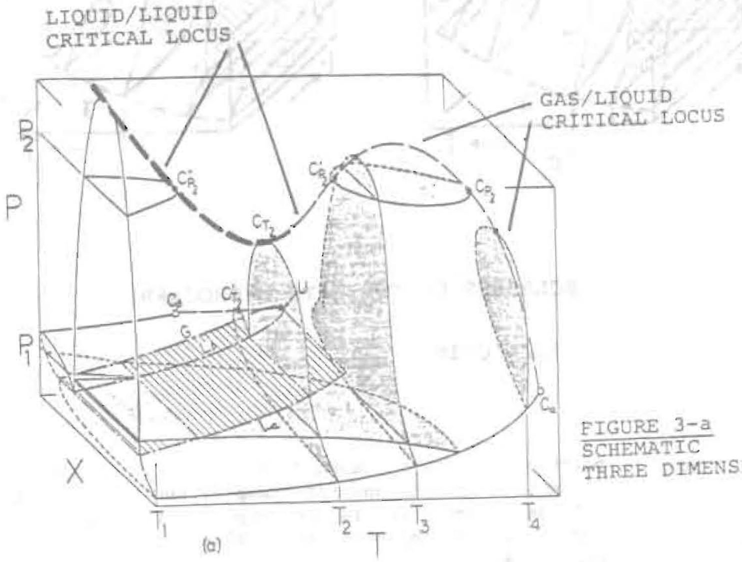

FIGURE 3-a
SCHEMATIC
THREE DIMENSIONAL

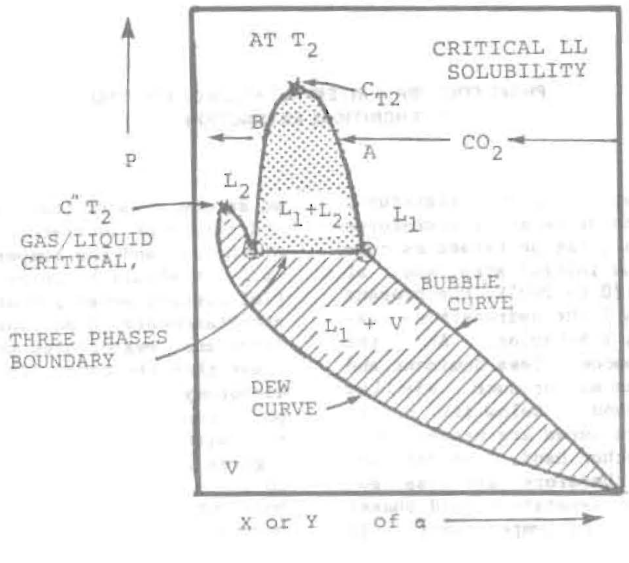

FIGURE 3-b
CROSSECTION ISOTHERM
AT T_2

FIGURE 3. SCHEMATIC OF CLASS III WITH LL CRITICAL IS A CONTINUATION OF ONE BRANCH OF THE LG CRITICAL.

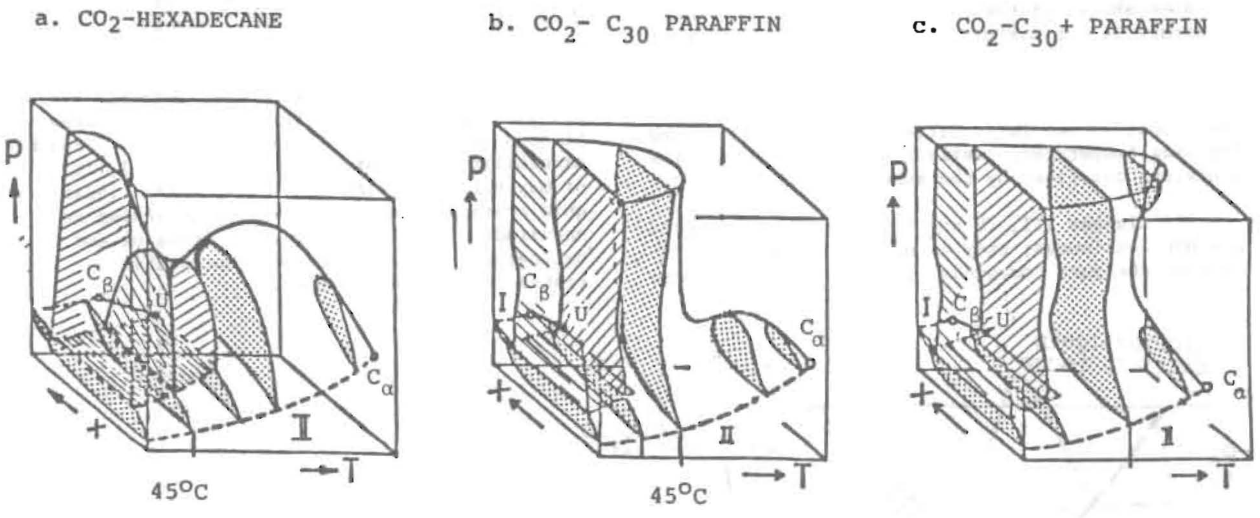

FIGURE 4. SCHEMATIC SKETCHES OF CLASS III SUBCLASSES OF CO_2 WITH HYDROCARBONS

▒ VAPOR/LIQUID OR VAPOR/SOLID   ▨ LIQUID/LIQUID

The behavior of binary mixtures of light hydrocarbons, e.g. C_1 to C_6 in heavier hydrocarbons, where the critical temperature differences are significant, are defined by Classes IV and V. Partial miscibility regions in the vicinity of the critical point of the light compound, as shown in Figures 2d and 2e, are common. For example, the process of propane deasphalting is an example of commercial application of the phenomenon illustrated in Figure 2e, Class V.

PHASE EQUILIBRIA INTERPRETATION OF EOR AND SUPERCRITICAL EXTRACTION

As has been pointed out in the literature, EOR with pressurized propane drive at temperatures below the propane's critical, can be termed as condensation/extraction, In the initial step, and at high enough temperatures, 120 to 200°F, the propane forms a separate phase with light hydrocarbons extracted from the oil, Class V behavior. As the front progresses, propane becomes less dominant and a single phase forms. Ethane may produce similar results at temperatures around or below its critical, 90°F, though higher pressures are needed. Methane and nitrogen, on the other hand, have very low critical temperatures and, therefore, are less soluble in oil and do not form separate liquid phases with extracted light ends at the temperatures in question. Consequently, these light compounds can be used only in immiscible EOR drives. Moreover, their presence reduces the efficiency of miscible drives.

Phenomena of EOR with CO_2 can each be explained as one or more steps in a series. The number and nature of such steps depend on the composition of the oil and the temperature and pressure in the well. It should be borne in mind that at the initial contact several unsteady-state transfers occur simultaneously. A portion of the oil, mainly its front end, evaportates and if the temperature is lower than the upper limit of observed liquid phase dichotomy, assumed around 135°F (20), when a dew point concentration is reached, a second phase, L_2, rich with CO_2 is formed along the LLG curves of Figures 2c, 2d and 2e. Both phases are rich with CO_2. The front of the drive extracts more hydrocarbons until the second phase, L2, disappears.At temperature above the postulated limit, no second liquid phase forms.

Mixtures of CO_2 with the bulk of the middle-distillate, C_{14} to C_{30} range, are assumed to behave as subclasses of Class III. As illustrated in Figures 3 and 4, the behavior of mixtures of the lower normal paraffinic components fo the middle distillate can be represented by the data and charts for normal hexadecane with CO_2, Figures 2c, 3a, 4a and 5.

In this system, the lower branch of the discontinuous critical locus stretches from the critical fo CO_2, C_B, to the point U, at T_u, which represents and abrupt termination of the two liquids and vapor three phase region. The other branch, which resembles a "camel's back and neck" is really composed of two merging curves. The branch starting at point C_α, in Figure 3a and Figures 4a, 4b and 4c, called here in the "camel's tail", extends to the camel's shoulders, at T_4, a point between C_{T_2} and C_{P_2}, the temperature of U, where the neck starts. It is the conventionally known gas-liquid critical locus. The neck section, heavy dashes in Figure 3a, is the liquid/liquid critical miscibility critical locus. In this case, the sections that of the gas-liquid and that of the liquid-liquid critical lici merge and form a continuous curve.

In Figure 3b, an isotherm at T_2, crossection at a temperature between C and T_u, the one for U, shows schematically the three phase equilibrium boundary and the region of miscible EOR. Starting with pure C_{16} along the arrow, at any pressure above that of the boundary, injected CO_2 dissolves into the C_{16}.

The C_{16} swells but does not throw up until point A is reached. Adding more CO_2, beyond the concentration of A causes the appearance of the second liquid phase L2 and when the mixture is very rich with CO_2, at point B, L1 disapperars, at point B, and only phase L2 exists. At a lower pressure, below that of C''_{T_2}, a vapor phase appears. More CO_2 will shift the whole system into the gaseous state. Needless to say, operating at the latter situation would be impractical economically.

At pressures above C_{T_2} one liquid phase exists throughout the entire composition range.

From viewing Figure 3, it is clear that at any temperature above T_u, only one liquid phase is possible. Thus, only a vapor and a liquid exist, as described by the dew-and-bubble envelopes at T_3 and T_4. Each of these envelopes ends at a true gas/liquid critical point of the camel-back locus. Different behavior is exhibited by systems containing CO_2 and heavier hydrocarbons. As illustrated in Figures 4b and 4c, the right hand branch of the critical curve turns upward at temperatures far above T_u. Figuratively, the camel has turned into a sitting ostrich in Figure 4b and into a charging swan (or Cobra) in Figure 4c.

Consequently, a gap exists, as shown by the dotted right side curve of Figure 2c; and more explicitly in Figures 4b and 4c. Within the temperature gap, the dew and bubble curves do not meet, at a critical point, at least at an attainable pressure. This may provide some understanding to the phenomena of EOR of heavy oils with CO_2 (6,11).

As metamorphoses in critical loci are directly influenced by the nature of the compounds, and differences in freezing and critical temperatures, presence of nitrogen and methane in either injection gas and/or the reservoir fluid can induce it. At static conditions, mixtures of CO_2 and a fraction within the gasoline/kerosene range of Classes II and IIIa can turn into a combination of Classes IIIb, IIIc and V. In reality, all phenomena may occur either simultaneously, or appear at one time, or a location, during and along the CO_2 drive path. When several different phenomena occur simultaneously, the overall system demonstrates an integral single type of behavior which may resemble any or none of them. For that reason, flash calculations of the entire bulk behavior are needed.

PRESENTACION OF AN OIL AS C_{7+}

The introduction of gas chromatography to the petroleum inspection laboratory greatly improved the accuracy of defining the light end part and the general nature of the oil. However, if insufficient information is provided, the advantage becomes a disadvantage. This is the case when the oil, which is the raison d'etre for EOR, is indequately defined, or worse, is only mentioned as C_{7+} in reports and publications.

The simplified approach of representing petroleum fractions as normal paraffins is easy to understand, since there are plenty of data on the latter compounds. However, from the statistical point, it introduces errors. Even among paraffins, isomers boil within a reasonably narrow range, but their freezing points vary significantly. For example the isomers of decane have a relatively narrow boiling range, 147°C for 2, 2dm-4-ethyl hexane, and 174°C for the normal. However, the freezing point of the normal decane is -29.66°C and that of 3-methyl nonane, with t_B = 165.7°C, is -98.7°C; the freezing point of the lowest boiling isomer is not available. It could be deduced that the critical phenomena that have been observed on system of CO_2 and light hydrocarbons with normal paraffins reflect the effect of the high freezing points of the normal paraffins and, therefore, do not represent the entire family. Oil fractions are not in the solid state; the contain solids and normal paraffins in solutions. They would be better described by isomers of alkyl cyclo compounds that have higher boiling points than normal paraffins and, with the exception of the rigid first members, have much lower freezing points.

Neglecting the importance of defining the oil in terms correlable by petroleum engineering procedures (1) is very common in EOR model programming. This subject will be discussed later in this presentation. It will be shown that significantly different computation results and conclusions may be reached even if the nature of the C_{40+} residue is not well defined (54, 55)

PREDICTION OF PHASE BEHAVIOR AND SIMULATIONS OF INSTANTANEOUS SITUATIONS

Equation 1, the classical "standard state", method, fails to meet the requirement that all K ratios equal unity at the critical point (27, 61, 62). It does not provide for reliable predictions at high pressures. However, equations of state can accommodate this requirement.

Predictions of K ratios with equations of state are rigorous, to the degree of validity of the empirical assumptions. Equilibrium is defined by Equations 3, below, where the fugacities $\hat{f}_{iL}$ and $\hat{f}_{iV}$ of component i in phases V and L are equal.

$$\hat{f}_{i_V} = \hat{f}_{i_L}$$

since $\hat{f}_{i_V} = \emptyset_{i_V} y_i P$ and $\hat{f}_{i_L} = \hat{\emptyset}_{i_L} X_i P$, the equilibrium is defined by

$$\emptyset_{iV} Y_i P = \hat{\emptyset}_{iL} X_i P \qquad (4)$$

Thus,

$$K_i = \frac{\emptyset_{i_L}}{\emptyset_{i_V}} \qquad (5)$$

Utilization of equations of state, such as the Redlich and Kwong (45)

$$p = \frac{RT}{V - b} - \frac{a}{T^{1/2} V(V+b)} \qquad (6)$$

and that of Peng and Robinson (42)

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V+b)+b(V-b)} \qquad (7)$$

requires establishing the coefficients a and b of the components, i, j, etc. and those of the mixture. Hence, different formulas for mixing coefficients have been employed by different researchers (9, 10, 27, 31, 53, 57, 58, 61). Predictions of K values encompass trial and error routines and results that qualitatively agree with experimental data are obtained.

Although the use of triangular digrams in modeling EOR with CO_2 has been proven valuable, it has been recognized that the changes in Classes and in the natures of fluids would impose quite a burden on the designers. Therefore, the use of equations of state has, naturally, gained wide acceptance.

The proposal of Joffe et al (27). Following earlier work by Wilson, that the Redlich-Kwong equation can be made to describe systems within the critical region and that it can describe petroleum fractions, has been much simplified by Hamam et al (19) and improved by Yarborough (61). In these prediction methods, the coefficients a and b along the vapor pressure curve of a compound are temperature dependent. They are established by trial and error by attempting to meet two criteria : (1) the fugacities of the vapor and the liquid must be equal, and (2) the experimental liquid density is reproduced.

Predictions of the phase behavior of mixtures have been done by the same equations of state. The parameters of the mixtures are established from combining equations modified by interaction parameters, k_{ij} or ν_{ij} for the R-K equation and C_{ij} and D_{ij} for the Peng Robinson equation. Deiters and Schneider (10) and Yarborough (61), and Turek et al (53) have proposed the use of a second interaction parameter for the coefficient b of the Redlich-Kwong equation. In all previous work, the interaction parameters were established from phase equilibrium data only; prediction of phase equilibrium being the objective.

A NEW CORRELATION APPROACH - INTERACTION PARAMETERS FROM BOTH PHASE AND DENSITY DATA

In this study, the objective is expanded. The interaction parameters of the equations of state were established from data on both phase equilibria and mixtures densities correlated simultaneously. Thus, the cross coefficients a_{ij} and b_{ij} of the Redlich-kwong equation equation were evaluated (10, 27, 61) as

$$a_{ij} = (1 - k_{ij})(a_{ii} \cdot a_{jj})^{1/2} \qquad (8)$$

and

$$b_{ij} = (1 - \nu_{ij})(b_{ii} + b_{jj}) \qquad (9)$$

The relationships which had been used by Turek et al. (53) for the cross coefficients of the Redlich-Kwong equation were used in this work for establishing the binary cross coefficients for the Peng-Robinson equation.

$$a_{ij} = (1 - C_{ij})\ (a_{ii}a_{jj})^{1/2} \qquad (10)$$

and

$$b_{ij} = \frac{(1 + D_{ij})\ (b_{ii} + b_{jj})}{2} \qquad (11)$$

The cross coefficients of equations 8 and 9, and of 10 and 11, were used with coefficients for pure compounds and fraction in Equations 6 and 7 respectively. However, there is a difference between the way coefficients a and b of the light hydrocarbons and CO_2 were established and the way these coefficient were established for compounds, heavier than propane.

In either correlation, the coefficients a and b at temperatures below their critical were established by the procedure outlined by Joffe, Schroeder and Zudkevitch (27). When the Peng-Robinson equation is used, the parameters a and b for any individual component, or a petroleum fraction, are calculated from

$$a = \Omega_a \frac{R^2T_c^2}{P_c} \qquad (12)$$

and

$$b = \Omega_b \frac{RT_c}{P_c}. \qquad (13)$$

The temperature dependence of the coefficients Ω_a and Ω_b is different from that for the function $\alpha(T_R,\omega)$ proposed by Peng-Robinson, since saturated liquid densities are included in the correlation.

The comparison in Table 3 illustrates how application of this multivariable correlation approach, i.e., making a and b temperature dependant, improves the capability of the P-R equation to predict the density of liquid CO_2.

Since supercritical gases play a most important role in EOR and its phenomena, emphasis was added to improving the correlations' capabilities to predict their properties within the range of 80°F and 250°F (300 K to 415K). For this reason, the coefficients a & b of Equations 6 and 7 for methane, and ethane and CO_2 at temperatures above their criticals, were established by the same procedure, i.e., at each temperature and pressure the coefficients were calculated from their densities and fugacities. IUPAC compendia of data, e.g.

Reference 2, were used. The procedure which will be described in detail in another publication is an expansion of that proposed by Wensel and Rupp (59) who used a single point for establishing representative (coefficients). It is very similar to the approach of Turek et al (53). For illustration, the variations of $_a$ and $_b$ for CO_2 as functions of temperature and pressure within the range of condition of "Hot EOR", above 88°F, are presented in Figures 6 and 7.

It has been recognized that when the coefficients a and b of any two parameter's equation of state become dependent variables, the nature of the equation changes (18,29). Consequently, the dependency equations $a = f'(T,P)$ and $b = f''(T,P)$ and their derivatives and integrals, etc. had to be built into the derivation of the fugacity coefficients and other derived variables.

The interaction parameters k_{ij} and ν_{ij} and C_{ij} and D_{ij} for various binaries of CO_2 and hydrocarbons from C_1 to C_{30}, and binaries of hydrocarbons, were established from literature data on phases at equilibrium and densities. For oils divided into petroleum fractions, a generalized empirical correlation was developed by fitting the interaction coefficients to polynomial functions of the hydrocarbon accentric factor .

This generalized equation however does not account for the effects of temperature and pressure that have been observed but neglected. For example, the binary system of CO_2 and hexadecane is probably the most studied member of Class III, Figures 2c, 3, 4a and 5. Portions of the isotherm at 90 °F given in Figures 3b and 5, show the parabola - like composition-pressure relation for the liquid-liquid equilibrium. As shown on Figure 5, several attempts to predict the boundries of the partial miscibility region with equations of state whereby the single interaction parameters (k_{ij} or C_{ij}) is a constant have not been very successful. However, when an effect of pressure on either interaction parameter was introduced, excellent agreements were found. Also, good agreement was found when predicted and experimental vapor and liquid equilibrium at a higher temperature (140°F or 60°C) were compared, as shown in Figure 11. Surprinsingly, the interaction parameters k_{ij}, for combining the a_i and a_j coefficients of the Redlich-Kwong equation, and C_{ij} the coefficient for combining the same coefficients of the Peng-Robinson equation, that represent the effect of pressure on the liquid/liquid equilibrium of this system vary as straight line functions of the system pressure. This is illustrated in Figure 8. Accounting for this effect, though of questioned thermodynamic basis (18), enabled the description of the liquid-liquid equilibrium curve and the critical miscibility pressure of the binary CO_2 - hexadecane at 90°F, shown in Figure 5.

In this study, the coefficients a and b of the equations of state of petroleum fractions were established for individual narrow cuts(10% volumes) of the TBP distillation curves. The methods of the API Data Book (1) were followed.

The method (correlation) for establishing parameters a, b, k_{ij}, ν_{ij}, D_{ij} and C_{ij} of the equations will be discussed separately.

TABLE 3

Comparison of Saturated Liquid Volumes for CO_2

Peng-Robinson Equation

T. K	P, Bar	Liquid Molar Volume,cc/mole				
		Lit.	Calc(1)	o/o Err.	Calc(2)	% Err.
280.00	41.595	49.773	51.580	3.63	50.093	0.64
284.00	45.960	51.559	54.072	4.87	51.937	0.73
288.00	50.665	53.460	57.135	6.87	54.083	1.17
292.00	55.734	55.981	61.059	9.07	56.589	1.09
296.00	61.198	59.376	66.436	11.89	59.502	0.21
300.00	67.095	64.690	74.876	15.75	62.872	-2.81
302.00	70.220	69.297	82.075	18.44	64.950	-6.27
303.00	71.830	73.123	88.051	20.41	66.488	-9.07
304.00	73.475	81.703	136.660	67.26	70.839	-13.30
304.21	73.825	94.440	116.640	23.51	94.442	0.00

NOTES: (1) Original Peng-Robinson Correlation (42)

(2) Modified Peng-Robinson, This work

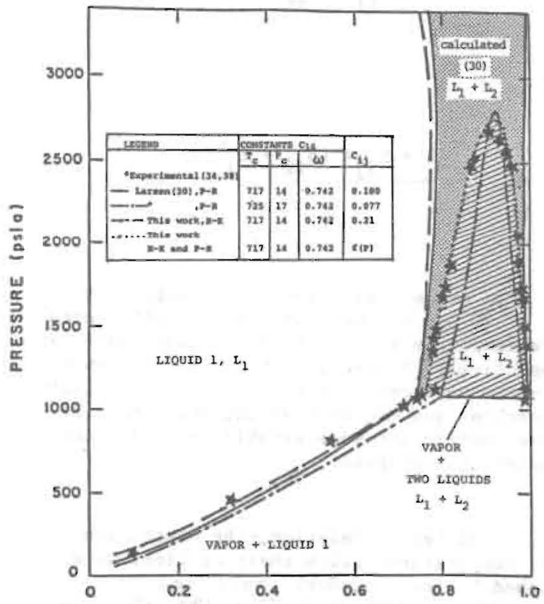

Fig. 5. Comparison of measured, *, and calculated phase compositions

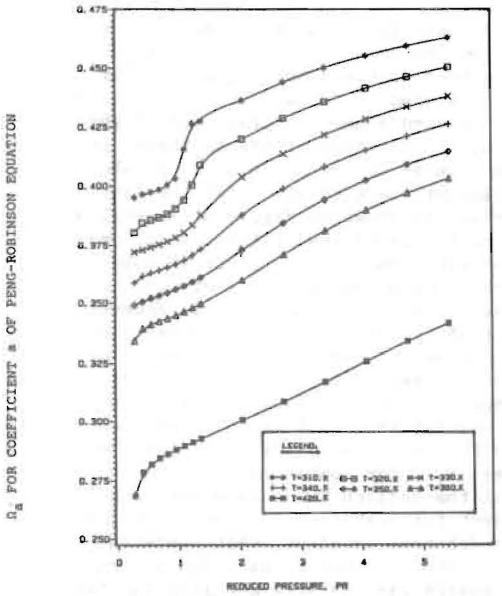

FIGURE 6 — COEFFICIENT Ω_a(27) FOR THE PENG-ROBINSON EQUATION(42) PURE CO_2(2) AT ENHANCED OIL RECOVERY CONDITIONS

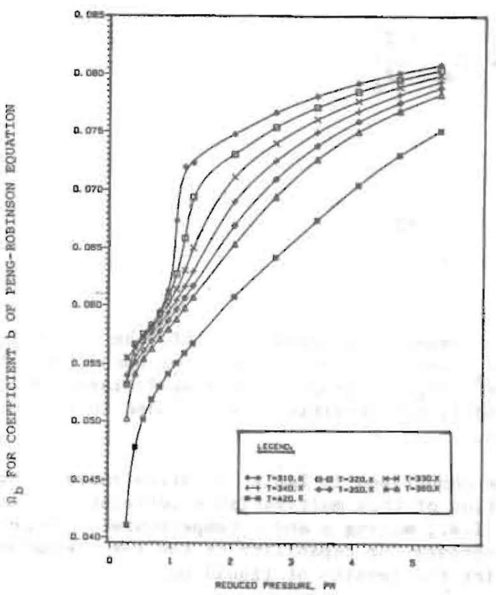

FIGURE 7. COEFFIEIENT Ω_b(27) FOR THE PENG-ROBINSON EQUATION(42) PURE CO_2(2) AT ENHANCED OIL RECOVERY CONDITIONS

PHASE DISTRIBUTION SIMULATION TRIAL DISCUSSION AND COMPARISON

The generalized correlation for parameters and interaction coefficients for the Peng-Robinson equation and the computer routine for simulating liquid dichotomy was tested. Two examples have been prepared to illustrate both strength and weaknesses of the theories and impressions from evaluations presented earlier in this manuscript. These examples were not selected but the result are presented as obtained with the authors' explanations. It is expected that highlighting and discussing weaknesses and needs wil promote future progress rather than criticism.

SIMULATIONS OF PHASE DISTRIBUTION

Oil A of Turek et al (53) was selected for the phase separation simulation. However, the preparation of the data was quite an undertaking. The data in Table 10 of Reference 53 provide a detailed analysis of the C_{7+} portion of the oil. Unfortunately the fractions are defined by their number of carbon atoms. This unfortunately leaves a reader/correlator uninformed about the characterization of the oil, i.e. boiling point, MW and gravity distribution, all of which are needed for establishing parameters for equations of state and defining interaction and behavior in mixtures. Additional information about oil A given in Table 10 of Reference 53, the molecular weight and the density of the C_{7+} oil at 288.7 K, were useful in the authors attempts to characterize the oil.

In preparation for phase equilibrium calculations, the oil was characterized in terms of petroleum engineering variables, NBP, °API gavity and molecular weight. The following procedure was used.

- The fractions were lumped into large ranging fractions, each encompassing three to five molecular weight groups. A representative compound was selected for each of the new fractions.
- Based on the assumption that there is less diversity in the normal boiling point of paraffins, than aromatics and naphthenes, each fraction was assigned the normal boiling point of the normal paraffins of the assigned molecular weight of the fraction. A TBP curve was then drawn to establish the molal average boiling point (MABP) of the oil and hence its characterization K.
- For the first trial, the API procedure for relating molecular weight, API gravity, and the Watson K was used to estimate the first - trial density (°API gravity) curve. Then the density of the oil was calculated and compared against the published experimental value.

Since the first trial value was far from the experimental, new TBP and gravity curves were drawn, values read and the trial procedure repeated until a reasonable agreement the experimental and calculated gravity of the oil was achieved.

The results from the final trial are shown in Table 5 and Figure 9. For a good match of the molecular weights and the oil gravity, the data on normal paraffins, used as an initial guess, dotted curve in Figure 9 was too far from describing the oil which has finally characterized to be naphthenic.

All initial trials did not yield reasonable characterization of the oil and its phase distribution after mixing with CO_2. Following the advice of Turek (54) Oil A of Reference 53 was redefined as Oil B2 of Reference 55. The characterization simulation/interpretation trial and error routine was repeated and the oil was finally satisfactorily characterized.

In phase equilibrium calculations a simulation of mixing/flashing the recombined oil (front - end combined with the C_{7+}) yielded the results in Table 6. With 75% overall (mole) CO_2 added, the mixture formed two liquid phases with the compositions split, molecular weights and gravities as presented and compared against the data of Turek et al (Table 11 of Reference 53). As shown in Table 6, the overall agreement between calculated and experimental values is very good. However, it highlights major weaknesses.

1. The correlation needs further refinement to improve predictions of phase distribution of the C_5 to C_6 compounds.
2. The characterization of the oil, in Table 5, is somewhat inadequate. The phase split simulation yielded somewhat erroneous molecular weights for the oils (liquids 1 and 2).

TRIAL SIMULATIONS OF OIL SWELLING AND CONTRACTION

Less satisfactory were the results from simulations of volume changes resulting from injecting CO_2 under pressure into oils. The objective was to reproduce the swelling-followed-by-contraction pattern illustrated by Holm and Josendall(23) for the Mead-Strawn Stock Tank Oil (STO), shown as curve 1 of Figure 10.

As presented in Column 2 of Table 1 of Reference 23 information on the Mead-Strawn STO is hardly adequate for characterizing the oil for sensitive computation. The same trial-and-error routine which had been for Amoco's Oil A (53, 54, 55) in preparation of the feed stream of Tables 5 and 6, yielded the assumed characterization of the STO shown in Table 7.

TABLE 4

COMPARISON OF PHASE DENSITIES OF CO2/HEXADECANE BINARY
TWO LIQUIDS AT EQUILIBRIUM AT 90 F
DATA (in gm/cc) OF ORR et.al. (31)

	C16 Rich Phase	CO2 Rich Phase
Pressure, psia	1350	1350
x CO2	0.770	0.991
Method	Density (gm/cc)	Density (gm/cc)
Original PR	0.705	0.693
Modified PR	0.828	0.761
Experimental	0.806±0.044	0.773±0.032
Pressure, psia	1680	1680
x CO2	0.799	0.986
Method	Density (gm/cc)	Density (gm/cc)
Original PR	0.716	0.746
Modified PR	0.834	0.805
Experimental	0.820±0.059	0.808±0.038
Pressure, psia	1800	1800
x CO2	0.804	0.983
Method	Density (gm/cc)	Density (gm/cc)
Original PR	0.725	0.768
Modified PR	0.839	0.827
Experimental	0.824±0.041	0.829±0.027
Pressure, psia	2480	2480
x CO2	0.865	0.959
Method	Density (gm/cc)	Density (gm/cc)
Original PR	0.751	0.808
Modified PR	0.853	0.860
Experimental	0.831 *	0.852 *

* ONLY ONE EXPERIMENTAL POINT

TABLE 6

COMPARISON OF LIQUID-LIQUID FLASH
OIL A OF TUREK ET AL (53)
C_7+ FRACTION FROM TABLE 5, REFERENCES (54, 55)
CASE 1, 75 MOLE % IN TOTAL FEED, 105°F AND 2204 PSIA

	Composition, Mole %			
	Liquid 1		Liquid 2	
Component	Exp.	Predicted	Exp.	Predicted
N_2	0.00	0.00	0.23	0.14
C_1	2.96	3.12	2.80	3.26
CO_2	66.71	68.70	85.98	88.90
C_2	1.99	1.76	1.94	1.47
C_3	1.89	1.90	1.94	1.36
C_4	1.62	1.83	1.69	1.01
C_5	0.99	1.57	1.48	0.76
C_6	0.46	0.92	0.55	0.37
C_7+	23.38	20.20	2.39	2.73
Density kg/m^3	864.8	884.9	766.3	727.3
Density % Error		2.3		-5.3
Mol. Weight	87.82	76.67	47.86	45.99
% Moles	65.2	68.3	34.8	31.7
% Volume	75.3	74.6	24.7	25.3

TABLE 5 INTERPRETATION/REPRESENTATION OF THE C_7 + OF OIL A OF TUREK ET AL. (53)
(MW=233, (55), SP. GR.@ 60°F=0.889)

SPECIES	MOLE %		NBP PARAFFIN °F	INTERPRETED AS			
	INC_7+	CUMM. IN C_7+		MW	NBP, °F	°API	SP. GR.
C_7	12.60	12.60	209.	100	210	68	0.7093
C_8	11.08	23.68	258.	114	250	60	0.7389
C_9	10.15	33.83	293.	130	336	53	0.7669
C_{10}	9.88	43.71	342.	142	385	46	0.7972
C_{12}	12.08	55.79	421.	170	428	38	0.8348
C_{15}	10.35	66.14	518.	212	530	32	0.8607
C_{18}	9.03	75.17	601.	254	620	26.5	0.8956
C_{21}	6.28	81.45	671.	296	690	23	0.9159
C_{24}	3.69	85.14	732.	338	745	20	0.9340
C_{27}	4.69	89.83	786.	380	812	17	0.9529
C_{31}	2.13	91.96	851.	436	875	14	0.9725
C_{36}	2.69	94.65	919.	506	962	9	1.0071
C_{40+}	5.35	100.00	968.	816	1165	2.6	1.0552
AVERAGE				233(55)		27.7(53)	

TABLE 7
INTERPREATION: MEAD-STRAWN STOCK-TANK-OIL (STO)

COMPOUND				Cumm-lative			V	Xi in C_6+
No.	Name	MW	Xi	ΣXi	°API	Sp. Gr. 60°F	cl/Mole	
1	C_3	44	0.0179	0.0179	147	0.508	1.55	
2	C_4	58	0.0332	0.0511	111	0.58	3.32	
3	C_5	72	0.0517	0.1028	127	0.630	5.908	
4	145.A72	83	0.0662	0.1690	72	0.6988	8.15	0.0738
5	230.A57	100	0.1111	0.28	57	0.7351	15.11	0.1238
6	320.A51	130	0.17	0.45	51	0.7753	28.58	0.1895
7	414 A41	162	0.15	0.60	41	0.8203	29.62	0.167
8	500 A33.5	190	0.10	0.70	33.5	0.8576	22.53	0.1114
9	585 A26.5	230	0.10	0.80	26.5	0.8956	25.68	0.1114
10	670 A20	275	0.10	0.90	20	0.9340	29.44	0.1114
11	790 A16	360	0.061	0.961	17	0.9529	23.00	0.068
12	950 A-9	495	0.039	100	9	1.0071	19.16	0.0435
	C_6+	193					212.5	
	Oil	180			317.5	0.837	212.5	0.8912

K = 11.8

Experimental 60/60 = 0.8203 = 41 °API

A simulation of the volume ratio vs. pressure of the CO_2 flooded STO was a tedious task. It was assume that the ratio of CO_2/PV was kept constant at all pressures. Consequently, the ratio of moles CO_2 to moles oil should have varied with pressure. The computed value of V/V_0 under different pressures at 135°F did not jibe with those of Holm and Josendal (curve 1 in Figure 10).

The authors postulated that the injection of CO_2 under pressure swells the oil until a point of incipient dichotomy (split) is reached. Beyond this point, around 1500 psia for curve 1 of Figure 10, a second liquid phase, containing CO_2 and a portion of the light end of the oil, forms. The oil-rich phase then, becomes denser and hence the sudden drop in the V/V_0 curve. However, the computations yielded a much milder decline in the V/V_0 ratio curve (curve 1a in Figure 10). It was assumed that the cause for the discrepancy was the authors' misinterpretations of Holm and Josendal's data. The computations were then carried out in an attempt to simulate the behavior of Oil A of Turek et al (53, 55) as defined in Table 6. The calculated volumetric behavior of the oil-rich phase of the system containing Oil A and CO_2 is presented as curves 2 and 3 of Figure 10. Curve 2 depicts the V/V_0 ratio of the oil-rich phase along the single phase incipient dichotomy curve and curve 3 represents the ratio for the same oil-rich phase at constant overall 75 mole % CO_2. In these cases too, the sharp drop in the V/V_0 curve which hac been anticipated to coincide with the formation of the light phase was not verified.

The disappointing failure to simulate / verify the sharp change in the density of the oil-rich phase could be attributed to any and/or combination of the following weaknesses in the definition of the problem and in the computer-programmed phase equilibrium prediction and the material balance simulation procedures.

- The procedure used to add CO_2 as pressure was increased. The description given in Holm and Josendall (23) was very general.
- Difficulties in the three flash algorithm to properly discern between the small differences in K valves and densities in the three phase region. An algorithm which works well for aqueous systems may not necessarily work well the two liquid phases are rich in CO_2.
- Can binary interaction parameters which have traditionally been assumed to be independent of temperature and pressure properly reflect the complicated mixtures inherent in EOR? The case illustrated in Figures 5 and 8 for the CO_2/C binary would indicate that this is not so.
- The equations used in the correlation of the a and b equation of state parameters for CO_2 may not properly reflect the rapid changes in these parameters near the critical point shown in Figures 6 and 7.
- The number of degree of freedom as determined by the Phase Rule is quite large (berween 19 and 21) for the systems used in Figure 10. Small differences in temperature or pressure or the bulk carbondioxide composition can lead to very different results, particularly in the region of incipient dichotomy.
- The section enclosed by the dashed lines of Figure 10 represents the region which the authors feel places the greatest demands on equation of state and the type of algorithm used. Failure in this region can be attributed to an algorithms inability to porperly predict phase splitting, as was mentioned above, or the mixture may be in the critical region, where any EOS will have difficulty.
- By using interaction parameters in the EOS, which are neither functions of temperature or pressure, one may get results which are encouraging on the one hand (flash calculation in Table 6) and completly erroneous on the other (failure to calculate the critical solubility pressure Figure 5).

In this study, the authors have tried to bring together, through the use of equations of state, some of the theories and observations of supercritical extraction as applied to EOR. Due to the inherent complexity of the EOR process, it is evident that much work remains to be done in this area before the same confidence that is applied to normal hydrocarbon processing is applied here.

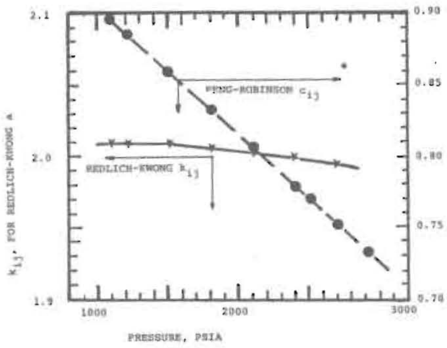

FIGURE 8. Interaction parameters varying with pressure for CO_2/Hexadecane(,) Liquid/Liquid Equilibria at 90°F

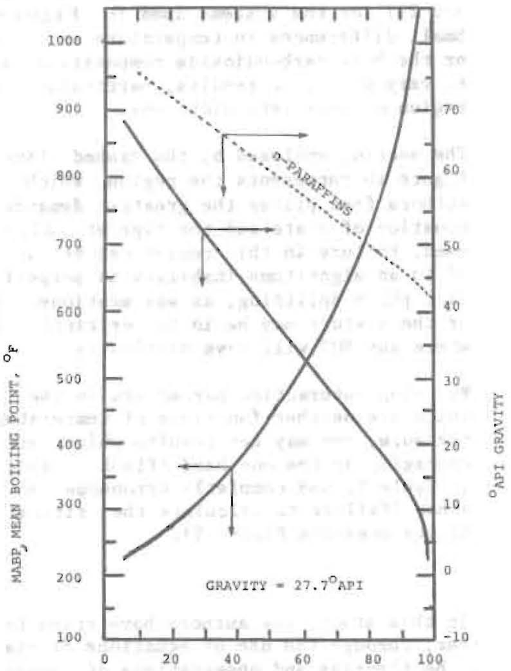

FIGURE 9. INTERPRETATION OF C_7+ FRACTION OIL A OF TUREK ET AL (53)

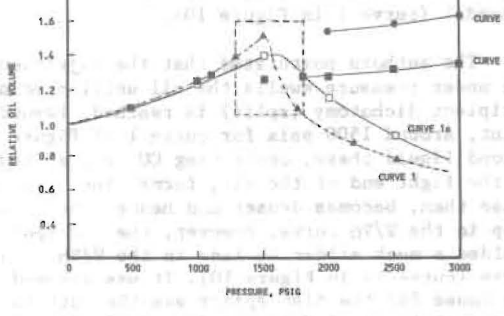

FIGURE 10 CHANGE IN OIL VOLUME UPON ADDITION OF CO2 AT INCREASING PRESSURE

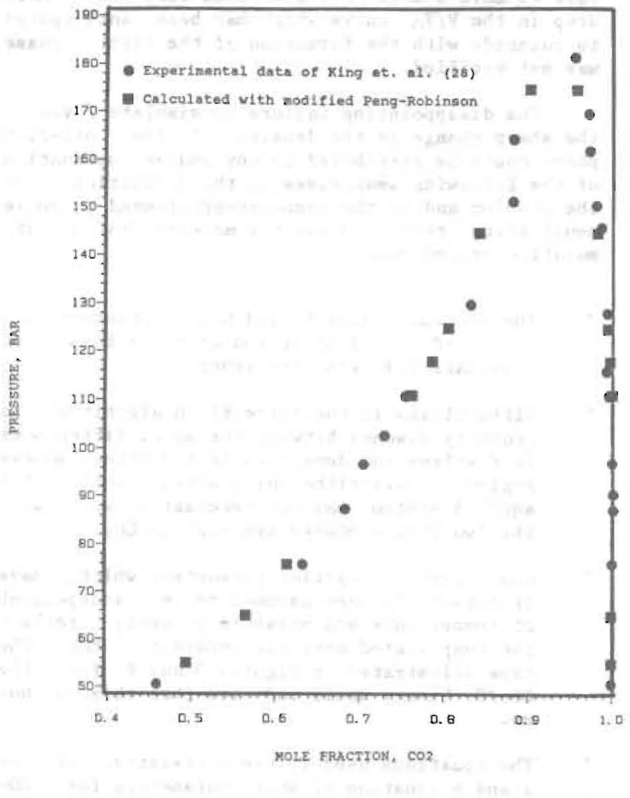

FIGURE 11. COMPARISON OF EXPERIMENTAL, ●, AND CALCULATED, ■, PHASE COMPOSITIONS FOR THE CARBON DIOXIDE - HEXADECANE SYSTEM AT 140 DEG F

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