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ABSTRACT

The main objective of this project is to provide basic laboratory data and analysis techniques for hydrocarbon/water and hydrocarbon/CO₂/water mixtures at pressures up to 10,000 psia and at temperatures up to 500 °F. Most of the published phase behavior studies have focused on hydrocarbon/CO₂ systems and hydrocarbon/water systems at low temperatures. At temperatures greater than 250 °F, the effects of an aqueous phase on the multiphase hydrocarbon separations in enhanced oil recovery processes and in chemical separation processes are significant.^{1-7*}

We designed and built two laboratory apparatus⁸⁻¹¹ for experimental tests to 500 °F and 10,000 psia. Stage-wise (sequential) isochoric tests using the apparatus provide basic high-temperature, high-pressure three-phase separation data for estimating three-phase equilibria and K-values. A high-pressure, mercury-free window cell PVT-VLLE apparatus is used to conduct three-phase equilibrium tests up to 8,000 psia and 375 °F to provide basic equilibrium phase-behavior data and verify the high-temperature, high-pressure results. Basic three-phase separation data are obtained for mixtures of pure n-alkanes (C₃ to C₂₀), CO₂ and water, and for mixtures of pseudocomponents of crude oils and water. Crude oils are characterized using an optimum number of pseudocomponents determined from a modified Whitson's¹² characterization procedure.

We also developed rigorous EOS computer simulators using conventional and the new Wong-Sandler mixing rules¹³⁻¹⁵ with Gibb's minimization procedures for laboratory data analysis, and *a priori* prediction of volumetric and phase equilibria properties. These simulators are validated with the experimental data for practical applications in compositional reservoir engineering and in enhanced oil recovery studies. Experimental data and EOS simulations are essential for practical applications in compositional reservoir engineering and for enhanced oil recovery studies. Results of the proposed research program have the following industrial applications: (1) provide a better description of hydrocarbon/CO₂/water equilibrium ratios for reservoir engineering calculations and (2) provide reliable data and techniques for predicting vapor/hydrocarbon liquid/water separation processes to improve the capability of numerical reservoir simulators.

* References at the end of the document

INTRODUCTION

Hydrocarbon/water and hydrocarbon/CO₂/water systems are frequently found in petroleum recovery processes, petroleum refining, and gasification of coals, lignites and tar sands. Techniques to estimate the phase volume and phase composition are indispensable to designing and improving the industry processes.

In petroleum reservoirs the aqueous phase always co-exists with hydrocarbons. Water is also extensively used in enhanced oil recovery processes such as steam flooding, CO₂ flooding, etc.¹⁻⁷ In a recent report⁷ the use of CO₂ in steamflooding shows many beneficial effects on oil recovery and economics. However, the aqueous effects upon the hydrocarbon equilibrium separation have not been fully quantified for reservoir and production engineering calculations. In steam-thermal recovery processes, steam is either injected into or generated within a reservoir where the hydrocarbons and water may coexist in three phases: vapor, liquid hydrocarbon and water. While steam distillation¹⁻³ is considered one of the most important thermal oil recovery mechanisms, simulation of steam injection processes often neglects the effect of the aqueous phase upon the hydrocarbon equilibrium separation. In miscible enhanced oil recovery processes where CO₂ is used as a displacing medium, the aqueous effects on the hydrocarbon/CO₂ phase behavior have not been fully investigated.¹⁶ Because of the aqueous phase vapor pressure and the mutual solubility of water and hydrocarbon/CO₂ in the liquid phases, neglecting the aqueous effects can induce serious error in the representation of hydrocarbon/CO₂ phase behavior.

Our extensive review of the existing literature on the effect of water and CO₂ on hydrocarbon phase behavior and our experimental view point indicate that water/hydrocarbon data are very difficult to analyze. Measurements of the mutual solubility of water/hydrocarbon/CO₂ systems is difficult because temperature changes in the sampling line can cause the solute to separate as a second phase and accumulate in the sample line, or to adsorb on the surface of this sample line. Both effects can alter sample characteristics. In addition, analysis for water by gas chromatography is very difficult, and most chromatography columns are not suited for analysis of water because the retention times for other compounds shift and interfere with the analysis of other species.^{17,18}

The solubility of water in a hydrocarbon-rich liquid phase at high pressure and temperature can be as high as 50 %.¹⁹ There is a strong effect of water presence on the phase behavior of reservoir crude oils at high temperatures. As an example, in the steam distillation processes, depending on oil gravity, 15 to 30 percent volume of oil could vaporize in the presence of steam at pressures of around 500 psia and at a temperature of

about 470 °F. In the absence of steam, there may be no vaporization at the same temperature and pressure.²⁰

From a computational perspective, initialization and solution techniques lead to common numerical difficulties in multiphase equilibrium calculations. The conventional initialization procedures based on reported experimental data, or derived from ideal conditions, are insufficient for aqueous mixtures. False solutions or nonphysical results may be encountered in multiphase calculation of aqueous mixtures.²⁰

Wu and Brown², and Wu and Elder²¹ provided laboratory crude oil steam distillation data with rough estimates of steam distillation yields of crude oils under dynamic, three-phase separation conditions. Langoff and Wu²² have reported some data on high-temperature, high-pressure separations for a n-hexane/n-decane/water system and for crude oil/water systems. Recently in our group, Beladi *et al.*²³ reported VLLE data on crude oil mixtures with water.

Billman,⁸ Lanclos,⁹ and Wu, *et al.*¹⁰ developed a stagewise three-phase distillation method, termed the Stage-Wise Isochoric Distillation (SWID) Test, that generated the phase compositions needed to estimate the three-phase K -values of selected hydrocarbons. To our knowledge, there is no comprehensive three-phase equilibrium separation of crude oil pseudo-components investigated in the laboratory for enhanced oil recovery process applications.

The correlation and prediction of multiphase, multicomponent equilibria usually require a computer simulator. The simulator model may consist of (1) an equation of state (EOS) and (2) mixture combining rules (MCR). Traditionally, the MCR contains binary interaction parameters k_{ij}^* which are found from "tuning" onto binary data for each binary pair in the multicomponent mixture. Tuning methods proposed by several investigators involve the use of different mixing rules for the EOS parameters and the use of temperature-dependent binary interaction parameters.^{24,25} For mixtures without polar components (e.g., hydrocarbon mixtures), good results are usually obtained when all the binary pair k_{ij}^* values are well established from binary measurements. However, when highly polar components (e.g., water) are present, the parameter k_{wj}^* , for water/HC interactions, varies with temperature, pressure and phase composition.

This phase dependency of k_{wj}^* was first recognized by Heidman, *et al.*²⁶ in a study of mutual solubilities of liquid hydrocarbons and water. Our research team has recently studied this problem in more detail and suggested an improved temperature-dependent correlation for k_{wj}^* .²⁷ This should be used in preference to the rough values of 0.48 ($N_c < 10$) and 0.46 ($N_c \geq 10$), where N_c is the carbon number, of Peng and Robinson.²⁸

Eubank *et al.*²⁷ provided further literature review and technical details concerning water/HC systems.

Wong and Sandler¹³ published a new MCR that include a liquid-phase parameter $A_{\infty}^E(T, x, P \rightarrow \infty)$ and a gas-phase parameter B_{12}^{EOS} not present in the usual van der Waals combining rules. These parameters can be determined from single-phase liquid mixture and single-phase gas mixture measurements, respectively. For "chemical systems" (e.g., methanol/benzene), Wong *et al.*¹⁴ showed that phase equilibria at high pressures and temperatures could be forecast from A_{∞}^E and B_{12}^{EOS} taken from measurements near atmospheric pressure. However, even in recent publications, Huang and Sandler²⁹ continue to tune both A_{∞}^E and B_{12}^{EOS} to liquid-phase measurements only. We have succeeded in relating the gas parameter B_{12}^{EOS} to experimental cross-second virial coefficients, B_{12}^{exp} , and thus convert the Wong-Sandler procedure from correlative (that is requiring parameter tuning) to *a priori* predictive. The new procedures for use of the W-S/MCR are reported by Eubank *et al.*³⁰ Our research of the past two years with these new mixing rules was performed with the ultimate objectives of this proposal in mind--the *a priori* prediction of the phase equilibria of HC/CO₂/water systems.

METHODOLOGY

Three tasks are carried out to accomplish the objectives of the project. They are briefly described below.

Task I. Experimental Stage-Wise Isochoric Distillation (SWID)

Two three-phase distillation apparatus are used for the high-temperature and high-pressure multiphase separation experiments. Figure 1 shows the distillation cell designed for experiments up to 500 °F and 10,000 psia. The other distillation apparatus is designed for tests at temperatures up to 500 °F and pressures up to 1,000 psia. The lower pressure distillation apparatus is used for mixtures of heavier hydrocarbon components (>C₅) and the higher pressure distillation apparatus is for mixtures of lighter hydrocarbon components and for mixtures including CO₂.

Figure 2 shows the high-pressure, high-temperature distillation apparatus. The distillation cell is monitored by an automation system which uses a temperature/pressure analog signal to control and monitor the distillation cell temperature. This experimental set-up is used to perform three different types of tests:

(1) *Static system pressure tests (SPT)* : These are runs for hydrocarbons (HC) without water phase (2-phase, V-L equilibria) and for hydrocarbons (HC) with water phase (3-phase, V-L-L equilibria). This test identifies the baseline for 3-phase behavior of the hydrocarbons. The results of these tests are used to tune parameters in EOS modeling.

(2) *Stage-wise isochoric distillation (SWID)* : These tests are conducted in a constant cell volume using two different approaches. The first one consists of removing vapor samples between equilibrium stages at successively higher temperatures. The second sets the system at a constant temperature and allows the pressure to drop and equilibrate after each vapor sample collected. Distillate includes a hydrocarbon (HC) phase and a water phase whose volumes are measured. The HC sample is collected for chromatography analysis. From the volumes of the distillates and the composition of the hydrocarbon phase, the over-all composition in the cell is calculated by a compositional material balance model.

(3) *Dynamic distillation tests (DDT)* : These tests help to investigate the effect of steam injection-rate on the steam distillation yields. This testing procedure is primarily used to obtain the maximum steam distillation yield.

The SWID can be considered as an isothermal, isochoric three-phase flash separation test. The three-phase K -values involved in the equilibrium equations are defined as

$$K_i^{yo} = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^l}{\hat{\phi}_i^v}, \quad K_i^{ya} = \frac{y_i}{w_i} = \frac{\hat{\phi}_i^a}{\hat{\phi}_i^v}, \quad \text{and} \quad K_i^{oa} = \frac{x_i}{w_i} = \frac{\hat{\phi}_i^a}{\hat{\phi}_i^l} \quad (1)$$

where the fugacity coefficients can be evaluated from an empirical or from an EOS model and the phase compositions are either measured, or determined, from material balance calculations.

Task II. Experimental PVT-VLLE Apparatus and Data Analysis

We designed and assembled a PVT-VLLE apparatus to simultaneously measure phase volumes and equilibrium compositions. We assembled a mercury-free Ruska PVT Model 2370 to a Hewlett Packard 5880 gas chromatograph (GC) with a specially designed sampling board capable of measuring compositions on-line at high pressures and temperatures. The significance of this experimental setup is a superior on-line sampling for compositional analysis and for accurate phase volume measurements. This is possible because a negligible volume (0.1 μl to 0.5 μl) is withdrawn and sent to the GC for compositional analysis. Since the volumes used for analysis represent less than $1 \times 10^{-5} \%$ of the sample volume, the mass withdrawn for analysis is negligible and does not disturb the equilibrium of the system. In addition we devised a procedure for analyzing and assessing the consistency of our experimental data.

The original Ruska Hg-Free PVT system had some shortcomings and was upgraded for experiments to be carried out at the required temperatures and pressures. In particular, four important changes were made:

1. A new fiber optics lighting system was installed for easy identification of the interface between two phases.
2. The viton seals being originally employed were not good for handling the water and carbon dioxide at desired temperatures, and were replaced with polymyte and fluoromyte seals.
3. These seals needed a change of the piston design and a piston with removable top was installed. The seal on the new piston can be changed without removing the piston from the jack.
4. Since the PVT cell, valves and the inter-connecting tubing are being heated by different controllers, there was a chance of non uniform heating. To insure uniform heating, three calibrated thermocouples were placed on these locations and the temperature is closely monitored throughout the experiment.

Figure 3 shows a schematic of the PVT system which consists of two cells: a pump cell (PC) and float piston cell (FPC). Figure 4 shows the sampling loop consisting of three sampling valves that has been incorporated between the two cells of the PVT system. Figure 5 shows the integrated experimental setup for the PVT-VLLE apparatus. The system has a unique dual-cell arrangement wherein the main cell volume is varied by the vertical movement of a dynamically sealed piston driven by a computer-controlled stepping motor. The second cell contains a floating piston operated by an external pump. The cells are connected by a small-bore tubing through a sapphire sight glass at the top of the main cell. This unique configuration allows phase volume measurements to be made by locating the phase boundary at a reference point in the sight glass. The volumes above and below the reference point are calculated by taking into account the cell dimensions, volume occupied by the magnetic stirrer, piston position, coefficients of thermal expansion, and modulus of elasticity of the cell wall.

Once a mixture is loaded into the main cell, we can make isothermal constant pressure (varying volume) or isothermal constant volume (varying pressure) experiments. The temperature can be set from 100 to 400 °F, and the pressure up to 10,000 psia with resolutions of 0.2 °F and 1 psia, respectively. Higher temperatures could also be attempted after a proper selection of sealing materials, calibration and adjustment of the controller.

The compositions of the equilibrium phases can be determined by taking a minute sample of each phase (of the order of 10^{-5} % of the phase volume) and analyzing the samples by chromatography. These compositions indicate the mutual solubilities of

hydrocarbon/water systems. By displacing the phases through the sight glass, we can sample up to three different phases: a gas phase, a hydrocarbon-rich liquid phase and a water-rich phase.

The PVT-VLLE apparatus allows the measurement of fully experimental K -values and phase densities for multiphase systems. For mixtures containing volatile compounds (C_1 - C_3), we will prepare the samples by gravimetry using high pressure sampling cylinders to assure a single phase. For liquid hydrocarbons, the proposed procedure is as follows:

1. Inject the required amount of water into the windowed combination cell at ambient conditions.
2. Inject the required amount of hydrocarbon mixture into the windowed combination cell at the same condition.
3. Turn on the oven and set the temperature to a value where the mixture will separate into coexisting phases. Maintain the total cell volume constant and wait until equilibrium is reached.
4. Displace the fluids until interphases are identified and determine phase volumes and compositions of each equilibrium phase using the in-line built GC.
5. Increase the temperature by a specified value and repeat steps 1. to 4. until the 375 °F limit is reached, or until multiphases exist.

Task III. *A priori* Simulator PR-EOS/WS-MCR/MEAR-GMIN

We use the Peng-Robinson EOS with usual values for the pure-component repulsion parameter b_i but with the attraction parameter $A_i(T)$ tuned to match the vapor pressure (P_i^s), using the original Maxwell Equal Area Rule (MEAR). The second element of any EOS model is the mixture combining rule (MCR). The Wong-Sandler MCR,¹³ introduced in 1992, contain more basic physics than do conventional van der Waals one-fluid MCR. However, they too used an adjustable binary interaction parameter, k_{12} . Eubank, et al.³⁰ evaluated independently this k_{12} from separate, dilute gas mixture data which provide the cross second virial coefficient, B_{12} . The complete PR/EOS with WS/MCR model is then completely predictive for mixture properties and phase equilibria.

The gas-phase parameter of the WS/MCR is

$$B_{12}^{EOS} = \left(\frac{1}{2}\right)(B_{11}^{EOS} + B_{22}^{EOS})(1 - k_{12}) \quad (2)$$

where $B_i^{EOS} = b_i - (a_i / RT)$ for the Peng-Robinson EOS, and k_{12} is the Wong-Sandler binary interaction constant. Unlike the usual interaction constant k_{12}^* discussed previously, k_{12} really is a constant. That is, it does not change with temperature. Particularly, it is not phase dependent. The bottom line is that only one value of k_{12} is needed to completely represent that binary pair. Our study shows that k_{12} can be found independently because of its connection to real virial coefficients, measurable in low-pressure gas mixtures. The procedure for HC/HC and HC/CO₂ pairs is to use $B_{12}^{EOS} = B_{12}^{EXP}$ for all temperatures. When experimental values are unavailable, B_{12}^{EXP} can be well estimated by the corresponding states method of Tsonopoulos³¹. When water is one component, B_{12}^{EOS} equals B_{12}^{EXP} only near the cross-reduced temperature 0.84 ± 0.04 , where

$$T_{r,12} \equiv (T / T_{c,12}); T_{c,12} \equiv \sqrt{T_{c1}T_{c2}}(1 - K_{12}) \quad (3)$$

The primary procedure for use of this method follows:

1. Use literature measurements of B_{12}^{EXP} (e.g., Dymond and Smith³²) at temperatures slightly below $\sqrt{T_{c1}T_{c2}}$ to calculate the correct K_{12} in the Tsonopoulos correlation.
2. Find the $B_{12}^{EOS} / B_{12}^{EXP}$ cross temperature from Eq. 3 and $T_{r,12} = 0.84$.
3. At the cross temperature, use Eq. 2 to find the Wong-Sandler k_{12} .
4. Use this value of k_{12} in Eq. 2 at all temperatures. When no B_{12}^{EXP} measurements are available, K_{12} must be assumed in keeping with numerous previous correlations.³²⁻³⁵

Phase Equilibria Calculations : Once the EOS/MCR model is set, it is the job of the phase-equilibria computer routine to perform the actual calculations, whether bubble-point, dew-point, flash or critical locus. We have built a large library of such routines over the years.

The computing routines can be divided into two basic types - those that use the conventional K -values approach and those that perform a minimization of the total Gibbs energy. The K -value approach is simpler and uses less computer time but sometimes provides incorrect results. This is due to an unfortunate initial guess that provides convergence into a local minimum of the Gibbs energy surface that is not the global minimum—the correct answer. Such problems were well demonstrated by Baker *et al.*³⁵ for CO₂/n-decane near the three-phase pressure curve. The possibility of false equilibria is increased when (1) components increase, (2) near three-phase boundaries, (3) near critical end points and (4) the components are similar. It is important to recognize this problem and to possess Gibbs' minimization routines. We have several such routines with somewhat different bases:

1. Michelsen tangent-plane algorithms.
2. our original Area Method (Eubank, *et al.*³⁶).

3. revised Area Method (Alvarado³⁷).

STAGE-WISE ISOCHORIC DISTILLATION

The SWID test is a stage-wise distillation test. This test is conducted under stepwise increase of temperature for each stage. For each stage, the system is assumed to reach equilibrium (the system is brought to equilibrium before the distillate sample is removed from the vapor phase), the vapor phase is removed as distillate for compositional analysis. Knowing the distillate volume and the distillate composition, the overall composition in the cell is calculated by material balance. The remaining components in the cell are used for the next stage of the test at a higher temperature. Detailed procedure is referred to Beladi's Ph.D. thesis.³⁸

SWID tests on pure components (C₈, C₁₀, C₁₂, C₁₄, C₁₅, C₁₆, and C₂₀), mixtures of these components, and crude oils are performed to obtain the basic data for calculating the K-values by the empirical material balance model (EMBM). The empirical material balance model considers the vapor phase to be a real gas mixture and the water-rich and hydrocarbon-rich liquid phases to be real solutions. It also considers the mutual solubility between the two liquid phases. The mutual solubility between the two liquid phases is modeled by considering the water as one of the components in the mixtures and using correlations of established laboratory data to approximate the mutual solubilities. At high temperature, the mutual solubilities of the two liquid phases become important. As indicated previously, at temperatures of 500 °F, the water solubility in the hydrocarbon-rich liquid phase exceeds 30%.

EMBM uses the measured P, T, V, z_i, and composition of distillate to calculate the phase compositions and the phase volumes in the distillation cell. The calculated phase compositions are used to calculate the K-values of each component in the mixture.

Pure Hydrocarbon/water Mixtures

Tables 1 through 7 present the calculated three-phase K-values for pure hydrocarbon/water binary systems. Table 8 presents the same data for ternary and quaternary systems of hydrocarbons with water. These three-phase K-values are presented in Figs. 6 through 9. Fig. 6 presents the vapor-oleic three-phase K-values, K^{VO} . The binary mixtures are C₈/water through C₂₀/water. The K-values increase as the temperature increases and appear to converge at a temperature greater than 500 °F.

Fig. 7 presents the vapor-aqueous three-phase K-values, K^{va} , for the same binary systems. The K^{va} for each hydrocarbon component tends to decrease as the temperature increases.

Fig. 8 presents the three-phase water K-values, K^{vo} for the binary systems. The water K^{vo} decreases as the temperature increases. The compositional effect on the K^{vo} for C10+ components appears to be insignificant.

Fig. 9 presents the three-phase water-K-values, K^{va} . The water K^{vo} decreases as the temperature increases except for the C8/water system.

Fig. 10 is a comparison of hydrocarbon K^{vo} for multi-component hydrocarbon/water mixtures. The K^{vo} behavior shows a compositional dependency, especially for C10 and C20. More laboratory experiments are needed to ascertain the nature of the compositional dependency. Fig. 11 is a comparison of the hydrocarbon K^{va} for the same mixtures.

Crude Oil Pseudocomponents

Four crude oils with °API gravities of 10 to 29 were selected for crude oil pseudocomponent K-value determination. Table 9 tabulates the compositions and properties of each crude oil. Fig. 12 shows the concentration profile of the crude oils.

SWID tests were conducted on crude oils A, B, C, and D. A trial and error approach based on Whitson's method was used to select the pseudocomponents. Proper selection of the hydrocarbon component range for each pseudocomponent can reduce the effects of component depletion in the pseudocomponent resulting in a more consistent pseudocomponent definition and better estimation of its K-values. This is because the K-values are sensitive to the compositional variation when the hydrocarbon components are depleted from the oleic phase. The heavier crude oils A and B did not have enough of lighted components, forcing the elimination of PC1. For dead oils, it is proper to reserve the PC1 as void pseudocomponent and start selection of the second pseudocomponent (PC2: C6 to C11).

PC8 is an arbitrary component representing the heavier fraction found in the crude oil. This fraction is not eluted at the temperature range of our experiments (250 °F through 500 °F), therefore, it is not found in the distillate samples. Since, the distillate samples do not contain enough of such heavier components (C37+) in order for the gas chromatography to detect, the PC8 K-values are not provided in this study.

Table 10 presents the pseudocomponent average properties that are used in EMBM. The properties of the distillate sample pseudocomponents are held constant and consistent with the characterized crude oil pseudocomponents.

Tables 11 through 14 present the calculated three-phase K-values and compositions of all phases for the water and pseudocomponents of crude oils A through D.

Figs. 13 through 16 are the plots representing the pseudocomponent K^{VO} each crude oil. These three-phase K-values data need to be verified with further laboratory tests as none of these data is currently available in the literature.

PVT-VLLE SEPARATION

We measured phase compositions and volumes for the following systems:

Hydrocarbons: (C_3+C_7) , (C_5+C_6) , $(C_3+C_5+C_8)$

Hydrocarbons + water: C_8/H_2O , C_6/H_2O , $(C_7+C_{12})/H_2O$, $(C_6+C_7+C_8)/H_2O$, $(C_3+C_5+C_8)/H_2O$

Hydrocarbons + CO_2 : $(C_3+C_5+C_8)/CO_2$.

The volume of both cells and connecting tubing was calibrated using a standard with known density. The difference between the observed and calculated volume was less than 0.68 %. This difference decreased with increasing volume and was less than .05 % for volumes larger than 300 cc. The gas chromatograph was calibrated and the calibration was checked using a known mixture of C_6 , C_7 and C_{10} . The difference between the observed and original compositions was less than 1 %.

After a successful calibration of the test apparatus, the experimental technique and procedure were validated using a mixture of 80 % C_5 and 20 % C_6 (molar basis). The experimental technique and procedure were used to determine the bubble point pressure, molar compositions of vapor and liquid phase, and K-values at four different temperatures ranging between 200 and 300 °F. The detailed procedure was presented in a previous report and additional information appears in our manuscript.³⁹

The running of these tests usually takes ten to fifteen days provided the system does not breakdown. The most common breakdown is leaks developed in the seals. The frequency of these breakdowns have been considerably reduced by improved piston design and better seals. The other breakdowns were due to gas chromatograph problem. We faced problems due to TCD and FID malfunction and processor board burn out. The frequency of these problems has been reduced with proper upkeep of the equipment. In addition, we signed a maintenance agreement with Hewlett Packard to avoid future downtimes and to operate the equipment efficiently.

We performed experiments on a quaternary system of $(C_6+C_7+C_8)/H_2O$. Phase compositions and K-values were obtained at temperatures ranging from 195 °F to 260 °F and at pressures up to 76 psig. These results are included in Table 15. The vapor phase

and oleic phase compositions compare well with the experiments done at this institution and from the EOS simulation. The hydrocarbon solubility in water appears to be too high. A tentative explanation for this could be the formation of a microemulsion, but additional research is needed before we could confirm this. The hydrocarbon solubility in water is too high. The gas chromatographic system and valves were thoroughly checked for any answer to the above mentioned problem of high hydrocarbon solubility in water. This problem was due to fast movement of the fluid while bringing this to the sampling loop and to a very small opening of 0.1 μl valve. These problems were solved by replacing the 0.1 μl rotor with a special rotor with two different size slots of 0.1 μl and 1 μl . The 1 μl slot was used for moving the fluids and the 0.1 μl slot for sampling.

Two binary systems C₈/water and C₆/water were selected to get basic data for comparison with published data (Heidman *et al.*²⁶ for C₈/water, and Tsonopolous and Wilson⁴⁰ for C₆/water.) Fig. 17 shows the phase compositions for C₆/water mixtures. The results for all three phase compare well, particularly at higher temperatures. Also compared are the saturation pressures at different temperature and an excellent agreement is observed (within ± 1 psia). Table 16 shows the phase compositions for the C₈/water system; and Fig. 18 shows the three-phase pressures as a function of temperature.

Quaternary Hydrocarbon/Water Systems

Results for the above mentioned binary systems established the validity of the technique for three phase separation analysis. A quaternary system of propane, pentane, octane and water was also tested. This analysis method was calibrated using external standards in such a way that phase densities were obtained directly from the compositional data. All three phase volumes and compositions were measured at six different temperatures ranging from 104 °F to 347 °F. These compositions are reported in Table 17. From these compositions, any of the three phase K-values can be calculated. The gas chromatograph was calibrated using external standards. Precisely same volume was injected for all the analysis and exact weights of all the components in three phases can be calculated.

Table 18 compares the molar phase fractions experimentally determined (using weights) with phase fractions determined by non-linear regression of material balance equation. The results differ minutely and well within the experimental error.

Phase Density by Chromatography

A well known fact is that gas chromatograph measures the weight % of different components in a mixture. This capability can be used for determination of density. There

are two main requirements for accomplishing this kind of analysis. These requirements are, a properly calibrated method using internal or external standards and exactly same volume injection in subsequent analyses. With our experimental setup and technique both these criteria can be met and the density determined. A method using external standard can be calibrated and with high pressure sampling valves, a precise volume can be injected.

A gas chromatographic method can be broadly defined as fixing of a set of GC parameters like oven temperature program, detector temperature, carrier flow rate, and a run table for operation of the GC. When a method is calibrated according to these fixed parameters the subsequent analyses are assumed to provide the similar results. Generally, an internal or external standard can be used to calibrate a method. In internal standard calibration one of the component whose amount is known even when the amount of the other components are not known is used as standard. This method is used when an external agent is used for dilution as solvent for gas chromatographic analysis. The second method of external standard is employed here. In this method a standard of known composition is used to calibrate the method and then the amount of same components in an unknown mixture are estimated based on this calibration.

After selecting the suitable parameters and oven temperature program a run table is established. The run table provides the instruction for operation of valves, chart speed, attenuation and integration of peaks. A standard of known components and density is injected. The basic chromatogram obtained thus gives the area counts for each individual component. As in case of known component standard, we know the weight percentage of each component response factors. If the response factor is used in this fashion the results will be in weight percent, but if at this juncture we include the density of the calibrating liquid the results will be in density units. We list the calibration and the response factors in the units of centigram per cubic centimeter per area count. The calibration can be performed for single component but that method is applied only when a homogenous mixture with that component can not be obtained, as in case of water and hydrocarbons.

This method of calibration is not new, similar calibrations procedure using external standards was employed by McAuliffe¹⁸ for determination of hydrocarbon solubility in water. McAuliffe¹⁸ calibrated the gas chromatograph using 1 ml of pure components or known composition mixtures as external standards. He then, compared the peaks of these components in 50 ml sample of water containing these components after trapping the water in the fractionator. The fractionator acted as a sample loop and was installed prior to the gas chromatograph column. The only difference in our technique and McAuliffe's technique is that in our case same volumes are injected for calibration and actual sample analysis and hence the sample injection volume can be eliminated as described above.

The above described method for density estimation was used for estimation of three phase density in a quaternary system of water and hydrocarbons. The method was first tested on pure gaseous carbon dioxide and a liquid ternary mixture of propane, pentane and octane. The results were compared with that from established laboratory data and correlations (e.g. modified Racket Equation). Results showed that the difference between the correlation value and experimentally determined value is less than 1 %.

Phase Densities of a Quaternary Hydrocarbon/CO₂ System

A quaternary system of propane, pentane, octane and carbon dioxide was tested. This system was tested at temperatures up to 250 °F and pressure to 1,000 psia. The samples and phase volumes were collected and analyzed for seven different temperatures and fifteen different pressures.

The vapor and liquid mole fraction for the experimental set of temperatures and pressures were also obtained from EOS and were compared with the experimental results. The equation used was Soave-Redlich-Kwong. These comparisons are tabulated in Tables 19 and 20 for vapor and liquid phase, respectively. The total weights data are tabulated in Table 21 along with the volumes of the phases. The total weight of the components are calculated and also listed in this table. These weights are compared with the originally charged weights of all the components as well as with the total weight. Weight difference is less than + 4 %, which is well within the expected experimental error.

Data Analysis by VLLESIM

The SWID cell is a fixed-volume blind cell which allows us to collect vapor phase samples. These samples are condensed and brought to room temperature, then separated into hydrocarbon- and water-rich parts. Chromatographic analysis of these parts and simple material balance calculations give us an estimate of the mole fractions of the components in the vapor phase. Sampling decreases the total mass of the system; thus, we need a scheme to account for this mass withdrawn at each step. We considered several types of experimental errors when sampling the vapor phase and selected a proper scheme for analysis.

During these experiments, sampling of the vapor phase may lead us to two types of experimental errors : 1) errors in identification of the hydrocarbon and water rich volumes, and 2) errors in the chromatographic analysis. We introduced several types of procedures considering different types of error and error propagation analysis within the experimental uncertainty. The types of outputs, or experiments, predicted by VLLE-SIM are:

Constant temperature (T) and pressure (P) and variable cell volume (V): The experimental mole fractions of the oleic, vapor, and aqueous phases, and the phase molar volumes are compared with the predicted values. This type of analysis is suitable for the experiments done on the Ruska Hg-Free PVT-VLLE apparatus. The following options are available :

1. For a given overall feed composition (z_i) and T , evaluate K -values for varying P .
2. For a given overall feed composition z_i and P , evaluate K -values for varying T .
3. For a given T and P , evaluate K -values for varying z_i .

Isochoric test (fixed cell volume) without sampling: Suitable for experiments performed using Ruska Hg-Free PVT-VLLE cell and static pressure tests on SWID cell. The following options are available:

1. For a given z_i , fix V and P and iterate on T . Compare the experimentally determined temperature, y_i , x_i , w_i , and phase volumes with the predicted values.
2. For a given z_i , fix V and T and iterate on P . Compare the experimental pressure, y_i , x_i , w_i , and phase volumes with the predicted values.

Isochoric test (fixed cell volume) with sampling of vapor phase. Suitable to analyze the experiments performed on the SWID cell. The same options discussed in the isochoric test without sampling are available.

An Equation of State (VLLESIM) simulator was developed using different EOS approaches with Van der Waals mixing rules, to predict the HC/CO₂/Water multiphase Equilibria. Experimental results obtained using PVT-VLLE apparatus, SWID cell and literature data were compared with results predicted by VLLESIM.

Following different types of experiment can be predicted by VLLESIM:

1. Varying cell volume (non-isochoric test) and fixed system T and P .
2. Fixed cell volume (isochoric test) and constant T or P .

These categories can further be divided into following sub-categories:

1. No sampling of any phase.
2. Variable or constant samples withdrawn from only vapor phase.
3. Variable or constant samples withdrawn from any or all phases.

Details about these experimental techniques and type of equipment used are discussed in following paragraphs.

Varying cell volume at fixed system temperature and pressure

These experiments can only be performed on PVT-VLLE apparatus. We can do either no sampling, or sampling of one or more phases, and compare predicted phase

compositions and phase volumes with experimental values. Following options are available while performing these experiments:

1. For a given feed composition z_i and T , we observe K-values for varying P .
2. For a given feed composition z_i and P , we observe K-values for varying T .
3. For a given T and P , we observe K-values for varying feed composition z_i .

Fixed cell volume at constant temperature and pressure

We can again do either no sampling, or sampling of one or more phases, and compare predicted phase compositions and phase volumes with experimental values. But only "variable sampling of vapor phase experiments" can be performed on SWID cell, whereas all other experiments including variable and constant sampling of one, two or three phases can be performed on PVT-VLLE apparatus. Following options are available while performing these experiments:

1. For a given feed composition z_i , cell volume and pressure, we iterate on temperature to get unique system temperature which will fix the thermodynamic state and make these experiments reproducible. Then, experimentally measured temperature, phase compositions and volumes are compared with predicted values.
2. For a given feed composition z_i , cell volume and temperature, we iterate on pressure to get unique system pressure which will fix the thermodynamic state and make these experiments reproducible. Then, experimentally measured pressure, phase compositions and volumes are compared with predicted values.

Samples withdrawn from vapor phase

During these experiments, sampling of the vapor phase may lead us to two types of experimental errors : 1) error in measurement of volumes of hydrocarbon and water rich parts, and 2) error in chromatographic analysis. Let's assume, we collected V_{total} amount of sample and this sample is physically separated at ambient conditions into $V_{hydrocarbon}$ and V_{water} parts. Chromatographic analysis of these parts after simple material balance calculations give us y_i^{sample} as mole fraction of components in vapor phase. To evaluate these errors or to study the propagation of these errors to experimental measurements for next step, we have the following options in VLLESIM:

1. Assuming measurements of $V_{hydrocarbon}$ and V_{water} are correct but, an error is introduced while doing material balance calculations using ambient condition pure component densities for calculation of y_i^{sample} . To account for these errors, we make adjustment for samples withdrawn for next step calculations using y_i^{EOS} (instead of experimental y_i^{sample}).

2. Assuming calculation of y_i^{sample} and measurement of V_{total} is correct, but errors are introduced while physically separating V_{total} into $V_{hydrocarbon}$ and V_{water} parts. So we calculate $V_{hydrocarbon}$ and V_{water} using y_i^{EOS} . These modified $V_{hydrocarbon}$, V_{water} (instead of experimental $V_{hydrocarbon}$ and V_{water}) and experimental y_i^{sample} are used to make adjustments for sampling.
3. Assuming only V_{total} is correct and there are errors in measuring $V_{hydrocarbon}$ and V_{water} parts, and calculating y_i^{sample} . So we calculate $V_{hydrocarbon}$ and V_{water} using y_i^{EOS} . And make adjustments for sampling using these modified $V_{hydrocarbon}$, V_{water} and y_i^{EOS} (instead of experimental $V_{hydrocarbon}$, V_{water} and y_i^{sample}).
4. Ignoring sampling adjustments. This option gives large errors for all the systems studied. This may be good for systems having heavier hydrocarbon components (higher than C₂₀).

Published experimental data show that these sampling errors are the major reason in the past for non-reproducibility of experimental data by different researchers for same experimental systems. These difficulties motivated researchers to use more sophisticated sampling techniques and resulted in modern on-line sampling equipments. But the equipments are still being used because those are built to withstand high temperature and pressures (500 °F and 10,000 psia), whereas on-line sampling equipments use sophisticated automatic sampling loops and can be used only up to 350 °F and 4,000 psia.

Modified multiphase equilibrium convergence procedure

VLLESIM is capable of predicting both three-phase (vapor-liquid-liquid) and two-phase (vapor-liquid) equilibria. At any system temperature and pressure we may have any one of the following situations:

1. Only vapor phase existing,
2. Vapor and oleic phases,
3. Vapor and aqueous phases,
4. Oleic and aqueous phases, or
5. Vapor, oleic and aqueous phases

For any system at any system temperature and pressure, we don't know which different types of phases exist. So we first run the three-phase flash loop for given temperature and pressure, if three-phase doesn't exist, we use the results predicted by the three-phase flash loop to decide what type of two-phase flash loop (vapor-oleic, vapor-aqueous, or oleic-aqueous) need to be executed.

We use conventional K-value approach to calculate multi-phase equilibria. A brief description of various steps used in the VLLESIM simulator are presented below:

- STEP 1. Read physical constants for each component (critical properties, molecular weight, room temperature densities etc.), feed composition, system parameters like T and P , and cell volume (when doing isochoric test).
- STEP 2. Provide initial guess for phase molar ratios (f_v and f_o) and K-values. Calculate phase compositions (y_i , x_i and w_i) using initial guess values.
- STEP 3. Go to EOS and mixing rules to calculate all pure component and mixture parameters.
- STEP 4. Calculate phase molar volumes v_v , v_o and v_a using a cubic solver.
- STEP 5. Calculate component fugacities for all phases.
- STEP 6. Calculate K-values and component mole fractions for each phase.
- STEP 7. Check whether convergence is achieved or not.

We assume convergence in flash is achieved when we satisfy following expressions:

Flash functions $< 10^{-8}$, that is

$$F^{3\phi,1} = \log \left(\frac{\sum y_i}{\sum x_i} \right) < 10^{-8} \quad \text{.....(4)}$$

$$F^{3\phi,2} = \log \left(\frac{\sum y_i}{\sum w_i} \right) < 10^{-8} \quad \text{.....(5)}$$

and,

$$\left| \left(y_i^{k+1} - y_i^k \right) \right| < 10^{-8} \quad i = 1, C \quad \text{.....(6)}$$

$$\left| \left(x_i^{k+1} - x_i^k \right) \right| < 10^{-8} \quad i = 1, C \quad \text{.....(7)}$$

$$\left| \left(w_i^{k+1} - w_i^k \right) \right| < 10^{-8} \quad i = 1, C \quad \text{.....(8)}$$

To ensure the presence of three-phase system, we check

$$\sum_{i=1}^C \left(z_i * K_i^{vo} \right) > 1 \quad i = 1, C \quad \text{.....(9)}$$

$$\sum_{i=1}^C \left(z_i * K_i^{va} \right) > 1 \quad i = 1, C \quad \text{.....(10)}$$

$$\sum_{i=1}^C \left(z_i / K_i^{vo} \right) > 1 \quad i = 1, C \quad \text{.....(11)}$$

$$\sum_{i=1}^C \left(z_i / K_i^{va} \right) > 1 \quad i = 1, C \quad \text{.....(12)}$$

To check whether the flash functions are within the desired tolerance (10^{-8}), we need to solve flash functions (Eqs. 4 and 5) using the Newton-Raphson iterative technique.

STEP 8. If convergence is not achieved, we update the values of f_v and f_o and go to STEP 2.

STEP 9. If we are evaluating an isochoric test, we check the volume constraint given by STEP 10, else we jump to STEP 11 and print the results.

STEP 10. For isochoric experiments we need to add volume constraint to the system or in other words the total volume of all three phases should be within the desired tolerance to the volume of the experimental cell.

$$|V_T - (V_v + V_o + V_a)| < 10^{-8} \quad \text{.....(13)}$$

where, V_T is the volume of the experimental cell, V_v , V_o , and V_a are the volumes of the vapor, oleic and aqueous phases respectively. In terms of molar volumes the volume constraint can be given as

$$F^{3\phi,v} = |v_T - (f_v v_v + f_o v_o + f_a v_a)| < 10^{-8} \quad \text{.....(14)}$$

we can call the volume constraint as a three-phase volume flash function $F^{3\phi,v}$. In the above equation, v_v , v_o , v_a are the molar volumes and f_v , f_o , f_a are the phase molar ratios of the vapor, oleic and aqueous phases respectively. According to Duhem's theorem, we need to fix only two variables for an isochoric test to completely define the system. Since we have already fixed the volume of the system, we need to fix either temperature or pressure of the system. We will again use Newton-Raphson iterative technique to solve the three-phase volume flash equation (Eq. 14). If we satisfy the convergence criteria given by Eq. 14, we move to STEP 11 and print results, or we go back to STEP 2 and continue doing iterations till convergence is achieved.

STEP 11. Print the results.

Chawla, *et al.*⁴¹ has more details on the procedure to detect the number of equilibrium phases.

Comparison of Experimental and Predicted Results

A semi-empirical model is developed which uses vapor phase compositions and the values of T and P for different SWID runs to give the phase volumes of three phases. Experiments under the same experimental conditions are conducted on the Hg-Free PVT-VLLE apparatus allowing direct on-line measurement of phase volumes and compositions. Phase volumes calculated using the semi-empirical model and those measured directly on

the Hg-Free cell were compared. The oleic phase volumes differ by $\pm 9\%$, aqueous phase by $\pm 6\%$, total liquid phase by $\pm 4\%$, and vapor phase by $\pm 4\%$. The differences in volumes obtained from the two experimental setups may be because of the limitations of the semi-empirical model which uses ideal gas law to evaluate vapor densities.

The procedure described in previous section is used to validate the VLLESIM for vapor-liquid-liquid equilibria calculations. As mentioned previously, we performed experiments for the different multicomponent hydrocarbon (C_6 to C_{20})/water systems on the SWID cell. Experimental results were compared with predicted values from VLLESIM and are found to be in excellent agreement. The overall mixture composition at experimental temperatures and three-phase equilibrium pressures for $(C_6+C_7+C_8)$ /Water, $(C_7+C_9+C_{12})$ /Water, $(C_{10}+C_{15})$ /Water, and $(C_{10}+C_{15}+C_{20})$ /Water systems are tabulated in Tables 22 through 25, respectively. Experimental and predicted molar compositions are plotted in Figures 19 through 33.

Quaternary mixtures of CH_4 , CO_2 , H_2S and Water in three-phase equilibrium at 100 °F - 908 psia and at 105 °F - 1,222 psia were reported by Huang *et al.*⁴² Experimental data and predicted results are compared in Table 26. Predicted three-phase compositions (vapor, H_2S -rich liquid and water-rich liquid) for all components, except H_2S in water-rich and water in H_2S -rich liquid phases, are in excellent agreement with experimental data. Deviations between experimental and predicted H_2S and water concentration in each other is not totally unexpected. It has already been very challenging to develop a simulator which may predict accurately multi-phase equilibria of pure hydrocarbon/water multi-component mixtures. The presence of CO_2 and H_2S makes the task of predicting three-phase hydrocarbon/water equilibria even more complicated, but excellent agreement between experimental and predicted data proves that PR-EOS based VLLESIM simulator, with some future modifications, would eventually predict accurately different and highly complex multi-component chemical systems.

A PRIORI SIMULATOR EOS-PR/WS-MCR/MEAR-GMIN

Our present predictive computer simulator may be summarized as a Peng-Robinson EOS/Wong-Sandler MCR *model* using the MEAR Gibbs minimization *procedure*. Predicted results are generally in close agreement with experiment as no errors are introduced by the MEAR procedure and the WS/MCR have considerably improved the model. A brief summary of these results is presented here.

To simulate HC/ CO_2 /water systems containing a number of hydrocarbons (for example, oil or a natural gas condensate), the phase behavior of various binary pairs must

be predicted and validated with experimental data. These pairs include (1) HC/HC, (2) HC/CO₂, (3) HC/water and (4) CO₂/water. While some work remains, we have now succeeded in predicting all four of these binary pairs using the above simulator (PR-EOS/WS-MCR/MEAR-GMIN). This result is most promising because water binaries have never been before predicted — only correlated with two or more adjustable parameters.

The HC/HC and HC/CO₂ predictions are described in a recent publication³⁰. Figure 34 is n-butane(1)/water(2) at 344.26 K and 8.844 bars (160°F and 128 psi). The heavy solid line is the vapor value of $g \equiv (\Delta G_m / RT)$, where (ΔG_m) is the Gibbs energy change upon mixing which represents the Gibbs energy itself in minimization procedures. The light solid line is g for the liquid state. Taken separately, the concavity of the vapor line means that vapors of different composition are miscible in all portions but the mostly convex liquid curve means that water and n-butane are nearly immiscible. For any fixed composition, x_1 , the phase with the lower value of g is stable with respect to the other phase. This feature is seen on Figure 35 which follows the derivative for the lower- g branch of Figure 34. Under MEAR, the area equalities of $A_1=A_2$ and $A_3=A_4$ means that we are exactly at the three-phase pressure with the phase point LW being the aqueous liquid, LHC the n-butane-rich liquid and V the vapor phase. There can be only one three-phase pressure and the composition of the three phases shown in Figure 35 are in very close agreement with experiment. If the simulator is run at a higher pressure, $A_1+A_3 = A_2+A_4$ but $A_1 \neq A_2$ so there is only LW-LHC equilibria. Below the three-phase pressure, an equal area is seen between points LW and V but not between V and LHC providing only aqueous liquid/vapor equilibria. This is also the dew-point of the aqueous liquid where $A_1=A_2$ remains but the liquid curve of Figure 34 remains well above that of the vapor to the right of cusp 1 meaning there is no cusp 2.

Of course, the dew-point pressure depends on the overall composition of the gas at V, which is always known in practice. By choosing the pressure, we can find the dew-point composition of the vapor (at V on Figure 35) as well as the amount of hydrocarbon in the first aqueous liquid drop (at LW). This result is especially valuable in determining the initial dew-point of wet natural gases.

For the CO₂/water binary, there exists a large experimental data base from 32 °F to 752 °F covering the region between the critical temperature of CO₂ (86 °F) and that of water (703.4 °F). We have correctly forecast the VLE measurements of Wiebe and Gaddy⁴³ below ≈ 88 °F and the numerous higher temperature VLE measurements. The latter measurements span ≈ 572 °F and include phase boundaries that are S-shaped. We are predicting all of this using only experimental cross second virial coefficients, $B_{12}(T)$, measured in 1987 in our P-V-T laboratory (Chemical Engineering). Of all binary systems,

CO₂/water is perhaps the most difficult to correlate, let alone predict as carbonic acid is formed in the aqueous liquid.

No serious difficulties are expected for the three triples as an additional hydrocarbon usually creates no new problems to HC/HC, HC/CO₂ and even HC/water binaries. The major test is the HC/CO₂/water triplet where our simulator could fail in prediction despite success in three constituent binary pairs. We are presently gaining experience with MEAR with simple liquid-phase activity coefficient models for ternary systems. MEAR can successfully provide regions of one, two and three coexisting phases.

We have recently succeeded in relating the cross virial coefficient obtained from EOS, (B_{ij} - EOS) to experimental cross second virial coefficients³⁰, and thus convert the Wong-Sandler procedure from correlative (that is, requiring parameter tuning) to apriori predictive. The interaction parameter k_{ij} can be calculated by the following equation:

$$B_{ij}^{Exp} = \frac{1}{2}(B_{ii}^{EOS} + B_{jj}^{EOS})(1 - k_{ij}) \quad (15)$$

evaluated at a reduced temperature of $T_{r,ij} = 0.84 \pm 0.04$.

Figure 36 show the diagram of k_{ij} with $T_{r,ij}$ of CO₂/water system. At $T_{r,12} = 0.84$, k_{12} is thus 0.318, which will be used over the whole range of temperatures and pressures.

Figures 37 and 38 each show the phase behavior for carbon dioxide-rich side and water-rich side of this system from 77°F to 167°F (25 °C to 75 °C). The solid lines are calculated by this model and the points are the experimental data from Wiebe and Gaddy^{43,44} and Corn and King⁴⁵. Good agreement is obtained for all pressures for the composition of both phases.

An important feature of this new model is that this model can use the same set of parameter to describe both phases well at the given temperature. However, in the simple vdW MCR, if the adjustable parameter is fitted to the composition of one phase, the results for the other phase will be very poor (Panagiotopoulos and Reid⁴⁶). Therefore, there will be two different parameters for each side.

In Figures 39 through 41 we show the comparison at the moderate temperature 212°F, 392°F and 482 °F (100°C, 200°C and 250°C). At these three temperature, the loops are not closed. Agreements between the prediction results and experimental data can be obtained up to 14,500 psi (1,000 bar).

At a fixed pressure and temperature (P,T), compositional computer simulators forecast (1) the number of phases present at equilibrium and their identity, (2) the relative amounts of these phases, and (3) the density and specific enthalpy of these phases. It is important to understand that all such simulators have two main components, the

background *model* and a *procedure* by which the simulator operates on the *model* to obtain the above *results* or predictions. The *model* tries to capture the physics of fluid mixtures and represent them by reasonably simple and tractable equations. In general, the model cannot provide the first forecast item above; it can give the gas density if a single-phase gas is present or it can give the liquid density if a single-phase liquid is present, but how can we be certain which phase it is or whether both phases are present? That is the job of the *procedure*. Very wrong *results* can occur due to either model failure or procedure failure. When a simulator *model* contains one or more tunable parameters, it is termed a correlation of experimental data. When it has no tunable parameters, it is termed an *a priori predictor* of experimental data (*results*). It is the long-term goal of this project to measure enough benchmark data for hydrocarbon(HC)/CO₂/water(H₂O) systems to test our predictive simulator over wide ranges of pressure, temperature and compositions and establish the reliability of the simulator in predicting accurately the millions of hydrocarbon combinations for which there are no mixture data.

CONCLUSIONS

1. Two three-phase distillation apparatus are designed and constructed for high-temperature and high-pressure multiphase separation experiments up to 500 °F and 10,000 psia. The lower pressure distillation apparatus is used for mixtures of heavier hydrocarbon components ($>C_5$) and the higher pressure distillation apparatus is ready for mixtures of lighter hydrocarbon components including CO_2 .
2. Pure components (C_8 , C_{10} , C_{12} , C_{14} , C_{15} , C_{16} , and C_{20}), mixtures of these components, and crude oil stage-wise isochoric distillation tests are performed to calculate the hydrocarbon/water and pseudocomponents/water three-phase K-values using the empirical material balance model (EMBM). Three-phase K-values of the pure components, pseudocomponents of crude oils and water are determined.
3. A new mercury-free PVT-VLLE apparatus are assembled and fully tested to simultaneously determine phase volumes and compositions on-line for multiphase systems. The pressure and temperature limits are 4,000 psia and 375°F, respectively. Binary, ternary, and quaternary systems of hydrocarbons plus water and hydrocarbons plus CO_2 are analyzed. Fully experimental molar phase densities and three-phase K-values are obtained.
4. A new technique to measure molar phase densities from Chromatography is developed and verified using material balance calculations.
5. A new method to determine experimental uncertainties from phase equilibria data of multiphase systems with a number of components greater or equal to four has been developed. The method is tested with literature data as well.
6. An EOS based simulator (VLLESIM) is developed and used to analyze isochoric and variable volume phase equilibria data for multiphase systems. The simulator has been validated with published and our own data.
7. A user-friendly, next-generation computer simulator based upon the Wong-Sandler mixing rules and the Peng-Robinson EOS is developed. The simulator affords *a priori* prediction of phase equilibria and critical loci without resorting to tuning to measurements for each particular system. Such a simulator could be used with any new crude oil system, provided the crude oil could be successfully represented by pseudo-components.

NOMENCLATURE

A_{∞}^E	=	Infinite dilution excess Helmholtz energy
B_{12}^{EOS}	=	Cross second virial coefficient determined from EOS
EMBM	=	Empirical material balance model
EOS	=	Equation of state
$F^{3\phi,i}$	=	Three-phase flash function
f_v	=	Phase molar ratio of vapor phase
f_o	=	Phase molar ratio of oleic phase
f_a	=	Phase molar ratio of aqueous phase
HC	=	Hydrocarbon
k_{ij}	=	Interaction parameter
K_i^v	=	Vapor-oleic three-phase K-value
K_i^a	=	Vapor-aqueous three-phase K-value
MCR	=	Mixing combining rule
PVT	=	Pressure-Volume-Temperature
VLE	=	Vapor-Liquid-Liquid-Equilibrium
V_T	=	Volume of the test cell
V_v	=	Volume of the vapor phase in the cell
V_o	=	Volume of the oleic phase in the cell
V_a	=	Volume of the aqueous phase in the cell
w_i	=	Water-rich liquid phase composition, mole fraction
x_i	=	Hydrocarbon-rich liquid phase composition, mole fraction
y_i	=	Vapor phase composition, mole fraction
z_i	=	Overall feed composition, mole fraction
$\hat{\phi}_i^v$	=	Fugacity coefficient of the i^{th} component in the vapor phase
$\hat{\phi}_i^l$	=	Fugacity coefficient of the i^{th} component in the hydrocarbon-rich liquid phase
$\hat{\phi}_i^a$	=	Fugacity coefficient of the i -th component in the water-rich liquid phase
ΔG_m	=	Gibbs energy change due to mixing

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LIST OF PAPERS AND PRESENTATIONS

The following is a list of the publications and presentations resulting from the two-year DOE Grant DE-FG03-93ER14357:

1. Beladi M. K., M. A. Barrufet, P. T. Eubank and C. H. Wu: *V-L-L Equilibria Data and K-values for Pseudo-components of a Crude Oil*, SPE paper 27873, presented in the SPE Western Regional Meeting in Long Beach, CA (March 23-25, 1994).
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5. Barrufet, M. A., Liu, K., Rhaman, S., Wu, C. H.: *A Method to Determine Experimental Uncertainties from Phase Equilibria Data of Quaternary Systems of Hydrocarbons + Water*, Submitted for publication to Fluid Phase Equilibria (Dec. 1995).
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APPENDIX I Tables

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Table 1 Three-phase K-values for the C ₈ /water system					
(SB1: 279.13cc C ₈ and 498.13cc water)					
Temperature	Pressure	K ^{vo}		K ^{va}	
(°F)	(psia)	C ₈	water	C ₈	water
250	42	0.38591	33.14	295771	0.6223
300	91	0.37423	16.81	102033	0.6412
350	181	0.36973	9.28	30307	0.6587
400	334	0.35555	5.63	7855	0.6918
450	573	0.36599	3.56	2180	0.7129
500	951	0.42885	2.36	746	0.7335

Table 2 Three-phase K-values for the C ₁₀ /water system					
(BS2: 208.1cc C ₁₀ and 500.0cc water)					
Temperature	Pressure	K ^{vo}		K ^{va}	
(°F)	(psia)	C ₁₀	water	C ₁₀	water
250	34	0.06979	47.76	264615	0.9316
300	76	0.09200	23.17	124123	0.9116
350	150	0.10726	12.37	43610	0.9005
400	278	0.11929	7.14	13131	0.8957
450	478	0.13052	4.41	3897	0.8961
500	777	0.23339	2.68	2212	0.8399

Table 3 Three-phase K-values for the C ₁₂ /water system					
(BS3: 193.56cc C ₁₂ and 500.0cc water)					
Temperature	Pressure	K ^{vo}		K ^{va}	
(°F)	(psia)	C ₁₂	water	C ₁₂	water
250	31	0.02837	48.59	530956	0.9722
300	74	0.03582	24.03	238460	0.9656
350	142	0.04887	12.90	97989	0.9547
400	259	0.05419	7.50	29397	0.9527
450	456	0.07810	4.56	11486	0.9380
500	738	0.13619	2.87	6353	0.9069

Table 4 Three-phase K-values for the C ₁₄ /water system					
(BS 4: 202.3cc C ₁₄ and 500.0cc water)					
Temperature	Pressure	K ^{vo}		K ^{va}	
(°F)	(psia)	C ₁₄	water	C ₁₄	water
250	33	0.00465	48.86	429442	0.9954
300	67	0.00842	24.32	276481	0.9919
350	139	0.01128	13.21	111620	0.9896
400	258	0.01886	7.67	50456	0.9836
450	444	0.02917	4.72	21145	0.9769
500	703	0.05332	3.03	12252	0.9636

Table 5 Three-phase K-values for the C ₁₅ /water system					
(BS5: 298.7cc C ₁₅ and 500.0cc water)					
Temperature (°F)	Pressure (psia)	K ^{vo}		K ^{va}	
		C ₁₅	water	C ₁₅	water
250	31	0.00215	48.63	441071	0.9979
300	68	0.00421	24.28	307609	0.9960
350	137	0.00623	13.20	137004	0.9942
400	253	0.01119	7.69	66498	0.9902
450	440	0.02488	4.72	40041	0.9803
500	691	0.03812	3.06	19447	0.9740

Table 6 Three-phase K-values for the C ₁₆ /water system					
(BS6: 205.1cc C ₁₆ and 500.0cc water)					
Temperature (°F)	Pressure (psia)	K ^{vo}		K ^{va}	
		C ₁₆	water	C ₁₆	water
250	34	0.00143	48.36	653282	0.9986
300	66	0.00279	24.18	452670	0.9973
350	138	0.00500	13.16	243873	0.9954
400	253	0.01023	7.67	134960	0.9911
450	435	0.01936	4.73	69208	0.9847
500	697	0.02718	3.08	30788	0.9815

**Table 7 Three-phase K-values for the C₂₀/water system
(BS7: 109.01cc C₂₀ and 500.0cc water)**

Temperature (°F)	Pressure (psia)	K ^{vo}		K ^{va}	
		C ₂₀	water	C ₂₀	water
250	30	0.00037	47.50	4134437	0.9996
300	68	0.00063	23.86	2496053	0.9994
350	139	0.00089	13.05	1062497	0.9992
400	256	0.00225	7.65	721709	0.9980
450	433	0.00325	4.76	282581	0.9974
500	687	0.00853	3.10	235001	0.9942

**Table 8 Three-phase K-values for the (C₁₀+C₁₅)/water and
(C₁₅+C₂₀)/water system**

T (°F)	P (psia)	K ^{vo}				K ^{va}			
		C ₁₀	C ₁₅	C ₂₀	H ₂ O	C ₁₀	C ₁₅	C ₂₀	H ₂ O
TS1: Ternary System									
250	31	0.05769	0.00212		48.3	261547	353948		0.9662
300	71	0.09131	0.00428		23.6	143325	263565		0.9485
350	147	0.10396	0.00714		12.7	47355	138802		0.9444
400	274	0.11565	0.01190		7.4	13538	66385		0.9426
450	473	0.15844	0.02132		4.5	4686	34600		0.9303
500	761	0.29732	0.05407		2.8	2450	31001		0.8923
TS2: Ternary System									
250	31		0.00126	0.00004	48.2		290244	366187	0.9992
300	68		0.00457	0.00020	24.1		372228	667983	0.9971
350	134		0.00870	0.00068	13.1		212247	686284	0.9947
400	240		0.01265	0.00142	7.7		82935	393862	0.9926
450	435		0.01971	0.00248	4.7		34613	189753	0.9896
500	692		0.03360	0.00582	3.1		18373	145059	0.9845
QS1: Quaternary System									
250	33	0.14094	0.00277	0.00004	46.6	753453	598601	383013	0.9577
300	74	0.21952	0.00365	0.00012	22.9	378089	291341	384358	0.9415
350	150	0.27859	0.00518	0.00018	12.5	117466	132856	189298	0.9413
400	274	0.49077	0.00918	0.00038	7.2	36326	69475	120797	0.9354
450	482	3.81571	0.01498	0.00067	4.5	11092	34517	66442	0.9317
500	748		0.02489	0.00166	2.9	3823	20749	62670	0.9322

Table 9 Crude oil compositions and C₄₅⁺ properties

SCN C#	MWt. g/gmole	Boiling Point (°R)	Normalized Compositions (Wt. fraction)			
			Crude A	Crude B	Crude C	Crude D
1	16	201	0.0000	0.0000	0.0000	0.0000
2	30	332	0.0000	0.0000	0.0000	0.0000
3	44	416	0.0000	0.0000	0.0000	0.0003
4	58	491	0.0000	0.0000	0.0000	0.0031
5	72	557	0.0000	0.0000	0.0100	0.0077
6	86	607	0.0000	0.0000	0.0160	0.0125
7	100	658	0.0002	0.0001	0.0203	0.0225
8	114	702	0.0003	0.0003	0.0246	0.0372
9	128	748	0.0012	0.0017	0.0272	0.0406
10	142	791	0.0033	0.0037	0.0298	0.0433
11	156	829	0.0067	0.0087	0.0326	0.0422
12	170	867	0.0093	0.0136	0.0355	0.0409
13	184	901	0.0139	0.0188	0.0367	0.0414
14	198	936	0.0173	0.0239	0.0379	0.0390
15	212	971	0.0195	0.0272	0.0363	0.0368
16	226	1002	0.0206	0.0298	0.0346	0.0322
17	240	1032	0.0210	0.0311	0.0327	0.0308
18	254	1055	0.0214	0.0320	0.0309	0.0304
19	269	1077	0.0211	0.0315	0.0301	0.0297
20	283	1101	0.0207	0.0305	0.0293	0.0281
21	297	1124	0.0196	0.0290	0.0267	0.0257
22	311	1146	0.0185	0.0279	0.0242	0.0235
23	325	1167	0.0175	0.0268	0.0223	0.0226
24	339	1187	0.0168	0.0260	0.0204	0.0213
25	353	1207	0.0162	0.0258	0.0190	0.0207
26	367	1226	0.0158	0.0262	0.0175	0.0194
27	381	1244	0.0157	0.0263	0.0166	0.0187
28	395	1262	0.0156	0.0259	0.0156	0.0185
29	409	1277	0.0154	0.0241	0.0148	0.0173

Table 9-(Continued)						
SCN	MWt.	Boiling Point	Normalized Compositions (Wt. fraction)			
C#	g/gmole	(°R)	Crude A	Crude B	Crude C	Crude D
30	423	1294	0.0151	0.0219	0.0140	0.0163
31	437	1310	0.0148	0.0192	0.0130	0.0162
32	451	1326	0.0137	0.0164	0.0121	0.0153
33	465	1341	0.0125	0.0146	0.0107	0.0143
34	479	1355	0.0114	0.0134	0.0093	0.0135
35	493	1368	0.0107	0.0126	0.0079	0.0129
36	507	1382	0.0101	0.0120	0.0065	0.0125
37	521	1394	0.0097	0.0110	0.0058	0.0121
38	535	1407	0.0091	0.0105	0.0051	0.0120
39	549	1419	0.0086	0.0101	0.0045	0.0103
40	563	1432	0.0083	0.0098	0.0040	0.0100
41	577	1442	0.0080	0.0095	0.0035	0.0097
42	591	1453	0.0077	0.0093	0.0030	0.0094
43	605	1464	0.0073	0.0090	0.0025	0.0091
44	619	1477	0.0070	0.0088	0.0020	0.0087
45+	-----	-----	0.5184	0.3210	0.2849	0.1118
°API gravity =			10.3	13.0	19	29
45+ normal Boiling point (°R)=			1850	1810	1740	1600
45+ average MWt. (g/gmole) =			1144	1074	959	757
45+ carbon number (SCN) =			81	76	68	54

Table 10 Pseudocomponent average property						
Pseudocomponent	Tb (°R)	SCN	MWt	γ	Pc (psia)	Tc (°R)
PC1	399	3	59	0.50	711	641
PC2	766	9	125	0.72	373	1091
PC3	905	13	178	0.76	291	1240
PC4	1015	17	231	0.78	240	1350
PC5	1110	21	283	0.80	203	1439
PC6	1205	25	339	0.82	171	1522
PC7	1316	32	411	0.84	141	1612
PC8	1695	64	687	0.89	73	1858

**Table 11 Pseudocomponents' three-phase K-values and phase compositions
for crude oil A**

Temperature (°F)	Pressure (psia)	PC2	PC3	PC4	PC5	PC6	PC7	H2O
K_{VO}								
250	29	4.66E-02	1.29E-02	2.10E-03	5.33E-04	1.69E-04	8.25E-05	45.62
300	69	5.51E-02	1.70E-02	2.97E-03	6.45E-04	2.19E-04	3.22E-05	23.06
350	138	5.82E-02	2.07E-02	4.51E-03	8.76E-04	2.51E-04	5.74E-05	12.68
400	253	4.79E-02	2.31E-02	5.98E-03	1.31E-03	3.33E-04	3.52E-05	7.48
450	429	6.05E-02	3.16E-02	9.11E-03	2.32E-03	6.10E-04	5.67E-05	4.67
500	692	6.45E-02	3.80E-02	1.20E-02	3.39E-03	9.10E-04	7.76E-05	3.07
K_{Va}								
250	29	5.73E+05	1.32E+06	3.31E+06	1.58E+07	1.68E+08	1.26E+10	0.9967
300	69	2.25E+05	6.06E+05	1.67E+06	6.85E+06	7.76E+07	1.75E+09	0.9961
350	138	6.65E+04	2.18E+05	7.61E+05	2.81E+06	2.68E+07	9.44E+08	0.9957
400	253	1.38E+04	6.34E+04	2.71E+05	1.14E+06	9.69E+06	1.57E+08	0.9959
450	429	4.34E+03	2.25E+04	1.11E+05	5.50E+05	4.85E+06	6.93E+07	0.9951
500	692	1.34E+03	8.15E+03	4.61E+04	2.56E+05	2.31E+06	3.04E+07	0.9951
Y_i								
250	29	1.63E-03	1.25E-03	3.27E-04	6.60E-05	1.80E-05	1.05E-05	0.9967
300	69	1.76E-03	1.58E-03	4.54E-04	7.85E-05	2.29E-05	4.03E-06	0.9961
350	138	1.67E-03	1.82E-03	6.64E-04	1.03E-04	2.54E-05	6.96E-06	0.9957
400	253	1.21E-03	1.85E-03	8.25E-04	1.46E-04	3.19E-05	4.04E-06	0.9959
450	429	1.27E-03	2.20E-03	1.14E-03	2.36E-04	5.36E-05	5.98E-06	0.9951
500	692	1.07E-03	2.16E-03	1.28E-03	2.98E-04	6.94E-05	7.11E-06	0.9951
X_i								
250	29	3.50E-02	9.71E-02	1.56E-01	1.24E-01	1.06E-01	1.27E-01	0.0218
300	69	3.20E-02	9.33E-02	1.53E-01	1.22E-01	1.04E-01	1.25E-01	0.0432
350	138	2.87E-02	8.78E-02	1.47E-01	1.18E-01	1.01E-01	1.21E-01	0.0785
400	253	2.52E-02	8.01E-02	1.38E-01	1.11E-01	9.58E-02	1.15E-01	0.1331
450	429	2.11E-02	6.98E-02	1.25E-01	1.02E-01	8.78E-02	1.05E-01	0.2130
500	692	1.66E-02	5.69E-02	1.06E-01	8.80E-02	7.62E-02	9.16E-02	0.3245
W_i								
250	29	2.85E-09	9.48E-10	9.90E-11	4.16E-12	1.07E-13	8.35E-16	0.999999996
300	69	7.84E-09	2.61E-09	2.73E-10	1.15E-11	2.95E-13	2.30E-15	0.999999989
350	138	2.51E-08	8.36E-09	8.73E-10	3.67E-11	9.45E-13	7.37E-15	0.999999966
400	253	8.75E-08	2.91E-08	3.04E-09	1.28E-10	3.29E-12	2.57E-14	0.999999880
450	429	2.94E-07	9.78E-08	1.02E-08	4.29E-10	1.11E-11	8.62E-14	0.999999598
500	692	7.97E-07	2.65E-07	2.77E-08	1.17E-09	3.00E-11	2.34E-13	0.999998909

**Table 12 Pseudocomponents' three-phase K-values and phase compositions
for crude oil B**

Temperature (°F)	Pressure (psia)	PC2	PC3	PC4	PC5	PC6	PC7	H2O
K_{VO}								
250	28	1.81E-02	5.84E-03	1.28E-03	2.00E-04	2.91E-05	1.03E-05	46.21
300	62	2.81E-02	1.45E-02	3.25E-03	4.15E-04	4.54E-05	1.27E-05	23.28
350	133	5.43E-02	3.43E-02	9.19E-03	1.45E-03	1.69E-04	4.30E-05	12.74
400	255	4.82E-02	3.98E-02	1.12E-02	1.77E-03	2.26E-04	5.01E-05	7.50
450	432	2.15E-02	2.04E-02	8.18E-03	2.13E-03	3.79E-04	6.77E-05	4.70
500	695	1.79E-02	1.81E-02	8.55E-03	2.92E-03	7.25E-04	1.61E-04	3.08
K_{Va}								
250	28	1.92E+05	4.91E+05	1.72E+06	4.97E+06	2.50E+07	1.03E+09	0.9984
300	62	9.98E+04	4.22E+05	1.55E+06	3.70E+06	1.40E+07	4.56E+08	0.9969
350	133	5.39E+04	2.87E+05	1.31E+06	3.92E+06	1.58E+07	4.70E+08	0.9931
400	255	1.25E+04	8.73E+04	4.33E+05	1.30E+06	5.76E+06	1.49E+08	0.9930
450	432	1.45E+03	1.17E+04	8.43E+04	4.25E+05	2.64E+06	5.50E+07	0.9963
500	695	3.73E+02	3.21E+03	2.76E+04	1.85E+05	1.61E+06	4.18E+07	0.9970
Y_i								
250	28	6.48E-04	6.55E-04	2.42E-04	3.07E-05	4.11E-06	1.47E-06	0.9984
300	62	9.27E-04	1.55E-03	5.99E-04	6.29E-05	6.32E-06	1.80E-06	0.9969
350	133	1.60E-03	3.38E-03	1.63E-03	2.13E-04	2.29E-05	5.93E-06	0.9931
400	255	1.29E-03	3.58E-03	1.87E-03	2.47E-04	2.91E-05	6.55E-06	0.9930
450	432	5.05E-04	1.61E-03	1.22E-03	2.71E-04	4.48E-05	8.13E-06	0.9963
500	695	3.52E-04	1.20E-03	1.09E-03	3.20E-04	7.41E-05	1.68E-05	0.9970
X_i								
250	28	3.58E-02	1.12E-01	1.89E-01	1.54E-01	1.41E-01	1.43E-01	0.0216
300	62	3.29E-02	1.07E-01	1.84E-01	1.51E-01	1.39E-01	1.41E-01	0.0428
350	133	2.95E-02	9.86E-02	1.77E-01	1.47E-01	1.36E-01	1.38E-01	0.0780
400	255	2.68E-02	9.00E-02	1.66E-01	1.39E-01	1.29E-01	1.31E-01	0.1324
450	432	2.35E-02	7.88E-02	1.49E-01	1.27E-01	1.18E-01	1.20E-01	0.2121
500	695	1.97E-02	6.61E-02	1.27E-01	1.10E-01	1.02E-01	1.04E-01	0.3234
W_i								
250	28	3.37E-09	1.34E-09	1.41E-10	6.17E-12	1.65E-13	1.43E-15	0.999999995
300	62	9.29E-09	3.68E-09	3.87E-10	1.70E-11	4.53E-13	3.94E-15	0.999999987
350	133	2.98E-08	1.18E-08	1.24E-09	5.44E-11	1.45E-12	1.26E-14	0.999999957
400	255	1.04E-07	4.10E-08	4.32E-09	1.90E-10	5.06E-12	4.40E-14	0.999999851
450	432	3.48E-07	1.38E-07	1.45E-08	6.36E-10	1.70E-11	1.48E-13	0.999999499
500	695	9.44E-07	3.74E-07	3.93E-08	1.73E-09	4.61E-11	4.01E-13	0.999998641

**Table 13 Pseudocomponent's three-phase K-values and phase compositions
for crude oil C**

Temperature (°F)	Pressure (psia)	PC2	PC3	PC4	PC5	PC6	PC7	H2O
K^{VO}								
250	34	9.09E-02	4.27E-03	4.61E-04	1.35E-04	7.88E-05	2.26E-05	45.99
300	80	5.07E-02	3.38E-03	3.77E-04	8.28E-05	5.17E-05	1.47E-05	23.44
350	151	4.07E-02	3.86E-03	3.88E-04	7.81E-05	4.76E-05	1.46E-05	12.87
400	265	3.88E-02	7.10E-03	6.67E-04	9.33E-05	5.26E-05	1.85E-05	7.56
450	455	3.99E-02	1.15E-02	1.14E-03	1.58E-04	7.03E-05	2.71E-05	4.71
500	701	7.04E-02	3.02E-02	3.77E-03	4.38E-04	1.41E-04	5.82E-05	3.06
K^{Va}								
250	34	1.65E+05	2.26E+05	3.90E+05	2.27E+06	4.22E+07	1.63E+09	0.9682
300	80	3.14E+04	6.46E+04	1.16E+05	5.06E+05	1.01E+07	3.84E+08	0.9831
350	151	7.33E+03	2.25E+04	3.65E+04	1.46E+05	2.84E+06	1.17E+08	0.9872
400	265	1.82E+03	1.13E+04	1.73E+04	4.82E+04	8.65E+05	4.09E+07	0.9884
450	455	4.87E+02	4.94E+03	8.20E+03	2.27E+04	3.21E+05	1.66E+07	0.9889
500	701	2.48E+02	4.06E+03	8.95E+03	2.09E+04	2.15E+05	1.19E+07	0.9832
Y_i								
250	34	3.11E-02	6.51E-04	6.63E-05	1.30E-05	5.51E-06	1.42E-06	0.9682
300	80	1.63E-02	5.14E-04	5.42E-05	7.96E-06	3.61E-06	9.20E-07	0.9831
350	151	1.22E-02	5.73E-04	5.48E-05	7.38E-06	3.26E-06	8.96E-07	0.9872
400	265	1.05E-02	1.00E-03	9.04E-05	8.47E-06	3.47E-06	1.09E-06	0.9883
450	455	9.47E-03	1.47E-03	1.44E-04	1.34E-05	4.31E-06	1.49E-06	0.9889
500	701	1.31E-02	3.28E-03	4.26E-04	3.35E-05	7.85E-06	2.90E-06	0.9831
X_i								
250	34	3.42E-01	1.53E-01	1.44E-01	9.63E-02	6.99E-02	6.26E-02	0.0211
300	80	3.22E-01	1.52E-01	1.44E-01	9.62E-02	6.98E-02	6.26E-02	0.0419
350	151	3.00E-01	1.48E-01	1.41E-01	9.45E-02	6.86E-02	6.15E-02	0.0767
400	265	2.72E-01	1.41E-01	1.36E-01	9.08E-02	6.59E-02	5.91E-02	0.1307
450	455	2.37E-01	1.28E-01	1.26E-01	8.45E-02	6.13E-02	5.49E-02	0.2101
500	701	1.86E-01	1.09E-01	1.13E-01	7.65E-02	5.56E-02	4.98E-02	0.3213
W_i								
250	34	1.89E-07	2.89E-09	1.70E-10	5.72E-12	1.30E-13	8.69E-16	0.99999981
300	80	5.20E-07	7.95E-09	4.68E-10	1.57E-11	3.59E-13	2.39E-15	0.99999947
350	151	1.66E-06	2.55E-08	1.50E-09	5.04E-11	1.15E-12	7.66E-15	0.99999831
400	265	5.80E-06	8.87E-08	5.23E-09	1.76E-10	4.01E-12	2.67E-14	0.99999411
450	455	1.95E-05	2.98E-07	1.75E-08	5.90E-10	1.35E-11	8.96E-14	0.99998022
500	701	5.28E-05	8.08E-07	4.76E-08	1.60E-09	3.65E-11	2.43E-13	0.99994632

**Table 14 Pseudocomponents' three-phase K-values and phase compositions
for crude oil D**

Temperature (°F)	Pressure (psia)	PC2	PC3	PC4	PC5	PC6	PC7	H2O
K_{VO}								
250	46	3.54E-01	2.16E-02	6.24E-03	1.61E-03	4.17E-04	1.54E-04	41.18
300	84	3.31E-01	2.41E-02	9.55E-03	4.68E-03	1.67E-03	7.02E-04	20.98
350	155	3.05E-01	2.71E-02	1.03E-02	6.49E-03	3.76E-03	8.52E-04	11.67
400	265	2.98E-01	4.03E-02	9.20E-03	3.88E-03	1.38E-03	5.81E-04	6.93
450	447	3.29E-01	5.27E-02	1.25E-02	4.02E-03	1.43E-03	6.02E-04	4.32
500	704	2.85E-01	1.06E-01	1.97E-02	3.95E-03	1.40E-03	5.90E-04	2.88
K_{Va}								
250	46	7.60E+05	9.75E+05	4.57E+06	2.37E+07	2.04E+08	1.24E+10	0.8556
300	84	2.46E+05	3.93E+05	2.53E+06	2.49E+07	2.96E+08	2.05E+10	0.8699
350	155	6.60E+04	1.35E+05	8.36E+05	1.06E+07	2.05E+08	7.65E+09	0.8865
400	265	1.66E+04	5.53E+04	2.09E+05	1.77E+06	2.10E+07	1.46E+09	0.8985
450	447	4.68E+03	2.00E+04	7.93E+04	5.16E+05	6.14E+06	4.25E+08	0.9022
500	704	1.23E+03	1.26E+04	4.08E+04	1.66E+05	1.98E+06	1.37E+08	0.9221
Y_i								
250	46	1.40E-01	3.31E-03	7.89E-04	1.37E-04	2.83E-05	1.14E-05	0.8556
300	84	1.25E-01	3.68E-03	1.21E-03	3.96E-04	1.13E-04	5.20E-05	0.8699
350	155	1.07E-01	4.05E-03	1.27E-03	5.40E-04	2.51E-04	6.22E-05	0.8865
400	265	9.42E-02	5.78E-03	1.11E-03	3.14E-04	8.96E-05	4.12E-05	0.8985
450	447	8.89E-02	7.02E-03	1.41E-03	3.07E-04	8.78E-05	4.04E-05	0.9022
500	704	6.36E-02	1.20E-02	1.97E-03	2.69E-04	7.67E-05	3.53E-05	0.9221
X_i								
250	46	3.96E-01	1.53E-01	1.26E-01	8.47E-02	6.79E-02	7.41E-02	0.0208
300	84	3.77E-01	1.52E-01	1.26E-01	8.46E-02	6.78E-02	7.40E-02	0.0415
350	155	3.52E-01	1.49E-01	1.24E-01	8.33E-02	6.68E-02	7.30E-02	0.0760
400	265	3.16E-01	1.43E-01	1.20E-01	8.08E-02	6.49E-02	7.09E-02	0.1297
450	447	2.70E-01	1.33E-01	1.13E-01	7.64E-02	6.14E-02	6.71E-02	0.2089
500	704	2.23E-01	1.12E-01	1.00E-01	6.80E-02	5.47E-02	5.98E-02	0.3200
W_i								
250	46	1.84E-07	3.40E-09	1.73E-10	5.77E-12	1.39E-13	9.21E-16	0.99999981
300	84	5.08E-07	9.36E-09	4.76E-10	1.59E-11	3.82E-13	2.54E-15	0.99999948
350	155	1.63E-06	3.00E-08	1.52E-09	5.09E-11	1.22E-12	8.13E-15	0.99999834
400	265	5.66E-06	1.04E-07	5.31E-09	1.77E-10	4.26E-12	2.83E-14	0.99999423
450	447	1.90E-05	3.51E-07	1.78E-08	5.96E-10	1.43E-11	9.51E-14	0.99998061
500	704	5.16E-05	9.52E-07	4.84E-08	1.62E-09	3.88E-11	2.58E-13	0.99994739

Table 15 Molar compositions and K-values for the (C₆+C₇+C₈)/water system

Feed Composition (mole %)							
	HEXANE	10.484	(C6)				
	HEPTANE	10.574	(C7)				
	OCTANE	10.743	(C8)				
	WATER	68.199	(H2O)				
			Oleic	Vapor	Aqueous		
P (psig)	T (°F)	Component	x _i	y _i	w _i	K _i vo	K _i va
13	195	C6	31.68	52.94	0.054	1.67	980.37
13	195	C7	32.30	28.01	0.054	0.87	518.70
13	195	C8	34.16	17.23	0.060	0.50	287.17
13	195	H2O	1.87	1.82	99.832	0.97	0.02
21	195	C6	32.63	50.49	0.050	1.55	1009.80
21	195	C7	31.96	29.68	0.059	0.93	503.05
21	195	C8	33.46	17.31	0.063	0.52	274.76
21	195	H2O	1.95	2.52	99.828	1.29	0.03
28	195	C6	32.68	48.53	0.065	1.49	746.62
28	195	C7	31.93	27.91	0.043	0.87	649.07
28	195	C8	33.36	21.44	0.062	0.64	345.81
28	195	H2O	2.03	2.12	99.830	1.04	0.02
33	230	C6	31.02	49.86	0.074	1.61	673.78
33	230	C7	31.61	29.07	0.057	0.92	510.00
33	230	C8	33.96	15.79	0.075	0.46	210.53
33	230	H2O	3.40	5.28	99.795	1.55	0.05
41	230	C6	30.99	49.85	0.074	1.61	673.65
41	230	C7	31.55	29.08	0.057	0.92	510.19
41	230	C8	34.07	15.74	0.075	0.46	209.81
41	230	H2O	3.39	5.34	99.793	1.57	0.05
50	230	C6	30.92	49.72	0.076	1.61	654.21
50	230	C7	31.56	29.17	0.058	0.92	502.93
50	230	C8	34.10	15.73	0.077	0.46	204.29
50	230	H2O	3.43	5.38	99.789	1.57	0.05
56	260	C6	30.98	29.99	0.078	0.97	384.49
56	260	C7	31.53	17.87	0.059	0.57	302.88
56	260	C8	33.90	9.99	0.078	0.29	128.08
56	260	H2O	3.59	42.14	99.784	11.74	0.42
65	260	C6	30.95	30.08	0.078	0.97	385.64
65	260	C7	31.51	17.94	0.064	0.57	280.31
65	260	C8	33.94	9.96	0.075	0.29	132.80
65	260	H2O	3.60	42.02	99.780	11.67	0.42
76	260	C6	31.13	29.53	0.081	0.95	364.57
76	260	C7	31.54	17.95	0.066	0.57	271.97
76	260	C8	33.68	10.43	0.078	0.31	133.72
76	260	H2O	3.65	42.09	99.775	11.53	0.42

Table 16 Phase compositions for the C₈/water system

T(F)	P(PSIA)	PHASE	MOLE % OCTANE	MOLE % WATER	HEIDMAN et al
100	5.7	VAPOR	20.73	79.57	NA
200	17.7	VAPOR	23.97	76.03	73.60
250	42.7	VAPOR	24.16	75.84	NA
300	95.7	VAPOR	27.13	72.87	73.60
350	189.7	VAPOR	27.71	72.29	
400	NA	VAPOR	NA	NA	70.40
100	5.7	AQUEOUS	TRACE	100.00	0.000012
200	17.7	AQUEOUS	0.00029	99.99971	0.000048
250	42.7	AQUEOUS	0.00030	99.99970	NA
300	95.7	AQUEOUS	0.00037	99.99963	0.000380
325	NA	AQUEOUS	0.00043	99.99957	NA
350	189.7	AQUEOUS	0.00190	99.99810	NA
400	NA	AQUEOUS	NA	NA	0.004000
100	5.7	OLEIC	99.54	0.46	0.1
150	NA	OLEIC	99.50	0.50	NA
200	17.7	OLEIC	99.25	0.75	0.62
250	42.7	OLEIC	98.06	1.94	NA
300	95.7	OLEIC	95.87	4.13	3.94
325	NA	OLEIC	94.20	5.80	NA
350	189.7	OLEIC	91.65	8.35	NA
400	NA	OLEIC	NA	NA	12.60

Table 17 Phase compositions for the (C₃+C₄+C₈)/water system

P (psia)	T (F)	PHASE	MOLE FRACTIONS			
			C3	C5	C8	H2O
107	104	VAPOR	0.95010	0.04598	0.00247	0.00144
107	104	OLEIC	0.51710	0.23411	0.24524	0.00355
107	104	AQUEOUS	0.00021	0.00001	0.00000	0.99978
172	149	VAPOR	0.92663	0.05373	0.00046	0.01918
172	149	OLEIC	0.50432	0.23546	0.25106	0.00916
172	149	AQUEOUS	0.00021	0.00001	0.00000	0.99977
295	212	VAPOR	0.90686	0.05072	0.01364	0.02878
295	212	OLEIC	0.47257	0.24943	0.26643	0.01156
295	212	AQUEOUS	0.00029	0.00002	0.00000	0.99969
382	248	VAPOR	0.75957	0.07219	0.03379	0.13444
382	248	OLEIC	0.45761	0.24362	0.26328	0.03549
382	248	AQUEOUS	0.00046	0.00003	0.00000	0.99951
570	302	VAPOR	0.69268	0.11540	0.03699	0.15494
570	302	OLEIC	0.42702	0.23736	0.27372	0.06190
570	302	AQUEOUS	0.00092	0.00008	0.00000	0.99899
747	347	VAPOR	0.68561	0.11683	0.04342	0.15414
747	347	OLEIC	0.37771	0.23170	0.27985	0.11074
747	347	AQUEOUS	0.00223	0.00030	0.00001	0.99746

Table 18 Molar phase fractions of the (C₃+C₅+C₈)/water system

P (psia)	T (F)	PHASE	GC	M.B	% DIFF
107	104	VAPOR	0.00982	0.01023	-4.25
107	104	OLEIC	0.23157	0.23080	0.33
107	104	AQUEOUS	0.75898	0.75897	0.00
172	149	VAPOR	0.01710	0.01602	6.35
172	149	OLEIC	0.22643	0.22653	-0.05
172	149	AQUEOUS	0.75720	0.75743	-0.03
295	212	VAPOR	0.03247	0.03212	1.08
295	212	OLEIC	0.21132	0.21137	-0.03
295	212	AQUEOUS	0.75611	0.75651	-0.05
382	248	VAPOR	0.04323	0.04309	0.31
382	248	OLEIC	0.21006	0.21014	-0.04
382	248	AQUEOUS	0.74698	0.74675	0.03
570	302	VAPOR	0.06159	0.06320	-2.61
570	302	OLEIC	0.20118	0.19852	1.33
570	302	AQUEOUS	0.73850	0.73831	0.03
747	347	VAPOR	0.08233	0.08090	1.74
747	347	OLEIC	0.19096	0.19116	-0.10
747	347	AQUEOUS	0.72747	0.72785	-0.05

Table 19 Vapor phase mole fractions of the (C₃+C₅+C₈)/ CO₂ system

T (F)	Experimental mole fractions				EOS mole fractions			
	C3	C5	C8	CO2	C3	C5	C8	CO2
100	0.2762	0.0379	0.0246	0.6614	0.2442	0.0174	0.0006	0.7378
125	0.2969	0.0415	0.0200	0.6417	0.2851	0.0254	0.0012	0.6882
150	0.3237	0.0483	0.0184	0.6096	0.3202	0.0356	0.0024	0.6418
175	0.3750	0.0694	0.0262	0.5294	0.3515	0.0484	0.0046	0.5956
200	0.3850	0.0771	0.0221	0.5159	0.3819	0.0645	0.0082	0.5454
225	0.4032	0.0975	0.0306	0.4686	0.4051	0.0835	0.0140	0.4975
250	0.4095	0.1067	0.0346	0.4493	0.4197	0.1046	0.0232	0.4525

Table 20 Liquid phase mole fractions of the (C₃+C₅+C₈)/ CO₂ system

T (F)	Experimental mole fractions				EOS mole fractions			
	C3	C5	C8	CO2	C3	C5	C8	CO2
100	0.4413	0.2088	0.1097	0.2401	0.4150	0.1810	0.0954	0.3082
125	0.4409	0.2135	0.1135	0.2321	0.4214	0.1894	0.1002	0.2889
150	0.4405	0.2163	0.1188	0.2244	0.4230	0.1939	0.1034	0.2801
175	0.4272	0.2142	0.1198	0.2388	0.4220	0.1971	0.1062	0.2748
200	0.4275	0.2210	0.1255	0.2260	0.4200	0.2035	0.1121	0.2641
225	0.4195	0.2215	0.1287	0.2303	0.4170	0.2086	0.1183	0.2567
250	0.4164	0.2238	0.1323	0.2274	0.4120	0.2100	0.1228	0.2555

Table 21 Four-component weight material balance for the (C₃+C₅+C₈)/CO₂ system

P (psia)	T (F)	Phase	Volume	DENSITY	WEIGHTS (gms)				TOTAL
				(gm/cc)	C3	C5	C8	CO2	
447	100	VAPOR	218.99	0.080	4.545	1.020	1.047	10.864	17.476
447	100	LIQUID	167.96	0.596	33.796	26.165	21.766	18.350	100.077
			386.95	TOTAL	38.341	27.185	22.814	29.214	117.552
				Diff. %	0.88	1.43	0.64	-0.77	0.56
472	100	VAPOR	154.07	0.088	3.494	0.847	0.897	8.349	13.587
472	100	LIQUID	172.88	0.604	35.125	26.837	22.007	20.411	104.380
			326.95	TOTAL	38.619	27.684	22.904	28.760	117.967
				Diff. %	0.16	-0.38	0.24	0.79	0.21
496	100	VAPOR	90.06	0.097	2.098	0.459	0.463	5.738	8.757
496	100	LIQUID	176.89	0.618	36.431	27.142	22.636	23.074	109.282
			266.95	TOTAL	38.529	27.601	23.098	28.811	118.039
				Diff. %	0.39	-0.08	-0.60	0.62	0.14
519	125	VAPOR	218.62	0.090	5.541	1.266	0.965	11.955	19.727
519	125	LIQUID	168.49	0.595	33.584	26.609	22.394	17.642	100.229
			387.11	TOTAL	39.125	27.875	23.359	29.597	119.956
				Diff. %	-1.15	-1.07	-1.74	-2.09	-1.48
549	125	VAPOR	153.32	0.099	4.212	0.987	0.768	9.221	15.188
549	125	LIQUID	173.79	0.598	34.745	26.658	22.296	20.260	103.959
			327.11	TOTAL	38.957	27.645	23.064	29.481	119.147
				Diff. %	-0.72	-0.24	-0.45	-1.69	-0.79
581	125	VAPOR	88.06	0.113	2.845	0.735	0.610	5.787	9.977
581	125	LIQUID	179.05	0.604	35.821	26.734	22.565	23.049	108.169
			267.11	TOTAL	38.666	27.469	23.175	28.836	118.146
				Diff. %	0.04	0.40	-0.94	0.53	0.05
604	150	VAPOR	217.89	0.096	6.392	1.562	0.941	12.014	20.909
604	150	LIQUID	169.44	0.577	32.455	26.080	22.669	16.499	97.703
			387.33	TOTAL	38.847	27.642	23.610	28.513	118.612
				Diff. %	-0.43	-0.22	-2.83	1.65	-0.34

(continued)

Table 21 Four-component weight material balance for the (C₃+C₅+C₈)/ CO₂ system

P(psia)	T (F)	Phase	Volume	DENSITY	WEIGHTS (gms)				TOTAL
				(gm/cc)	C3	C5	C8	CO2	
644	150	VAPOR	154.88	0.112	5.238	1.427	0.799	9.948	17.411
644	150	LIQUID	172.45	0.579	33.271	25.944	22.151	18.529	99.895
			327.33	TOTAL	38.509	27.371	22.950	28.477	117.306
				Diff. %	0.44	0.76	0.04	1.77	0.76
687	150	VAPOR	83.58	0.123	3.004	0.778	0.458	6.028	10.267
687	150	LIQUID	183.75	0.576	34.965	26.356	22.338	22.269	105.928
			267.33	TOTAL	37.969	27.134	22.795	28.297	116.195
				Diff. %	1.84	1.62	0.72	2.39	1.70
694	175	VAPOR	215.71	0.115	8.589	2.600	1.555	12.104	24.849
694	175	LIQUID	171.77	0.540	29.877	24.514	21.705	16.665	92.760
			387.48	TOTAL	38.466	27.114	23.260	28.769	117.609
				Diff. %	0.55	1.69	-1.31	0.76	0.51
734	175	VAPOR	149.59	0.125	5.967	1.708	0.836	10.236	18.746
734	175	LIQUID	177.89	0.556	32.839	25.645	21.925	18.581	98.990
			327.48	TOTAL	38.805	27.353	22.761	28.817	117.737
				Diff. %	-0.32	0.82	0.87	0.60	0.40
791	175	VAPOR	80.92	0.154	3.654	1.329	0.783	6.665	12.430
791	175	LIQUID	186.56	0.559	34.527	25.839	21.921	21.940	104.228
			267.48	TOTAL	38.181	27.167	22.704	28.605	116.657
				Diff. %	1.29	1.50	1.11	1.33	1.31
770	200	VAPOR	214.72	0.138	10.509	3.441	1.561	14.053	29.564
770	200	LIQUID	172.94	0.512	28.235	23.881	21.478	14.902	88.498
			387.66	TOTAL	38.744	27.323	23.039	28.956	118.061
				Diff. %	-0.17	0.93	-0.34	0.12	0.13
845	225	VAPOR	214.30	0.154	11.965	4.735	2.355	13.880	32.935
845	225	LIQUID	173.54	0.488	26.407	22.810	20.977	14.468	84.663
			387.84	TOTAL	38.372	27.545	23.332	28.348	117.597
				Diff. %	0.80	0.13	-1.62	2.21	0.52
925	250	VAPOR	212.29	0.170	13.151	5.605	2.877	14.403	36.036
925	250	LIQUID	175.73	0.469	25.374	22.316	20.886	13.832	82.408
			388.02	TOTAL	38.525	27.921	23.763	28.235	118.444
				Diff. %	0.40	-1.24	-3.50	2.60	-0.20

Table 22 Experimental conditions for the (C₆+C₇+C₈)/water system

Temperature (°F)	Pressure (psia)	Overall Feed Composition			
		n-Hexane	n-Heptane	n-Octane	Water
260	65.7	0.1035	0.1045	0.1084	0.6835
290	99.7	0.1022	0.1041	0.1086	0.6851
330	187.7	0.1011	0.1036	0.1086	0.6867
360	285.7	0.0999	0.1029	0.1084	0.6888
390	392.7	0.0992	0.1025	0.1085	0.6898
420	530.7	0.0982	0.1019	0.1083	0.6916
460	766.7	0.0978	0.1018	0.1086	0.6919

Table 23 Experimental conditions for the (C₇+C₉+C₁₂)/water system

Temperature (°F)	Pressure (psia)	Overall Feed Composition			
		n-Heptane	n-Nonane	n-Dodecane	Water
269	54.7	0.1184	0.0718	0.0481	0.7617
290	88.7	0.1179	0.0722	0.0488	0.7611
330	152.7	0.1168	0.0724	0.0496	0.7612
360	222.7	0.1161	0.0726	0.0504	0.7600
390	319.7	0.1149	0.0724	0.0511	0.7616
420	433.7	0.1144	0.0725	0.0519	0.7612
460	622.7	0.1136	0.0722	0.0526	0.7616
490	815.7	0.1125	0.0715	0.0530	0.7630

Table 24 Experimental conditions for the (C₁₀+C₁₅)/water system

Temperature (°F)	Pressure (psia)	Overall Feed Composition		
		n-Decane	n-Pentadecane	Water
250	30.94	0.016493	0.012096	0.97141
300	71.44	0.016493	0.012096	0.97141
350	146.56	0.015855	0.012313	0.97183
400	273.51	0.015007	0.012548	0.97244
450	472.58	0.013951	0.012783	0.97327
500	760.63	0.012841	0.012892	0.97427

Table 25 Experimental conditions for the (C₁₀+C₁₅+C₂₀)/water system

Temperature (°F)	Pressure (psia)	Overall Feed Composition			
		n-Decane	n-Pentadecane	n-Isosane	Water
250	32.64	0.0069618	0.0072778	0.0092819	0.97688
300	73.76	0.0069618	0.0072778	0.0092819	0.97688
350	149.79	0.0062619	0.0073696	0.0094189	0.97695
400	274.07	0.0050545	0.0075160	0.0096559	0.97777
450	481.50	0.0035054	0.0076509	0.0099333	0.97891
500	748.08	0.0016346	0.0077448	0.0102550	0.98037

Table 26 Comparison of experimental and predicted phase compositions for the (CH₄+CO₂+H₂S)/water systems (Huang et al. 1985)

Component	Feed	Phase Compositions					
		Vapor Phase		Water Rich Liquid		H ₂ S Rich Liquid	
		Exp.	Predict.	Exp.	Predict.	Exp.	Predict.
CASE 1 : T = 100 °F , P = 908 psia							
CH ₄	0.0504	0.32130	0.35727	0.00049	0.00055	0.0653	0.0669
CO ₂	0.0503	0.17390	0.16187	0.00350	0.00349	0.1049	0.0902
H ₂ S	0.3986	0.50280	0.47786	0.02840	0.03020	0.8197	0.7818
WATER	0.5008	0.00214	0.00300	0.96770	0.96889	0.0101	0.0610
CASE 2 : T = 150 °F , P = 1,222 psia							
CH ₄	0.0501	0.18720	0.20151	0.00038	0.00038	0.0580	0.0582
CO ₂	0.0499	0.14840	0.11643	0.00272	0.00272	0.0904	0.0878
H ₂ S	0.4016	0.65570	0.67404	0.03210	0.00105	0.8287	0.8377
WATER	0.4984	0.00866	0.00802	0.96840	0.99584	0.0212	0.0163

APPENDIX II Figures

Figure 1 High-temperature, high-pressure distillation cell

Figure 2 High-temperature, high-pressure, 3-phase separation apparatus

Figure 3 Schematic of the PVT system, pump cell and float piston cell.

Figure 4 Upgraded gas chromatograph sampling device

Figure 5 Integrated Experimental PVT-VLLE setup

Figure 6 Hydrocarbon K^{vo} of C₈/water through C₂₀/water binary systems Figure 7 Hydrocarbon K^{va} of C₈/water through C₂₀/water binary systems

Figure 10 Multi-component Hydrocarbon K^{VO} Figure 11 Multi-component Hydrocarbon K^{Va}

Figure 12 SCN Concentration of the four crude oils

Figure 13 Pseudocomponents' K^V for crude oil A

Figure 14 Pseudocomponents' K^{VO} for crude oil B Figure 15 Pseudocomponents' K^{VO} for crude oil C

Figure 16 Pseudocomponents' K^{VO} for crude oil D Figure 17 Comparison of phase compositions for C_6/H_2O obtained in this work with those reported by Tsonopolous and Wilson (1983)

Figure 18 Three-phase equilibrium pressure for C₈/water system

Figure 19 Experimental and predicted mole fraction of C₆ in vapor phase for the (C₆+C₇+C₈)/water system

Figure 20 Experimental and predicted mole fraction of C₇ in vapor phase for the (C₆+C₇+C₈)/water system

Figure 21 Experimental and predicted mole fraction of C₈ in vapor phase for the (C₆+C₇+C₈)/water system

Figure 22 Experimental and predicted mole fraction of water in vapor phase for the (C₆+C₇+C₈)/water system

Figure 23 Experimental and predicted mole fraction of C7 in vapor phase for the (C7+C9+C12)/water system

Figure 24 Experimental and predicted mole fraction of C9 in vapor phase for the (C7+C9+C12)/water system

Figure 25 Experimental and predicted mole fraction of C₁₂ in vapor phase for the (C₇+C₉+C₁₂)/water system

Figure 26 Experimental and predicted mole fraction of water in vapor phase for the (C₇+C₉+C₁₂)/water system

Figure 27 Experimental and predicted mole fraction of C₁₀ in vapor phase for the (C₁₀+C₁₅)/water system

Figure 28 Experimental and predicted mole fraction of C₁₅ in vapor phase for the (C₁₀+C₁₅)/water system

Figure 29 Experimental and predicted mole fraction of water in vapor phase for the (C₁₀+C₁₅)/water system

Figure 30 Experimental and predicted mole fraction of C₁₀ in vapor phase for the (C₁₀+C₁₅+C₂₀)/water system

Figure 31 Experimental and predicted mole fraction of C₁₅ in vapor phase for the (C₁₀+C₁₅+C₂₀)/water system

Figure 32 Experimental and predicted mole fraction of C₂₀ in vapor phase for the (C₁₀+C₁₅+C₂₀)/water system

Figure 33 Experimental and predicted mole fraction of water in vapor phase for the (C₁₀+C₁₅+C₂₀)/water system

Figure 34 Plot of dg/dx_1 for the n-butane(1)/water(2) system

Figure 35 Plot of Gibbs Energy of Mixing, g , for the n-butane(1)/water(2) system Figure 36 Diagram of k_{ij} vs. $T_{r,ij}$ for CO_2 /water system

Figure 37 Phase diagram for CO₂/water from 25°C to 75°C at CO₂-rich phase Figure 38 Phase diagram for CO₂/water from 25°C to 75°C at water-rich phase

Figure 39 Phase diagram for CO₂/water at 100°C Figure 40 Phase diagram for CO₂/water at 200°C. Experimental data are from Todheide and Franck (1963) and Muller (1988)

Figure 41 Phase diagram for CO₂/water at 250°C. Experimental data is from Todheide and Franck (1963)

ATTACHMENTS - Papers

1. Beladi M. K., M. A. Barrufet, P. T. Eubank and C. H. Wu: *V-L-L Equilibria Data and K-values for Pseudo-components of a Crude Oil*, SPE paper 27873, presented in the SPE Western Regional Meeting in Long Beach, CA (March 23-25, 1994).
2. Eubank, P.T., C. H. Wu, J. F. J. Alvarado, A. Forero and M. K. Beladi: *Measurement and Prediction of Three-Phase Water/Hydrocarbon Equilibria*, *Fluid Phase Equilibria*, **102**, 181-203 (1994).
3. Alvarado, J.F.J., Eubank, P.T.: *Re-examination of Collinearity Tests for Density-Dependent Mixing Rules*, accepted by *Fluid Phase Equilib.*, Aug. 1995.
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