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TRANSPORT AND PHASE EQUILIBRIA PROPERTIES FOR STEAM
FLOODING OF HEAVY OILS

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Transport and Phase Equilibria Properties for Steam Flooding
of Heavy Oils

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**TRANSPORT AND PHASE EQUILIBRIA PROPERTIES FOR STEAM FLOODING OF
HEAVY OILS**

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TRANSPORT AND PHASE EQUILIBRIA PROPERTIES FOR STEAM FLOODING OF HEAVY OILS

ABSTRACT

Hydrocarbon/water and CO₂ 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 design and improve oil recovery processes such as steam, hot water, or CO₂/steam combinations of flooding techniques typically used for heavy oils.

We propose an interdisciplinary research program to quantify transport, PVT, and equilibria properties of selected oil/ 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.

The objectives of this research include experimental determination and rigorous modeling and computation of phase equilibria, volumetric, and transport properties of hydrocarbon/CO₂/water mixtures at pressures and temperatures typical of steam injection processes for thermal recovery of heavy oils.

The project is divided in an experimental and a theoretical part. For the experimental part, we measured bubble points and pressure-volume relations for four different oil samples. For the theoretical part a computer program to implement the technique to determine phase equilibria known as the area method was developed. Calculations involving several binary pairs have been performed. The results are presented here.

TRANSPORT AND PHASE EQUILIBRIA PROPERTIES FOR STEAM FLOODING OF HEAVY OILS

STATEMENT OF WORK (SOW)

Under this Statement of Work (SOW), Dr. Jorge Gabitto from the Chemical Engineering Department at Prairie View A&M University (PVAMU), Dr. Maria Barrufet from the Petroleum Engineering Department at Texas A&M University (TAMU) and Dr. Rebecca Bryant from Bio-Engineering Inc. (B-E) will conduct research and training in the area of transport and thermodynamic properties determination for heavy oils. A research project is proposed to develop theoretical models, develop computer algorithms, and measure experimentally transport and thermodynamic properties of heavy oils.

Training of graduate and undergraduate students will be part of the project. Technology transfer of the results generated by the project will be achieved through BDM PT and publications in referred journals.

Dr. Gabitto will act as coordinator of the research team. Drs. Barrufet and Bryant will act as subcontractors to Dr. Gabitto.

TECHNICAL DESCRIPTION

INTRODUCTION

Water and CO₂ are used extensively in enhanced oil recovery processes such as steam flooding and CO₂ flooding. These methods are the most important thermal/miscible oil recovery processes (Wu, 1977; Harding et al.; 1983; Leung, 1983; Hornbrook et al., 1991). Steam and/or CO₂ are injected into reservoirs where hydrocarbons and brines coexist. Intermolecular interactions of CO₂ with water and hydrocarbons will affect the species partitioning into the coexisting equilibrium phases, i.e., the hydrocarbon K-values (K_i's) will likely be different from those obtained at the same pressure and temperature, but in the absence of water or of CO₂.

The effect of water on phase equilibrium has been recognized by many investigators. It has not been taken into account in most engineering calculations due to lack of sufficient experimental data. This omission can result in serious errors in the design and simulation of the recovery and separation processes.

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 and two liquid phases, hydrocarbon and water. While steam distillation 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 using CO₂ as a displacing medium, the aqueous effects on the hydrocarbon/ CO₂ phase behavior have not been fully investigated. 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. In Hornbrook et al., 1991, reported the use of CO₂ in steam flooding shows many beneficial effects on oil recovery and economics.

The solubility of water in a hydrocarbon-rich liquid phase at high pressure and temperature can be as high as 50 %. 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.

Numerous K-value equations exist for hydrocarbons, but these are not appropriate when CO₂ and water are present. Rigorous methods are available to estimate the K-values from EOS; however, the conventional use of EOS produce large deviations between measured and computed solubilities of CO₂ and hydrocarbons in water. Several procedures can improve the computation of both the densities of the coexisting equilibrium phases and their compositions. These EOS optimization methods involve use of different mixing rules for the EOS parameters (Wong Sandler, 1992; Eubank et al., 1995), volume translation for better density predictions (Peneloux et al. 1982), etc.

Some of the material presented in the previous semiannual report is also presented here for the sake of completeness.

THEORETICAL PART

INTRODUCTION

Phase equilibria of fluid mixtures are important to process and oil recovery industries. They are important to operate and model satisfactorily equilibrium based separation processes and for accurate prediction of water, oil and gas mixtures under reservoir conditions. In reservoir simulation one needs accurate prediction of the correct number and equilibrium compositions of the different phases present in the reservoir. Binary mixtures consisting of, for example, Carbon Dioxide (CO₂)/hydrocarbon and CO₂/alcohol, have received increased attention as solvent/cosolvent pairs in the supercritical extraction of biomaterials, coal products and are also important to natural gas and petroleum processing (see for example, Prausnitz et al., 1986; Sadus, 1992). In the past CO₂/hydrocarbon mixtures have been investigated in detail using equations of state and experiments (see for example, Graboski and Daubert, 1978; Kato et al., 1981; Lin, 1984; Gasem et al., 1993).

Phase equilibrium calculations are usually performed by means of either the activity coefficient methods or equations of state (EOS). In the so-called activity-fugacity approach, the activity coefficient represents the non-ideality of the liquid phase whereas fugacity coefficient is used to represent that of the vapor phase. The application of the activity-fugacity approach to high-pressure systems containing supercritical components is impossible unless hypothetical reference states are assumed (Anderko, 1990).

In the equation of state method, a single equation is used to represent all fluid phases. Generally, this approach is based on the van der Waals type EOS, which accounts for the effects of both the attractive and the repulsive forces in mixtures. Several two-parameter van der Waals type equations of state are now available. The most commonly used EOS in industrial applications are Redlich-Kwong (RK), (Redlich and Kwong, 1949), a modified form of RK known as Soave-Redlich-Kwong (SRK), (Soave, 1972), Peng-Robinson (PR), (Peng and Robinson, 1976). The phase equilibrium is calculated for example, using a well-defined EOS and mixing rules (MR), such as the van der Waals and one-fluid mixing rules (VDW MR). The material balance equations and equality of chemical potentials are then used to calculate the phase equilibrium compositions. Using this approach one can determine phase equilibria directly using flash equilibrium calculations. However, it has been realized in the past that the equality of chemical potentials is a necessary, but not a sufficient condition for minimizing the Gibbs energy of mixing of the entire system (Null, 1970; Eubank et al., (1992)). One must, therefore, use means of minimizing the Gibbs energy of mixing such that in a phase equilibrium calculation the Gibbs energy of mixing should be a global minimum.

It may be noted that the EOS/MR model may be analytical, but the calculation of phase equilibria is always numerical, and the implementation of the numerical scheme is based on the particular numerical technique used. Although, the final results can be no better than the model itself, a numerical method that fails to provide a sufficient criteria for Gibbs minimization can yield incorrect results. This situation does not imply fault of the theoretical model.

A recently proposed approach for computing phase equilibria in binary mixtures has been found to provide the necessary and the sufficient conditions for *Gibbs minimization* of the entire system, Eubank et al. (1992). In this approach, known as the *area method*, two compositions in the region of the mixture are found. The condition that should be satisfied is that the difference between the absolute area under the straight line connecting these two compositions and the absolute area of the Gibbs energy curve integrated between these same compositions should be positive and a maximum (Figure 1). This condition implies that the two compositions represent the equilibrium compositions for the mixture. When the area is negative in the entire composition range, there exists only a single phase. This method is stable because it does not use derivatives, but rather integrates under the Gibbs energy surface. It can predict phase equilibria close to the critical locus of the mixture reliably where, for some cases, most of the iterative methods may become unreliable Eubank et al. (1992). In their study, Eubank et al. (1992), tested the area method by applying it to a very few selected mixtures.

Equation of State and Mixing Rules

We consider a binary fluid mixture consisting of components 1 and 2. Thermodynamic properties of this mixture are described by the following two parameter SRK EOS (Soave, 1972),

$$P = RT / (V - b_m) - a_m / (V(V + b_m)) \quad (1),$$

where, P, T, V and R are pressure, absolute temperature, molar volume and ideal gas constant, respectively. Here a_m is the energy parameter and b_m is the excluded volume parameter. In the present work, these parameters are represented by the simple Van der Waals one-fluid mixing rules (VDW MR),

$$a_m = \sum_i \sum_j X_i X_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad (2), \text{ and}$$

$$b_m = \sum_i X_i b_i \quad (3),$$

with the pure component parameters given by (Soave, 1972),

$$a_i = \alpha_{ai} R^2 (T_{ci}^2 / P_{ci}) \left[1 + (0.48 + 1.574\omega_i - 0.176\omega_i^2) (1 - T_{ri}^{0.5}) \right] \quad (4), \text{ and}$$

$$b_i = \alpha_{bi} RT_{ci} / P_{ci} \quad (5),$$

where T_{ci} and P_{ci} are critical temperature and critical pressure of the pure components, respectively, and $T_{ri} = T / T_{ci}$. The temperature dependence of the constant a_i has been given by eqn.(4) in terms of ω_i . Both a_i and b_i are determined by the properties of the pure fluids. For the SRK EOS, the values of α_{ai} and α_{bi} parameters are $\alpha_{ai} = 0.42748$ and $\alpha_{bi} = 0.08664$. The acentric factor ω_i is specific to the particular fluid. k_{ij} is a binary interaction parameter characteristic of each binary pair. Here, k_{ij} is assumed to be an adjustable parameter. Using only two parameters in addition to the acentric factor ω , the SRK EOS is known to describe thermodynamic properties of the pure fluids reasonably well (Anderko, 1990).

Application of the Area Method

In the *area method*, area (A) is confined between the tie lines and the nonuniformly continuous curve on the Gibbs energy of mixing $\phi = \Delta G_m / RT$ versus X curve. This area must be positive in its absolute value and corresponds to the equilibrium compositions X_I and X_{II} . It has been defined as that area which lies between the trapezoid $cdef$ and the integrated Gibbs energy curve from X_I to X_{II} (shown in Figure 1). Mathematically, if the following equation holds,

$$A(X_I, X_2) = \left| (\phi(X_2) + \phi(X_I))(X_2 - X_I)/2 - \int_{X_I}^{X_2} \phi(X) dX \right| \quad (6), \text{ then}$$

$$A(X_p, X_H) = \max A(X_I, X_2) \text{ subject to } A > 0.$$

Note that (X_p, X_H) represent phase equilibrium compositions of liquid and vapor phases of the mixture only if the area is positive and maximum Eubank et al. (1992).

Calculation of phase equilibria using the *area method* requires acknowledgement of the Gibbs energy of mixing ϕ for a given EOS. In this approach, no derivatives of the Gibbs energy are needed to calculate the vapor/liquid phase equilibria. Here, we present an explicit form of the Gibbs energy of mixing for the SRK EOS. In general, ϕ can be expressed in terms of activity coefficient γ_i of the components (Reid et al., 1987),

$$\phi = X_1 \ln X_1 \gamma_1 + X_2 \ln X_2 \gamma_2 \quad (7)$$

In terms of compositions, pressure, volume and temperature of the mixture, eqn.(7) can be further written as,

$$\phi = X_1 \ln X_1 + X_2 \ln X_2 + \frac{1}{RT} \int_0^P V dP - \frac{X_1}{RT} \int_0^P V_1 dP - \frac{X_2}{RT} \int_0^P V_2 dP \quad (8)$$

Using the simple SRK EOS, eqn.(8) can be solved to yield an analytical expression for the Gibbs energy given as,

$$\begin{aligned} \phi_{SRK} = & X_1 \ln X_1 + X_2 \ln X_2 + \frac{PV_m}{RT} - \ln(V_m - b_m) - \frac{a_m}{RTb_m} \ln((V_m + b_m)/V_m) \\ & - X_1 \left[\frac{PV_1}{RT} - \ln(V_1 - b_1) - \frac{a_1}{RTb_1} \ln((V_1 + b_1)/V_1) \right] \\ & - X_2 \left[\frac{PV_2}{RT} - \ln(V_2 - b_2) - \frac{a_2}{RTb_2} \ln((V_2 + b_2)/V_2) \right] \end{aligned} \quad (9)$$

The important equations related to the calculations of phase equilibria and critical properties using SRK EOS are given in Appendix A. Similar expression for the Gibbs energy of mixing could be obtained for the simpler, but less reliable EOS, known as the Redlich-Kwong (RK) EOS, which has also been investigated. It should be noted that the *area method* offers several advantages over the previously used numerical methods in phase equilibrium calculations:

- (a) it avoids the need of any starting values,
- (b) it does not involve the derivatives of the free energy; and

(c) it is stable and more accurate than the previously available methods for calculating the phase behavior, in particular, very close to the critical loci of the mixtures Eubank *et al.* (1992).

RESULTS AND DISCUSSION

In this section, we first focus on the CO₂/hydrocarbon mixtures. In recent years, extensive experimental data have become available for such mixtures against which the accuracy of the model can be tested reliably. Critical temperature, critical pressure and acentric factor of the pure fluids of the mixtures investigated here are taken from Reid *et al.*, (1987). They are given in Table 1. The binary interaction parameter k_{12} for each mixture was determined by fitting isothermal vapor/liquid equilibrium data at a selected condition of the low pressure and low temperature of each mixture using the following objective function

$$\Delta X_1 = \frac{1}{n} \sum_{i=1}^n \left[ABS(X_{1,exp} - X_{1,cal}) \times 100 / X_{1,exp} \right] \quad (10)$$

where $X_{1,exp}$ and $X_{1,cal}$ represent, respectively, the experimental and calculated values of the liquid phase compositions at equilibrium, and n being the number of data points. In the present calculations, $n=1$. More explicitly, the error in mole fraction of the liquid phase is minimized ($\Delta X_1 < 10^{-4}$) by setting temperature and pressure, and evaluating mole fraction of the vapor phase. To check the accuracy in the composition of the vapor phase, similar function was defined for the vapor phase composition at equilibrium,

$$\Delta Y_1 = \frac{1}{n} \sum_{i=1}^n \left[ABS(Y_{1,exp} - Y_{1,cal}) \times 100 / Y_{1,exp} \right] \quad (11),$$

where $Y_{1,exp}$ and $Y_{1,cal}$ are, respectively, the experimental and calculated values of the vapor phase compositions at equilibrium.

The determined values of k_{12} together with the fitted conditions for several mixtures are contained in Table 2. In order to examine the accuracy of the SRK EOS/VDW MR predictions, these values of k_{12} are then used to generate phase equilibrium results at all other pressures and temperatures.

We first report results for a binary mixture of CO₂/Decane using the SRK EOS/VDW MR. Though, this system was investigated previously using the *area method* but with the RK EOS. In those studies only a few selected temperature and pressure conditions were considered (Eubank *et al.*, 1992). It is well-known that the RK EOS is less accurate than the SRK EOS in representing thermodynamic properties of the pure fluids and fluid mixtures. Therefore, we examine the accuracy of the SRK EOS/VDW MR model in detail in predicting the phase behavior of CO₂/Decane system over a range of temperature and pressure.

Figures 2a-2d show comparisons between calculated and experimental results at temperatures T=463K, 477K, 543K and 584K, respectively. These temperatures correspond to the supercritical conditions for CO₂ while the subcritical conditions for

Decane. In general, SRK EOS/VDW MR predictions are seen to be in good agreement with experimental data. Only at the highest temperature $T=584\text{K}$ (Figure 2d) the agreement is not as good as at lower temperatures, in explaining the liquid phase compositions at relatively high pressures ($P>30\text{bar}$). This may be due to the reason that the VDW MR may not be adequate to properly represent the temperature and density dependences of the binary interaction parameter k_{12} . Also shown in Figures 2a-2d are the results obtained from the RK EOS/VDW MR. In this latter case, calculated results in the liquid phase are seen to agree well with experimental data. However, a severe disagreement between the RK EOS/VDW MR and experiment is seen in the vapor phase. These comparisons show that the results based on SRK EOS/VDW MR are in better agreement with experimental data than those based on RK EOS/VDW MR.

The above comparisons suggest that the *area method* along with the SRK EOS/VDW MR is a suitable model to predict phase equilibria in CO_2 /hydrocarbon mixtures reliably. Therefore, we extend our calculations to other mixtures, namely; CO_2 /Butane, CO_2 /Pentane, CO_2 /Cyclopentane, CO_2 /Cyclohexane, CO_2 /Hexane, CO_2 /Octane, CO_2 /Hexadecane, CO_2 /Docosane and CO_2 /Dotriacontane, for which accurate experimental data are available.

Figures 3a and 3b show results for the vapor/liquid phase equilibria in CO_2 /Butane. In Figure 3a, phase equilibria at a subcritical isotherm (both components being under subcritical condition of the temperature) are shown, while in Figure 3b, the first component (CO_2) is under supercritical condition. In both cases the SRK EOS/VDW MR predictions agree well with experimental results. Similar results are obtained for CO_2 /Pentane as shown in Figures 4a ($T=312\text{K}$) and 4b ($T=394\text{K}$), all in the supercritical conditions of CO_2 . However, a slight discrepancy between calculated and experimental results are seen in Figure 4b in the vapor phase composition at $T=394\text{K}$ and $P>20\text{bar}$.

In order to further test the accuracy of the SRK EOS/VDW MR model using the area method, Figures 5a and 5b show an extensive comparison between calculated and experimental results for the vapor/liquid phase equilibria in CO_2 /Cyclopentane at very high temperatures, $T=375\text{K}$ and 478K . Both isotherms are in the supercritical condition of CO_2 . These figures show that at relatively low pressures ($P<60\text{bar}$) SRK EOS/VDW MR predictions are in good agreement with experimental results. However, such a good agreement between calculated and experimental results does not extend beyond $P=60\text{bar}$ and close to the critical loci of the mixtures. Nevertheless, calculated results are still consistent with experimental data. It appears that the value of k_{12} ($= 0.16$) of Table 2 (determined at low temperature $T=277\text{K}$ and low pressure $P=2\text{bar}$) is inadequate to represent the phase diagram of this system at high pressures and temperatures of the mixtures. Therefore, we adjusted k_{12} at a relatively high pressure $P=28\text{bar}$ keeping the same low temperature $T=277\text{K}$. A slightly lower value of $k_{12}=0.13$ has been obtained. As can be seen in both Figures 5a and 5b, this results into a significant improvement of the SRK EOS/VDW MR predictions when compared with experimental data at all pressures and temperatures. However, close to the critical loci of the mixtures the new value of k_{12} is still insufficient in explaining experimental compositions, especially at the highest temperature $T=478\text{K}$. In order to further improve the predictions at $T=478\text{K}$ and close to

the critical point, we refitted k_{12} at a sufficiently high pressure $P=81\text{bar}$ (close to the critical pressure of the mixture) to reproduce the liquid phase composition of the mixture. This gave a slightly higher value of $k_{12}=0.18$, but the vapor phase compositions near the critical locus of the mixture could not be reproduced very well. These comparisons suggest that k_{12} may be a function of both the temperature and pressure and that the SRK EOS/VDW MR may not be adequate enough to describe such a mixture close to its critical locus.

Figures 6a and 6b illustrate phase equilibrium results for a more complex system, $\text{CO}_2/\text{Cyclohexane}$, at $T=366.5\text{K}$ and 410.9K , respectively. As with the $\text{CO}_2/\text{Cyclopentane}$, SRK EOS/VDW MR predictions for the vapor/liquid phase equilibria agree well with experimental results at the lower temperature ($T=366.5\text{K}$) and low pressures. Close to the critical loci those predictions are found to deviate significantly from the experimental results, in particular at $T=410.9\text{K}$.

Similar comparisons are presented in Figures 7a-7c for $\text{CO}_2/\text{Hexane}$ and in Figures 8a and 8b for $\text{CO}_2/\text{Hexadecane}$ where CO_2 is again in its supercritical condition. In the case of $\text{CO}_2/\text{Hexane}$ the temperature range is relatively lower than that of $\text{CO}_2/\text{Hexadecane}$. Comparisons between SRK EOS/VDW MR and experiment are very good for $\text{CO}_2/\text{Hexane}$ at all temperatures (Figures 7a-7c), while they are not as good for $\text{CO}_2/\text{Hexadecane}$, especially at the very high temperature, $T=664\text{K}$ (Figure 8b).

Figures 9 and 10 show comparisons between calculated and experimental results for more asymmetric mixtures $\text{CO}_2/\text{Docosane}$ and $\text{CO}_2/\text{Dotriacontane}$, containing heavy hydrocarbons. Only the liquid phase composition is compared, for the the vapor phase composition is unavailable from the experiment and is set to unity (as also done in the experiment of Fall and Luks (1984)). Even in these mixtures, the area method based SRK EOS/VDW MR predictions are in very good agreement with experimental data, away from the critical loci of the mixtures. Again, a discrepancy between experiment and prediction can be seen close to the critical loci.

To check the accuracy of the SRK EOS/VDW MR for the less complex mixtures, calculations were also performed for the vapor/liquid phase equilibria of $\text{CH}_4/\text{Propane}$ and $\text{CH}_4/\text{Pentane}$ at several temperatures and pressures. Sample results are presented at a single temperature in Figure 11 for $\text{CH}_4/\text{Propane}$ ($T=278\text{K}$) and in Figure 12 for $\text{CH}_4/\text{Pentane}$ ($T=228\text{K}$). In these mixtures the first component (CH_4) is in its supercritical condition, while the second component is in its subcritical condition. In general, the SRK EOS/VDW MR has been able to describe experimental data over a range of pressure and temperature adequately.

In an effort to examine the predictive power of the present approach in describing nonpolar/alcohol systems, we extended our calculations to investigate mixtures consisting of $\text{CO}_2/\text{alcohol}$. Comparisons of the phase equilibria for two systems $\text{CO}_2/\text{Ethanol}$ and $\text{CO}_2/\text{Linalool}$ are presented in Figures 13 and 14, respectively, as examples. As can be seen, SRK EOS/VDW MR predictions are seen to be in very good agreement with

experimental results for CO₂/Ethanol, while they are not as good for CO₂/Linalool, again close to the critical locus of the mixture.

Since the numerical accuracy of the *area method* over the existing numerical methods for calculating vapor/liquid phase equilibria in binary fluid mixtures has been demonstrated before (Eubank et al., 1992), we did not present here such comparisons again. However, in order to emphasize the importance of the *area method*, Figure 15 presents sample results for compositions of the liquid and vapor phases of a mixture, CO₂/Propane, using two different numerical methods: *fugacity method* (FM) and *area method* (AM).

In the *fugacity method*, vapor/liquid phase equilibria are determined by equating the fugacities of the liquid and the vapor phases simultaneously. This method requires appropriate starting values of the compositions to solve for the equilibrium compositions of the vapor and liquid phases numerically. FM is reliable at conditions away from the critical temperature and critical pressure of the mixtures. However, in the vicinity of the critical point of the mixtures, it may become unreliable for some mixtures, even for relatively less complex mixtures such as those investigated in this work. This is demonstrated in Figure 15. Unlike the calculations presented above, where k_{12} was determined at relatively low temperatures and pressures, in this particular example, k_{12} has been determined at the temperature, $T=311\text{K}$ and the pressure, $P=54.861\text{bar}$, leading $k_{12}=0.14$. This k_{12} value is able to describe the vapor/liquid phase equilibria of CO₂/Propane mixture at this temperature within 0.7% of the average absolute deviation in liquid composition and 1.2% of that in the vapor composition. As can be seen from Figure 15, FM is less reliable than AM in predicting the vapor/liquid phase equilibria in the vicinity of the critical point of the mixture, beyond $P=50\text{bar}$. On the other hand, AM is essentially better in describing the vapor/liquid phase equilibria in CO₂/Propane, even close to the critical locus of the mixture. Similar results were obtained at higher temperatures, therefore, those results are not presented here.

Similar to CO₂/Propane, AM and FM results for the phase equilibria are compared in Tables 3 and 4, respectively, for CO₂/Octane and CO₂/Linalool, for which experimental results for the liquid and vapor compositions exist very close to the critical loci. In the former case, FM is unable to predict the phase separation at $T=313\text{K}$ and $P=75.5\text{bar}$, and at $T=348\text{K}$ and 113.5bar , and leads to the trivial solutions of the compositions. On the other hand, AM is able to describe that phase separation at both conditions. Similar observation can be made in Table 4 for CO₂/Linalool, at the lower temperature $T=313\text{K}$ and $P=79.9\text{bar}$. At the higher temperature, $T=333\text{K}$, however, no difference between AM and FM can be seen. This may be due to the reason that the calculations are performed at the experimental points only away from the critical locus of the mixture, and that the experimental results close to the critical locus are unavailable.

CONCLUSIONS

Our results show that the *area method* based SRK EOS/VDW MR calculations can describe phase diagrams of several mixtures consisting of CO₂ (or CH₄) and hydrocarbon systems reliably even close to the critical loci of the mixtures. In these

calculations, only a single binary interaction parameter has been adjusted at a low temperature and low pressure. Comparisons of theoretical results with experimental data for the vapor/liquid phase equilibria of several mixtures, namely, CO₂/Propane, CO₂/Butane, CO₂/Cyclopentane, CO₂/Pentane, CO₂/Cyclohexane, CO₂/Hexane, CO₂/Octane, CO₂/Decane, CO₂/Hexadecane, CO₂/Docosane, CO₂/Dotriacontane, CH₄/Propane and CH₄/Pentane show a very good performance of the SRK EOS/VDW MR model. Similar results could also be obtained for some CO₂/alcohol systems, for example, CO₂/Ethanol and CO₂/Linalool. However, discrepancies between theory and experiment are also seen for some mixtures, such as CO₂/Cyclopentane and CO₂/Cyclohexane, and more asymmetric mixtures CO₂/Docosane, CO₂/Dotriacontane, and CO₂/Linalool, especially at high temperatures and pressures close to the critical loci of the mixtures. Our results for CO₂/Propane, CO₂/Octane and CO₂/Linalool show that AM is more reliable than the FM for predicting the phase separation close to the critical loci of the mixtures. Since the *area method* of calculating phase equilibria is sufficiently accurate, the remaining discrepancies between theory and experiment of the mixtures can be attributed to: (1) the inadequacy of the SRK EOS/VDW MR model close to the critical loci of the mixtures, and (2) the inherent error in the experimental data.

It may be possible to minimize the difference between calculated and experimental results for some systems using the conventional mixing rules containing more than one unlike parameters, which can be functions of temperature, density and compositions (Gasem *et al.*, 1993). However, such conventional mixing rules usually become unreliable for the predictions of phase equilibria under the conditions not included in the fit. Moreover, even if the numerical method is accurate, the accuracy of the EOS predictions cannot be tested unambiguously. Since we are interested more in predictions rather than correlations of the phase equilibria in mixtures, in our future studies we propose to investigate more complex mixtures at very high temperatures and pressures by developing theoretically based mixing rules and more accurate equations of state. Moreover, we will extend this study to ternary and multicomponent fluid mixtures so that the model can be integrated into one of our reservoir simulators.

In order to check the efficiency of the two numerical methods, we cite here the CPU time (central processing unit time at a HP700 series workstation) required for a typical run of the phase equilibrium calculation, say for CO₂/Dotriacontane at T=348K and P=42.25bar. In FM the CPU time is 0.03 seconds, while in AM it is 0.08 seconds. Both methods result into the liquid composition $X_1=0.3992$ and the vapor composition $Y_1=1.0$ (with the accuracy up to four significant figures). However, if one desires the accuracy of compositions up to three significant figures only this CPU time in AM can be lowered significantly (0.04 seconds). It can be further lowered (0.02 seconds) if the accuracy required in compositions is up to two significant figures only.

APPENDIX A

Derivatives of the Gibbs energy of mixing for SRK EOS

Using the SRK EOS (eq.(10)) analytical expressions for the derivatives of the Gibbs energy of mixing are given below.

$$\frac{PV_1}{RT} = \frac{V_1}{V_1 - b_1} - \frac{a_1}{RT(V_1 + b_1)} \quad (A1)$$

$$\frac{PV_2}{RT} = \frac{V_2}{V_2 - b_2} - \frac{a_2}{RT(V_2 + b_2)} \quad (A2)$$

and the derivatives of a_m and b_m with respect to X_i are given by

$$a'_m = 2X_1a_1 - 2X_2a_2 + 2(a_1a_2)^{0.5}(1 - k_{12})(X_2 - X_1) \quad (A3)$$

$$a''_m = 2a_1 + 2a_2 - 4(a_1a_2)^{0.5}(1 - k_{12}) \quad (A4)$$

$$a'''_m = 0 \quad (A5)$$

$$b'_m = b_1 - b_2 \quad (A6)$$

$$b''_m = 0 \quad (A7)$$

$$b'''_m = 0 \quad (A8)$$

In the above equations, 1 and 2 denote mixture components and k_{12} is a binary interaction parameter.

First derivative of the Gibbs energy:

$$\begin{aligned} \left[\frac{\partial \phi_{SRK}}{\partial X_1} \right] = & \ln \left(\frac{X_1}{X_2} \right) + \left(\frac{b'_m}{b_m} \right) \left(\frac{PV_m}{RT} - 1 \right) + \left(\frac{a_m b'_m - b'_m a_m}{RT b_m^2} \right) \ln \left(\frac{V_m + b_m}{V_m} \right) \\ & - \left\{ \frac{PV_1}{RT} - \ln(V_1 - b_1) - \frac{a_1}{b_1 RT} \ln \left(\frac{V_1 + b_1}{V_1} \right) \right\} \\ & + \left\{ \frac{PV_2}{RT} - \ln(V_2 - b_2) - \frac{a_2}{b_2 RT} \ln \left(\frac{V_2 + b_2}{V_2} \right) \right\} \end{aligned} \quad (A9)$$

Second derivative of the Gibbs energy:

$$\left[\frac{\partial^2 \phi_{SRK}}{\partial X_1^2} \right] = \frac{1}{X_1 X_2} + \frac{PV_m' b_m'}{b_m RT} + \left(\frac{PV_m}{RT} - 1 \right) \left(\frac{b_m^* b_m - b_m^2}{b_m^2} \right) + \left(\frac{a_m b_m^* - b_m a_m'}{RT b_m^2} \right) \ln \left(\frac{V_m + b_m}{V_m} \right) \quad (A10)$$

$$+ \left(\frac{b_m a_m' b_m' - a_m b_m'^2}{b_m^3 RT} \right) \left[2 \ln \left(\frac{V_m + b_m}{V_m} \right) - \frac{b_m}{V_m + b_m} \right] + \frac{V_m' (b_m a_m' - a_m b_m')}{V_m b_m RT (V_m + b_m)}$$

Third derivative of the Gibbs energy:

$$\left[\frac{\partial^3 \phi_{SRK}}{\partial X_1^3} \right] = \left[\frac{(X_1 - X_2)}{(X_1 X_2)^2} \right] + \left(\frac{P}{RT b_m^2} \right) \left[2 V_m' (b_m b_m^* - b_m'^2) + b_m b_m' V_m' \right]$$

$$+ \left(\frac{PV_m}{RT} - 1 \right) \left[\frac{b_m'}{b_m^2} \left(\frac{2 b_m'^2}{b_m} - 3 b_m' \right) + \frac{b_m''}{b_m} \right] + \left[\frac{1}{b_m^2 RT} \ln \left(\frac{V_m + b_m}{V_m} \right) \right]$$

$$\left[3 a_m'' b_m' + 3 a_m' b_m'' + \frac{6 a_m b_m'^3}{b_m^2} - \frac{6 a_m' b_m'^2}{b_m} - \frac{6 a_m b_m' b_m''}{b_m} + a_m b_m''' - b_m a_m''' \right]$$

$$- \frac{1}{b_m RT (V_m + b_m)} \left[a_m'' b_m' + a_m' b_m'' + \frac{3 a_m b_m'^3}{b_m^2} - \frac{3 a_m' b_m'^2}{b_m} - \frac{2 a_m b_m' b_m''}{b_m} \right]$$

$$+ \left(\frac{a_m b_m''}{b_m} - a_m'' \right) \left[\frac{V_m'}{b_m RT (V_m + b_m)} + \frac{b_m'}{b_m RT (V_m + b_m)} - \frac{V_m'}{V_m RT (V_m + b_m)} \right]$$

$$- \left(\frac{a_m b_m'}{b_m} - a_m' \right) \left[\frac{V_m'}{b_m V_m RT} \right] + \left(a_m' b_m' - \frac{a_m b_m'^2}{b_m} \right) \left[\frac{2 V_m^2 V_m' + 2 V_m^2 b_m'}{b_m^2 RT (V_m + b_m)} - \frac{2 V_m'}{b_m^2 V_m RT} \right] \quad (A11)$$

$$- \left(\frac{b_m'}{b_m^2 RT (V_m + b_m)} \right) + \frac{(V_m' + b_m')}{b_m^2 RT (V_m + b_m)^2} + \left(a_m' - \frac{a_m b_m'}{b_m} \right) \left(\frac{1}{V_m RT (V_m + b_m)} \right)$$

$$\left[V_m' - \frac{V_m'^2}{(V_m + b_m)} - \frac{V_m' b_m'}{(V_m + b_m)} - \frac{V_m'^2}{V_m (V_m + b_m)} - \frac{V_m' b_m'}{b_m (V_m + b_m)} \right]$$

APPENDIX B

The Redlich-Kwong equation of state (*RK EOS*) is given by

$$P = \frac{RT}{V - b_m} - \frac{a_m}{T^{0.5} V (V + b_m)}$$

The Gibbs energy of mixing for a binary mixture using the *RK EOS* can be expressed as

$$\phi_{RK} = X_1 \ln X_1 + X_2 \ln X_2 + \frac{PV_m}{RT} - \ln(V_m - b_m) - \frac{a_m}{RT^{1.5} b_m} \ln \left(\frac{V_m + b_m}{V_m} \right)$$

$$- X_1 \left[\frac{PV_1}{RT} - \ln(V_1 - b_1) - \frac{a_1}{RT^{1.5} b_1} \ln \left(\frac{V_1 + b_1}{V_1} \right) \right] - X_2 \left[\frac{PV_2}{RT} - \ln(V_2 - b_2) - \frac{a_2}{RT^{1.5} b_2} \ln \left(\frac{V_2 + b_2}{V_2} \right) \right]$$

Table 1. Parameters of pure fluids (Reid *et al.*, 1987)

System	T_c (K)	P_c (bar)	ω
Carbon Dioxide	304.2	73.98	0.225
Methane	190.6	46.00	0.008
Propane	369.8	42.50	0.152
Butane	425.2	37.96	0.193
Cyclopentane	511.6	45.09	0.192
Pentane	469.6	33.64	0.251
Cyclohexane	553.4	40.73	0.213
Hexane	507.5	30.12	0.299
Octane	568.8	24.98	0.399
Decane	617.6	20.90	0.49
Hexadecane	717.0	14.18	0.74
Docosane *	785.0	9.44	0.952
Dotriacontane *	847.9	5.29	1.295
Ethanol	516.2	63.83	0.635
Linalool	630.5	24.20	0.748

* Data from Gasem *et al.* (1993).

Table 2. Binary interaction parameters

Mixtures	k_{12} (SRK)	k_{12} (RK)
CO ₂ /Propane	0.140 (T=311K, P=55bar)	-
CO ₂ /Butane	0.134 (T=278K, P=3bar)	-
CO ₂ /Cyclopentane	0.160 (T=277K, P=2bar)	-
CO ₂ /Pentane	0.120 (T=253K, P=30bar)	-
CO ₂ /Cyclohexane	0.110 (T=367K, P=18bar)	-
CO ₂ /Hexane	0.121 (T=313K, P=8bar)	-
CO ₂ /Octane	0.159 (T=313K, P=15bar)	-
CO ₂ /Decane	0.140 (T=463K, P=20bar)	0.095
CO ₂ /Hexadecane	0.085 (T=190K, P=20bar)	-
CO ₂ /Docosane	0.114 (T=323K, P=14bar)	-
Methane/Propane	0	-
Methane/Pentane	0	-

Table 3. Vapor/liquid phase equilibria of CO₂/Octane from AM and FM (experimental data are from Weng and Lee, 1992).

P (bar)	Exp.	x_i (Liq.) Calc.	Calc.	Exp.	y_i (Vapor) Calc.	Calc.
		<i>FM</i>	<i>AM</i> T=313K		<i>FM</i>	<i>AM</i>
15.0	0.1433	0.1433	0.1433	0.9947	0.9961	0.9961
30.0	0.2910	0.2788	0.2788	0.9960	0.9971	0.9971
45.0	0.4550	0.4099	0.4099	0.9956	0.9969	0.9969
58.9	0.6160	0.5338	0.5338	0.9953	0.9960	0.9960
65.0	0.7110	0.5927	0.5927	0.9952	0.9952	0.9952
75.5	0.8900	0.9822	0.7250	0.9920	0.9829	0.9913
			T=348K			
20.0	0.1450	0.1412	0.1412	0.9860	0.9861	0.9861
40.0	0.2750	0.2719	0.2719	0.9891	0.9895	0.9895
52.6	0.3600	0.3492	0.3492	0.9898	0.9895	0.9895
71.0	0.4855	0.4568	0.4568	0.9874	0.9879	0.9879
91.0	0.6310	0.5693	0.5693	0.9824	0.9832	0.9832
97.0	0.6770	0.6028	0.6028	0.9786	0.9808	0.9808
108.0	0.7540	0.6650	0.6650	0.9620	0.9736	0.9736
113.5	0.8130	0.9421	0.6971	0.9581	0.9421	0.9675

EXPERIMENTAL PART

INTRODUCTION.

A good understanding of volumetric and phase behavior of petroleum reservoir fluids is required for accurate prediction of reservoir performance and production forecasting. Phase behavior data dictates reservoir development strategies for ordinary gas drives to more technologically intensive carbon dioxide or steam flooding projects (Wu, 1977, Harding et al., 1983). Phase behavior data have been obtained traditionally by experimental testing or by use of generalized correlations. Of these two methods the later is often favored by researchers because it is easier to use and less expensive; however, predictions using general correlations can be highly inaccurate mainly due to varying chemical and physical properties of reservoir fluids from one reservoir to another.

Highlighting the importance of phase behavior, researchers insist on obtaining truly representative reservoir fluids samples for experimental analysis. Similar efforts have been done for accurate prediction of phase compositions especially for mixtures of hydrocarbons and water and/or CO₂ (McKetta and Katz, 1947; Mehra et al., 1982; Shibata et al., 1989; Langasan and Smith, 1993). In more recent times (Weng and Lee, 1992; Barrufet and Rahman, 1995) very accurate gas chromatographs along with PVT apparatus have been employed for determination of phase compositions.

The objective of this part of the project is to determine bubble point and pressure-volume relationships for several oil samples already available. This work will be repeated using producers provided heavy oil samples.

APPARATUS AND EXPERIMENTAL SET-UP

The laboratory set-up consists of three main parts:

I - VACUUM SYSTEM

II- HYDRAULIC SYSTEM

III. RECOMBINATION APPARATUS

I –Vacuum System. The vacuum system consists of a vacuum pump, two traps to protect the vacuum pump from liquid, and tubing.

II- Hydraulic System. Hydraulic System consists of a Ruska positive displacement pump, a pressure gauge, high-pressure valves and tubing. The purpose of this system is to charge the volume in the upper portion of the recombination cell.

The capacity of the pump is 500 cc (0.01765 cu. ft.).

The maximum working pressure is 340.25 ATM (5000 psia).

The displacement pump is equipped with a discharge volume scale. This is used to monitor the volume of the discharge and, indirectly, the volume of the recombination cell. This scale can be read within 0.02 cc (7.062 e -7 cu. ft.).

III- Recombination Apparatus.

a). The Temperature Controlled Air-Bath Oven with maximum operating temperature 200 C (392 F). The temperature can be set with an accuracy of 0.2 C. Uniform air bath temperature distribution ± 1 C.

b). The Recombination Cell

JEFFREY Recombination cell model No 1000-10-P-REC

Floating piston.

Capacity of the Cell 1,000 cc (0.0353 Cu. ft.).

Maximum working pressure 689.48 bar (10,000 psia).

Maximum working temperature 200 C (392 F).

c). The Rocking Mechanism

Laboratory set-up. This rocking mechanism is provided to mix efficiently a multi component fluid such the desired equilibrium condition can rapidly be obtained.

The laboratory set-up was constructed according the standard set-up suggested in manual hook of the recombination apparatus. The recombination Cell is connected from the bottom with hydraulic system and with the Sample Cylinder from the top. The hydraulic system is connected with the bottom of both recombination cell and simple cylinder. The sample cylinder is connected with hydraulic system from the bottom and with the recombination cell from the top. The vacuum system is used with all the system depending of step of experiment.

Procedure to charge the hydraulic oil into the system:

- 1- Before charging oil into the hydraulic system, all air has to be removed from the system by using vacuum (from the hydraulic pump until the bottom of recombination Cell).
- 2- Injecting the hydraulic oil into the bottom of the recombination cell until the floating piston arrive on the top of the Recombination Cell.
- 3- Do the same procedure for the preparation of Sample Cylinder.
- 4- Charge the crude Oil into the Sample Cylinder.
- 5- Before Charging the Oil from the Sample Cylinder, all air has to be removed from the system between the top of the Recombination Cell until the connection with the Sample Cylinder.
- 6- Charge the oil from the Sample Cylinder into the top of the Recombination Cell by using the hydraulic pump.
- 7- Close the top of the Recombination Cell.
- 8- Heat the System until the wanted Temperature.

Composition of the Oil Samples:

The characteristics of the oils used in the bubble point pressure experiments are:

Oil A

Paradis crude oil (Stock Tank Oil). The volume injected into the recombination cell of this oil is:

$V = 500 \text{ cc}$ at $T = 22 \text{ }^{\circ}\text{C}$ and 1 ATM . API # 40 density = 0.82 g/cc so the mass of this oil is 410 g

Oil B

A mixture of 95.7% mass of Oil A and 4.3% mass of Methane.

The mixture is 1.71% volume of black oil and 98.29 % volume of Methane and at $T = 22 \text{ }^{\circ}\text{C}$ and Atmospheric Pressure.

Oil C

Oil B plus 5 cc (5g) of distilled water. Then the total mass of mixture is 433.45 g (410 g black oil + 18.45 g Methane + 5 g water). The water was added to the recombination cell at a pressure above the pressure inside the cell (2100 psi we used this pressure to keep the system under the liquid phase), and to avoid the back flash.

Oil D

Oil C plus 20 cc of distilled water. Thus then the total mass of mixture is 453.45 g (410 g black oil + 18.45 g Methane + 25 g water). The same procedure of Oil C is used.

EXPERIMENTAL RESULTS

Evaluation of Water Effect on Bubble Point Pressures of a Crude Oil Bubble Point Pressure for Crude Oil (A) and of this crude oil with Methane and Water, have been measured in the range $212\text{-}315 \text{ }^{\circ}\text{F}$ ($100\text{ }^{\circ}\text{C}$ to $175 \text{ }^{\circ}\text{C}$). The result gives us a very good idea about what happens in a reservoir while injecting the water or steam for the Enhanced Oil Recovery, especially the change in the bubble point pressure which is a more important variable for oil production.

The objective of this study is to know the influence of the water injection on the value of the bubble point pressure at the conditions of reservoir and to find the relation between the quantity of water added to the reservoir and the amount of pressure reduced from the bubble point.

Figures 1 to 4 show the isothermal pressure volume behavior of these oils. Bubble point pressures were determined by least square regression of the two curves indicating liquid phase and two-phase regions.

Table IIa.10 Indicates the differences in bubble point pressures obtained for all these experiments. The purpose of adding methane was to be able to detect the bubble point

pressure experimentally. The effect of water in the P_b can be considered negligible, and within experimental uncertainty.

Equations of state predicting 2-phase equilibria, rather than three phase equilibria, predict a substantial increase in the bubble point pressure of an oil when water is added. This is mainly an artifact of predicting 2-phase equilibria instead of three-phase equilibria.

Currently we are working in the comparison of predicted bubble point pressures as a function of water composition using the Peng Robinson EOS using two and three-phase flash algorithms.

Determination of Isothermal Compressibility from Pressure Volume Behavior.

Pressure volume pairs were recorded for selected isotherms in the single and in the two-phase regions. The bubble-point pressure was determined from intersecting these two curves. The isothermal compressibility can be determined from the fitted equation.

$$P = a - bV \quad 0$$

$$C_o = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{bV} \quad 0$$

Fig IIa. 4 Pressure Volume relation for Oil A at various temperatures.

Fig IIa. 5 Pressure Volume relation for Oil B at various temperatures.

Fig. Ila. 6 Pressure Volume relation for Oil C at various temperatures.

Fig IIa. 7 Pressure Volume relation for Oil D at various temperatures.

Table IIa.10 Bubble Point Pressure and Total Volume at Bubble Point Pressure point for the crude oils A, B, C, and D.

Temp °C Oil-D	Bubble Point Pressure, PSI				Total Volume, cc		
	Oil-A	Oil-B	Oil-C	Oil-D	Oil-A	Oil-B	Oil-C
100 629	<14.7	2108	2079	2062	-	607	610
125 -	36	2123	-	-	586	633	-
150 678	43	2156	2179	2169	611	657	660
175 705	60	2186	2249	2185	636	681	685

The purpose of adding methane was to be able to detect the bubble point pressure experimentally.

The effect of water in the Pb can be considered negligible, and within experimental uncertainty.

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Determination of Isothermal Compressibility from Pressure Volume Behavior

Pressure volume pairs were recorded for selected isotherms in the single and in the two-phase regions. The bubble-point pressure was determined from intersecting these two curves. The isothermal compressibility can be determined from the fitted equation.

$$P = a - bV$$

$$C_o = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{bV}$$

Oil	a	b	Temperature	R ²
A	5.8681x10 ⁴	-104.41	100	0.998
A	5.2569x10 ⁴	-89.58	125	0.998
A	5.0024x10 ⁴	-81.83	150	0.999
A	4.146x10 ⁴	-65.07	175	0.998
B	5.7154x10 ⁴	-90.715	100	0.999
B	4.676x10 ⁴	-70.472	125	0.985
B	5.008x10 ⁴	-72.902	150	0.999
B	4.713x10 ⁴	-65.938	175	0.999
C	5.784x10 ⁴	-91.304	100	0.999

C	5.114×10^4	-74.232	150	0.999
C	4.621×10^4	-64.119	175	0.999
D	5.7629×10^4	-88.339	100	0.999
D	5.03×10^4	-70.926	150	0.999
D	4.7146×10^4	-64.092	175	0.999

The variation in compressibilities among oils is not significantly different. Therefore, we can infer that the solubility of water in the oil phase is negligible.

Oil	Pressure (psia)	Temperature ($^{\circ}\text{C}$)	C_o (psia^{-1})
A	167	100	$2.37\text{e-}5$
A	1189	100	$1.81\text{e-}5$
A	3817	100	$1.86\text{e-}5$
D	1773	100	$1.81\text{e-}5$
D	3918	100	$1.73\text{e-}5$

FUTURE WORK

Theoretical Part

- a). We are going to finish the write-up of the computer code to implement the area method to calculate phase equilibria.
- b). We are going to search for available methods in literature to reduce the number of components in typical heavy oils. A "pseudo-component" technique will be used. We envision reducing the number of components to 8-10.
- c). Results will be computed for binary mixtures H_2O /Hydrocarbon and CO_2 /Hydrocarbon using the area method.
- d). Critical comparison between experimental and computed data will be performed.

Experimental Part

- a). Bubble points will be determined for the oil samples described in this report.
- b). PVT data will be measured for the aforementioned oils.
- c). Samples of heavy oils will be obtained.

NOMENCLATURE

A	Area
a_m	Energy parameter
b_m	Size parameter
G	Gibbs energy
k_{12}	Binary interaction parameter
P	Pressure
R	Gas constant
T	Absolute temperature
V	Total volume
X	Composition

Greek Symbols

α	Constant in the equation of state
ϕ	Reduced Gibbs energy of mixing
γ	Activity coefficient
ω	Acentric factor
μ	Chemical potential

Abbreviations

EOS	Equation of state
MR	Mixing rules
RK	Redlich-Kwong EOS
SRK	Soave-Redlich-Kwong EOS
VDW	Van der Waals

Subscripts

- 1 Mixture component
- 2 Mixture component

Superscripts

- L Liquid phase
- V Vapor phase

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