High-Pressure and High-Temperature Pressure Composition Diagram of Hexadecane, Water and Carbon Dioxide Systems

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To carry out a feasible exploitation of the pre-salt Brazilian reserves, it is crucial to understand the phase behavior of these highly non ideal systems well and to obtain accurate models for the simulation of such severe operational conditions. In this work, the performance of two thermodynamics models based on Peng-Robinson cubic equation of state (PREOS) are compared to achieve the best representation for the ternary hexadecane, water and carbon dioxide system. The interaction parameters obtained from each model were compared and then the pressure composition diagram for the multicomponent system was created. Further research is going on to determine the experimental phase envelope data points of this system.

1. Introduction

Since new large oil fields have been discovered off the Brazilian coast, specific research projects related to offshore oil production are required. These new oil fields are in the pre-salt layer, under extreme temperature and pressure conditions. A successful predictive approach for mixtures containing different kinds of hydrocarbons under high pressure and temperature conditions would be very valuable for pre-salt exploitation. An important consideration for a predictive approach is the model used.

Equations of state (EOS's) are often used for phase equilibrium calculations, but the success of such models depends upon the choice of mixture combining rules. Cubic equations of state are widely used to provide knowledge of oil and natural gas thermodynamic properties and, in particular, of their phase behavior. Moreover for this purpose, their application remains unchallenged at present in reservoir simulation (Fenghour et al., 2001).

In order to encourage petroleum exploitation, new aspects such as the phase behavior of the CO_2 - H_2O - $C_{16}H_{34}$ system must be carefully investigated. Due to the scarcity of

experimental equilibrium data for CO_2 - H_2O and H_2O - $C_{16}H_{34}$ binary mixtures under high pressures, few or no modeling papers have been published about this ternary system. In this work, we used the PREOS together with van der Waals (VDW) and Mathias-Klotz-Prausnitz (MKP) mixing rules for each binary pair. For the determination of the binary parameters values, a robust optimization routine was developed. The results of this study include a pressure composition diagram for the ternary CO_2 - H_2O - $C_{16}H_{34}$ system at 573.15K and ranging over 101 - 201bar.

1.1 Phase Equilibrium data

Only one study for a CO_2 - H_2O - $C_{16}H_{34}$ system was found. The VLE have been measured at pressures between 101 to 301bar and at temperatures between 473.15 and 573.15K by Brunner et al. (1994).

On the one hand abundant phase equilibrium data exist for the CO_2 - H_2O and CO_2 - $C_{16}H_{34}$ systems, on the other for H_2O - $C_{16}H_{34}$ no experimental data was found. The principal high pressure VLE experimental data used in this paper are in Spee et al. (1991), D'Souza et al. (1988), Brunner et al. (1994), Teng et al. (1997), Bamberger et al. (2000) and Koschel et al. (2006). They reported important VLE data of the binaries CO_2-H_2O and CO_2-$C_{16}H_{34}$ systems.

1.2 Thermodynamic Modeling

Within a few years following its publication in 1976, the PREOS became a standard tool for the calculation of VLE for fluid mixtures, especially for those mixtures encountered in the natural-gas and petroleum industries (Wu and Prausnitz, 1998).

As an EOS is used to describe the non-ideality of both phases in the $\phi - \phi$ (fugacity coefficient) approach, the EOS suggested by Peng and Robinson (1976) along with the VDW and MKP mixture rules was used to calculate the phase equilibria behavior at high pressure. The Peng-Robinson EOS is:

$$P = \frac{RT}{V-b} - \frac{a}{V(V-b)+b(V-b)} \tag{1}$$

where P is the pressure, T is the temperature, V is the molar volume, R is the universal gas constant, b is the co-volume parameter and a is the energy parameter. For pure components, the parameters a and b were determined from the critical temperature (T_c), the critical pressure (P_c) and the acentric factor (ω) provided in Poling et al. (2001).

$$a(T_c) = 0.45724 \frac{R^2 T^2}{P_c}$$

$$b(T_c) = 0.07780 \frac{RT_c}{P_c} \tag{2}$$

First model

For this approach, the van der Waals mixing rules are applied with cross interaction parameters k_{ij} and l_{ij}. For a mixture of N components, a and b are generally given by:

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$b = \sum_i \sum_j x_i x_j b_{ij}$$

$$(3)$$

where

$$aij = (1 - k_{ij})(a_{ii} a_{jj})^{1/2}$$

$$bij = 0.5(b_{ii} + b_{jj})(1 - l_{ij})$$

$$(4)$$

where x_i, x_j are the mole fractions of component i and j. It is knowed that at thermodynamic equilibrium, the fugacities f_i of each component i must be equal in the vapor and liquid phases. Thus, the liquid and vapor fugacities come from:

$$f_i^L(P,T) = \phi_i^L x_i P$$

$$f_i^V(P,T) = \phi_i^V y_i P$$

$$(5)$$

where ϕ_i^V and ϕ_i^L are the fugacity coefficients of vapor and liquid phase. The x_i, and y_i, are the mole fractions of component i in the liquid and vapor phase respectively.

Second Model

The MKP is a mixture rule dependent on the concentration with three adjustable parameters. According to Mathias et al. (1991), the major advantage of the MKP mixture rule is the fact that there is no influence from the increase in the number of components in the results. Furthermore, it is not only applicable to PREOS, but also to other equations of state and excess-Gibbs-energy models for calculating activity coefficients. Here, the parameters a and b become

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \sqrt{a_i a_j}\,(1 - k_{ij}) + \sum_{i=1}^n x_i \left(\sum_{j=1}^n x_j \left(\sqrt{a_i a_j}\, \lambda_{ij} \right)^{1/3} \right)^3$$

$$b_{ij} = (1 - l_{ij}) \frac{(b_i + b_j)}{2}$$

$$(6)$$

where x_i, x_j are the mole fractions of component i and j. The cross interactions parameters are presented through $\lambda_{ij}, k_{ij}, l_{ij}$, where

$$\lambda_{ij} = -\lambda_{ji}$$
$$k_{ij} = k_{ji} \qquad (7)$$
$$l_{ij} = l_{ji}$$

2. Correlation of Experimental Results

To determine the interactions parameters a robust optimization routine was developed in. FORTRAN language. The bubble points were calculated using experimental data obtained by the authors cited previously and the deviations were evaluated using eq 8, where PEXP represents the experimental pressure and PCAL the calculated pressure. The objective function (F_{OBJ}) is presented in eq 9, where NP represents the number of experimental points.

$$AAD = \left(\frac{\left| P^{EXP} - P^{CAL} \right|}{P^{EXP}} \right) \qquad (8)$$

$$F_{OBJ} = \sum_{i=1}^{NP} \left(\frac{P_i - P^{CAL}{}_i}{P_i} \right)^2 \qquad (9)$$

The procedure of modeling is as follows:
1. Estimate the k_{ij} and l_{ij} of each system using eq 4 by means of guesses in an attempt to establish a pair of parameters to represent all experimental temperatures;
2. Fix the k_{ij} and l_{ij} obtained by first model and then adjust the third parameter using eq 6 in order to minimize the deviations.
In table 1 are listed the absolute average deviations (AAD) obtained by means of the modeling, as well as experimental temperature (TEXP) and pressure (PEXP) used. As a result, figure 1 shows the bubble pressure curves calculated with the PREOS together with VDW and MKP mixing rules for the ternary system at 573.15 K.

Table 1: Thermodynamic modeling data and results.

Reference data	TEXP (K)	PEXP (bar)	1st Model AAD (%)	2nd Model AAD (%)
CO_2 - $C_{16}H_{34}$				
D'Souza et al. (1988)	314.15, 333.15, 353.15	76.9-161.2	4.59	4.58
Spee et al. (1991)	393.2	101-256	8.1	3.12
Brunner et al. (1994)	473.15, 573.15	101-257	7.19	3.16
CO_2- H_2O				
Teng et al. (1997)	278, 283, 288, 293	64.4-294.9	21.73	1.33
Koschel et al. (2006)	323.15, 371.3	20.6-203.03	0.9	0.96
Bamberger et al. (2000)	323.2, 333.2, 353.1	40.5-141.1	1.38	1.37
CO_2 - H_20 - $C_{16}H_{34}$				
Brunner et al. (1994)	473.15, 573.15	101, 201	11.23	6.99
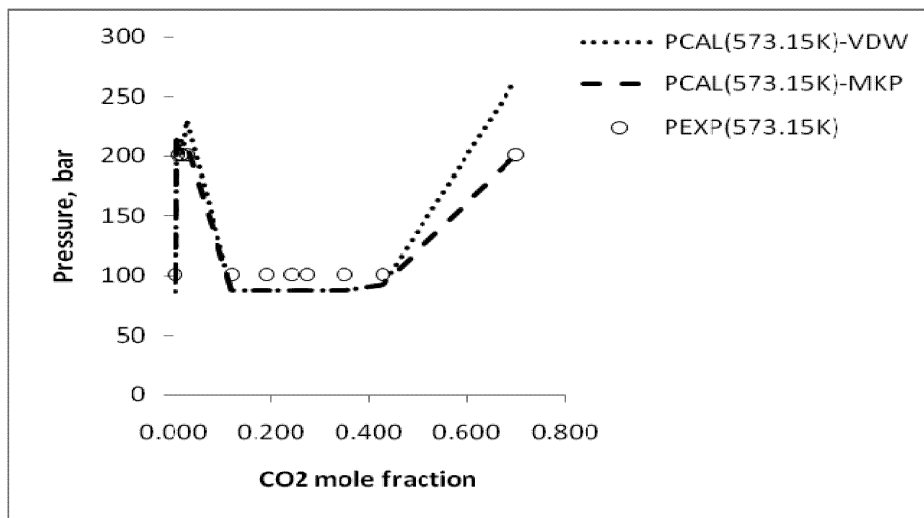
Figure 1: Pressure composition diagram of the CO_2-H_2O-$C_{16}H_{34}$ system at T=573.15K.

3. Discussion

In general, the representation of the experimental results was satisfactory taking into consideration the good agreement between the calculated and experimental pressures. However, for each of the systems investigated the MKP mixing rule performed better than the VDW as seen in Spee et al. (1991), Brunner et al. (1994) and Teng et al. (1997) reference data modeling (table 1). Overall there were no significant differences between the performances of the models used.

For the CO_2 - H_2O - $C_{16}H_{34}$ system it can be observed that the MKP mixing rule correlated very well the vapor-liquid equilibria data. Probably this model can be used to predict the complete behavior of this system that presents two or three phases according to Brunner et al. (1994).

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