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Predictions of three-phase regions in CO_2–oil mixtures

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Abstract

Petroleum fluids can in the presence of CO_2 present a complex phase behavior. Both two-phase (VLE and LLE) and three-phase regions (VLLE) might occur within certain ranges of pressure and temperature.

It is important in EOR to be able to predict the phase behavior of these systems for both the design of CO_2 flooding processes and reservoir simulation. No purely predictive method for the description of the three-phase region (VLLE) of these systems was previously reported in the literature. The correlation of experimental data has only been possible by means of a severe tuning of the oil properties or the equation of state employed.

A predictive model, using a cubic equation of state for description of the phase behavior of CO_2–oil mixtures, is presented. A tuning procedure, based on the use of binary interaction parameters, was developed for systems where a fair description of the phase behavior is not achieved with the proposed model. It is shown that good predictions are usually obtained for temperatures below 314 K and that the tuning procedure can successfully describe the phase behavior in the remaining cases.

1. Introduction

The design of CO_2 flooding processes, the evaluation of laboratory CO_2 corefloods, and reservoir simulators require knowledge of the phase equilibria that exist between CO_2 and oil over the entire CO_2/oil composition range. Most reservoir simulators employ only two hydrocarbon phases to describe CO_2–oil systems. The interest in reservoir simulators dealing with three-phase equilibria is increasing due to their improved predictive ability. Khan et al. (1992) and Lim et al. (1992) have recognized that the effect of a third hydrocarbon phase may be significant in simulation results and that a higher degree of correspondence between experimental and simulated slim-tube data can generally be obtained by use of a three-phase solution. Wang and Stenby (1993) showed that the ultimate oil recovery using four-phase flow simulation can be 10% higher compared with the three-phase case.

Several methods attempting the description of the three-phase regions with cubic equations of state have been presented in the literature. Many of these methods are just correlations tuning the parameters of the model to match the experimental phase behavior (Khan et al., 1992; Negahban and Kremesec, 1992). Some models displaying a more predictive character have also been reported (Turek et al., 1984; Nghiem and Li, 1984, 1986; Chaback and Turek, 1986), but they are either of limited applicability and no indication is provided on how to avoid or overcome their limitations or, although to a lesser extent, they also make use of tuning.

To correlate the measured phase behavior all parameters of the models have already been tuned by different authors (Chorn and Mansoori, 1989). The properties of the heavy oil fraction (Mw, Sg, T_c, P_c and

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ω) as well as the composition, the constants Ω_a and Ω_b of the equation of state a and b parameters, and the binary interaction parameters (K_{ij}) have been employed regardless of the risk of their use for this purpose. Some rules are well established concerning the tuning of light oils and the dangers of using certain parameters for tuning (Gani and Fredenslund, 1987; Pedersen et al., 1988, 1989a, 1989b) but very little is known about the tuning of heavy oils.

In continuation of previous works (Jørgensen and Stenby, 1993; Coutinho et al., 1993, 1994) it is the purpose of this article to present a systematic approach to the prediction of phase behavior of CO_2–oil mixtures presenting three-phase regions. An oil characterization and a cubic equation of state are used to develop a predictive model for the description of the phase behavior. The model shortcomings are well identified and a tuning procedure, using binary interaction parameters, is presented to correlate the data for which prediction is not possible.

2. Multiphase behavior predictive model

2.1. Oil characterization

The Pedersen et al. (1988, 1989a,b) model is used for the oil characterization. It provides a composition distribution of the plus fraction and the pseudocomponent properties. The lumping is performed describing the C_{7+} fraction with 2 to 4 pseudocomponents depending on the C_{7+} mole fraction (Khan et al., 1992). The usual lumping for the defined components is $CO_2/C_1/C_2$–C_3/C_4–C_6. The total number of pseudocomponents is thus 6–8. This number was found to be a good compromise between accuracy and computational time.

2.2. Multiphase calculation procedure

The phase boundaries are calculated with a multiphase flash (Michelsen, 1982a, b). The phase equilibrium calculations are performed employing the SRK-EOS (Soave, 1972) along with the van der Waals one fluid mixing rules. The binary interaction parameters between CO_2 and hydrocarbons for the a parameter mixing rule are given by Eq. 1.

$$K_{ij} = 1 - 0.885\left(\frac{2\sqrt{b_i b_j}}{b_i + b_j}\right)^{-0.036} \quad (1)$$

where b_i is the equation of state parameter b for the component i, K_{ij} is the binary interaction parameter between species i and j, referring to CO_2 and the oil pseudocomponents. The interaction parameters between hydrocarbons are assumed equal to zero, and no interaction parameters are used in the b parameter mixing rule.

Eq. 1 is obtained from the work by Coutinho et al. (1994) combining the interaction parameter values for aliphatic and aromatic hydrocarbons in a proportion that reflects an average PNA distribution of heavy oils. It also takes into account the results by Larsen et al. (1986) and Nutakki (1991) showing that binary interaction parameters for LLE are smaller than for VLE.

3. Results and discussion

The model presented was applied to several CO_2-crude oil systems whose phase diagrams have been reported in the literature (Shelton and Yarborough, 1977; Orr et al., 1981; Chaback and Turek, 1986; Turek et al., 1988; Winzinger et al. 1991; Khan et al. 1992; Creek and Sheffield, 1993). In these examples the tem-

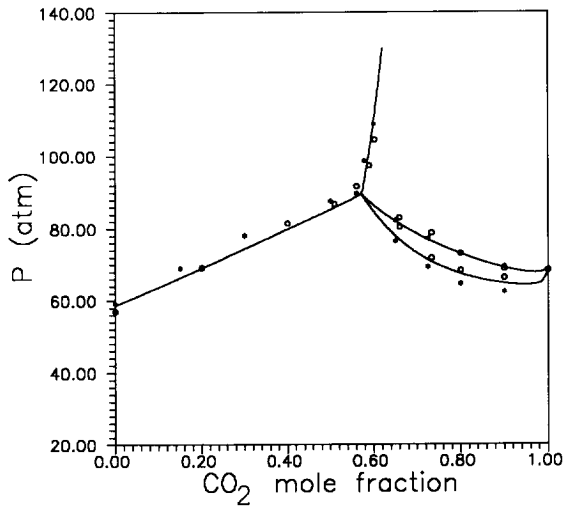

Fig. 1. Experimental (*) and predicted (–) phase diagram for NWE oil at 301.5 K. The circles are calculated using the method by Khan et al. (1992). Experimental data from Winzinger et al. (1991).

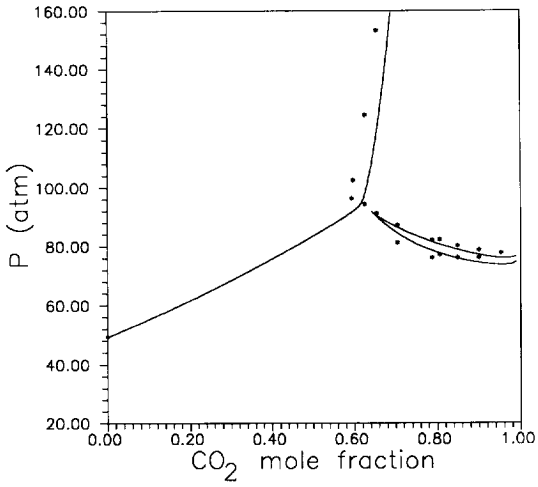

Fig. 2. Experimental (*) and predicted (–) phase diagram for OILB oil at 307.6 K. Experimental data from Shelton and Yarborough (1977).

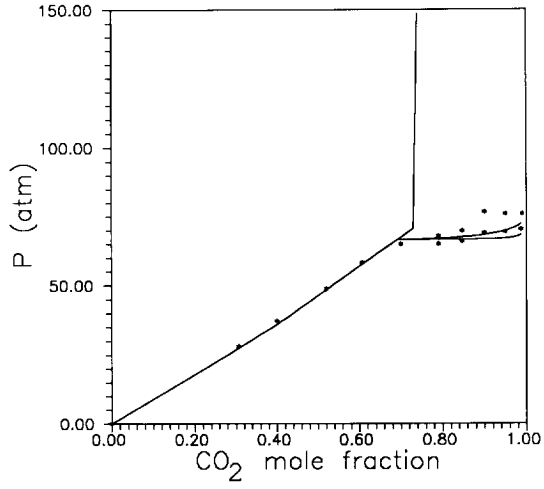

Fig. 3. Experimental (*) and predicted (–) phase diagram for Maljamar separator oil at 305.4 K. Type I diagram. Experimental data from Orr et al. (1981).

perature ranges from 301.5 to 316.5 K. The predicted P–x projections of the phase diagram are presented in Figs. 1-5. For temperatures below 314 K the predictions are always accurate enough for use in a reservoir simulator. The model is able to perform predictions of both types of three-phase regions, I and II according to the definition by Orr et al. (1981). Fig. 3 is an example of type I behavior for Maljamar separator oil (Orr et al., 1981) at 305.4 K. Type I is characterized by a three-phase region that is found at progressively higher pressures as the mixture becomes richer in carbon dioxide. This phase behavior occurs for reservoir fluids devoid of light ends. Despite the composition being almost completely described by the characterization model, which makes the predictions for these oils particularly difficult, the three-phase region is fairly well predicted. All the other phase diagrams are examples of type II

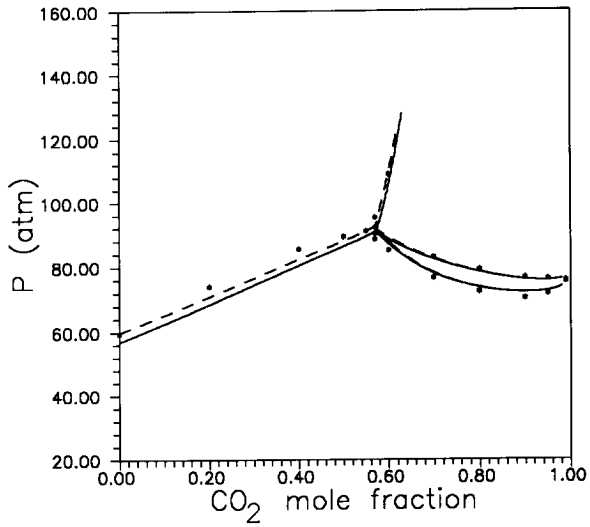

Fig. 4. Experimental (*), predicted (solid line) and tuned (dashed line) phase diagram for OILG oil at 307.6 K. Experimental data from Creek and Sheffield (1993).

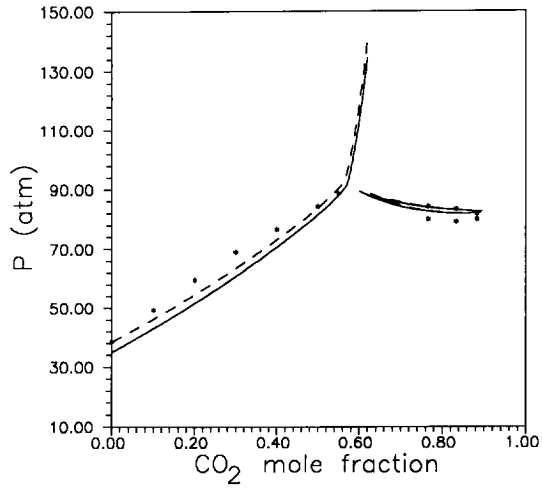

Fig. 5. Experimental (*), predicted (solid line) and tuned (dashed line) phase diagram for BSB oil at 313.7 K. Experimental data from Khan et al. (1992).

behavior with the three-phase region being found at lower pressures with an increasing concentration of carbon dioxide. A comparison between the predictions obtained by the proposed model and the results by Khan et al. (1992) is shown in Fig. 1.

The presence of a solid phase is very often reported to appear in the three-phase region (Shelton and Yarborough, 1977, Simon et al., 1978; Orr et al., 1981; Stalkup, 1984; Turek et al., 1984, 1988; Creek and Sheffield, 1993). Some efforts in modeling the appearance of this phase due to the effect of CO_2 have been done (Kawanaka et al., 1991). The model presented in this work does not take into account the formation of solid phases. Further work is currently being carried attempting to model the four-phase (SLLV) equilibrium.

The model has two shortcomings that are evident in the phase diagram of BSB oil (Fig. 5):

- Deviations in the saturation pressure predictions.
- Predicted three-phase region smaller than experimental.

The first problem is less frequent and is related with the characterization procedure employed. Pedersen et al. (1989a) report that saturation pressure calculations using this characterization procedure have an average deviation inferior to 5% and that errors larger than this value occur in less than 10% of the cases. A deviation inferior to 5% in the saturation pressure is required for use of a phase diagram in reservoir simulators (Wang, 1993). Examples of deviations in the oil saturation pressure are shown in Fig. 4 for oil OILG and for oil BSB in Fig. 5. The first case presents an acceptable deviation of 4%, whereas BSB shows a somewhat larger deviation of about 9%. Errors in the saturation pressure predictions affect only the boundary between the Liquid and Liquid + Vapor regions. The three-phase region predictions, however, are not significantly influenced by the deviations in the saturation pressure as is clear in Figs. 4 and 5 comparing the predicted and tuned three-phase region. In all other cases the error is inferior to 1%. A correct estimate of the saturation pressure demands that the light, non organic, gases present in the oil, principally nitrogen, are taken into account.

The second problem is a limitation common to all three-phase region calculations previously presented in the literature (Chaback and Turek, 1986; Nghiem and Li, 1986; Khan et al., 1992; Creek and Sheffield, 1993).

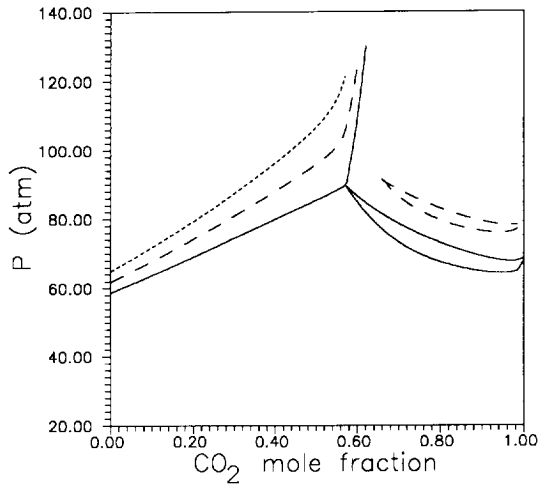

Fig. 6. Calculated phase diagrams for NWE oil at 301.5 K (solid line), 308.7 K (dashed line), and 316.5 K (dotted line).

This behavior is clear in Fig. 5, but to a lesser extent it is already present in the phase diagrams shown in the previous figures. It deserves some further attention. The phase diagram for NWE oil (Winzinger et al., 1991) at three different temperatures from 301.5 to 316.5 K is shown in Fig. 6. The behavior described here has been experimentally observed before and is well documented in the works by Turek et al. (1984, 1988). The three-phase region decreases with increasing temperature and disappears for temperatures that, depending on the oil, range from 310 to 320 K (Orr and Jensen, 1984; Turek et al., 1984, 1988). The error on the size of the predicted three-phase region may be recognized as a temperature dependency error: The three-phase region is "correctly" predicted but at a "wrong" temperature. This problem seems thus to be related to the temperature dependence of the equation of state and not to an oversimplification of the oil description. This is manifest in the work by Deak et al. (1993) where a similar problem on the temperature dependence of the three-phase region predictions appears for a defined ternary mixture. The predicted and experimental three-phase region boundaries have a similar shape but predictions present a displacement of around 3 K towards lower temperatures.

The inaccurate description of the temperature dependence lead to a prediction of the three-phase region at temperatures lower than the experimental. This is the explanation for the difficulties of the model

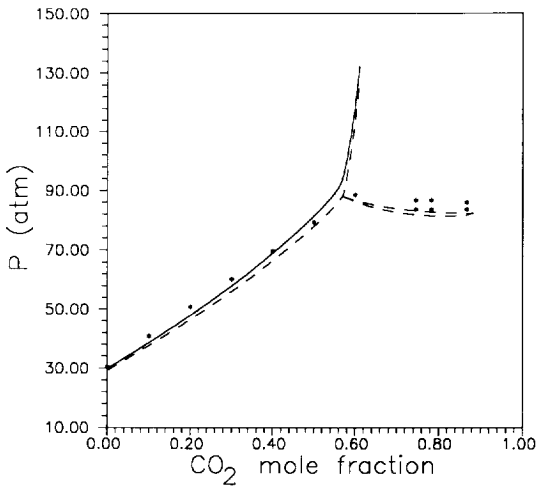

Fig. 7. Experimental (*), predicted phase diagrams for JEMA oil at 316.5 K (solid line) and at 315 K (dashed line). Experimental data from Khan et al. (1992).

dealing with systems at high temperatures, meaning temperatures close to the temperature where the three-phase region disappears, which is usually around 314 K (110°F). This behavior is exemplified in Fig. 7 for JEMA oil (Khan et al. 1992) at 316.5 K. The model is unable to predict the existence of the reported three-phase region. This does not mean that the model does not predict the existence of a three-phase region for this oil in presence of CO_2 as it is evident from the prediction at 315 K, but that with the increasing temperature, the predicted three-phase region has already disappeared at 316.5 K.

These two limitations to the proposed model reduce its predictive character and cannot be handled within the frame of a pure predictive model without performing some changes in both the characterization procedure and the temperature dependency of the equation of state.

It has been shown that the proposed model is able to perform pure predictions of phase diagrams for CO_2–oil mixtures, within a degree of accuracy that allows their use in reservoir simulation, in 90% of the systems for temperatures below 314 K. To obtain good descriptions for systems at temperatures above 314 K and for the remaining 10% of cases below this temperature the pure prediction demand has to be abandoned. Based on this consideration a tuning procedure using binary interaction parameters was developed to overcome the above-mentioned limitations of the model.

4. Tuning

Several parameters can be and have been regularly used by different authors, for tuning the models to correlate experimental data:

- The critical properties and the acentric factor of both light and heavy fractions.
- Measurable properties of the plus fraction such as molar fraction, molecular weight, and specific gravity.
- The constants Ω_a and Ω_b of the parameters of the equation of state.
- The binary interaction parameters.

To develop a tuning procedure for heavy oils and their mixtures with carbon dioxide, the potential tuning parameters were analyzed. The ability of a parameter to fit experimental data and the physical significance of its use were employed as criterion.

The critical properties of the light components are accurately known and, therefore, their use as tuning parameters is not physically acceptable. For the heavy fractions the critical properties are not known. They are obtained by using the correlations of the characterization procedure that relate them to the molecular weight and the specific gravity of the fractions and, at least in principle, their use as tuning parameters seems justified. There is, however, no reason to modify the properties estimated by the characterization, because it has been extensively employed with very good results.

A large error is associated with the measured values of the molecular weight and the specific gravity of the plus fraction that is of 5–10% for the first and around 5% for the latter (Pedersen et al., 1989a). The molecular weight of the plus fraction is successfully used for tuning light oils; however Jørgensen and Stenby (1993) have shown that even a 10% adjustment in this property has only a small effect on heavy oils. The same authors have shown that the specific gravity could be used to tune OILG and correctly calculate the saturation pressure. The danger of applying the specific gravity to tune the description of the phase behavior of CO_2–oil mixtures is apparent in Fig. 8. For low concentrations of carbon dioxide a good description of the phase boundary is obtained, but for oil concentrations below 0.5, the prediction is totally wrong. This shows how risky tuning can be when it is not carefully performed.

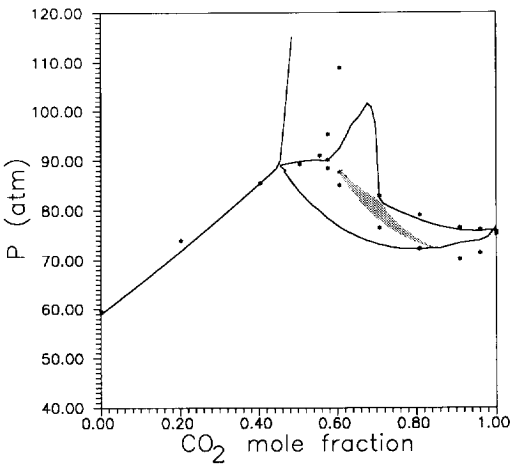

Fig. 8. Experimental and predicted phase diagram for OILG at 307.6 K tuned with a 5% change in C_{7+} density. In grey: a four-phase region.

Some authors (Coats and Smart, 1984; Whitson, 1984; Khan et al., 1992) have suggested tuning the constants of the EOS parameters (Ω_a and Ω_b). In spite of being a very powerful tuning tool, it does not seem a physically acceptable tuning procedure. Changing the constants Ω_a and Ω_b alters the behavior of the equation at the critical point. The equation no longer obeys the critical point restrictions:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \tag{2a}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \tag{2b}$$

and the predictive power of the equation is destroyed (Merril, 1993). This is particularly significant in three-phase region predictions because the CO_2 is very close to its critical point.

The major uncertainties of an equation of state are related to the binary interaction parameters. For a long time they have been looked at as purely empirical and have been employed as tuning parameters (Katz and Firoozabadi, 1978; Chaback and Turek, 1986; Gani and Fredenslund, 1987; Helle and Friedemann, 1989), but only marginally and not in a systematic approach. It was shown by Coutinho et al. (1994) that binary interaction parameters have a physical meaning. In that work, the authors also showed the difference between the binary interaction parameters for CO_2/aliphatic and CO_2/aromatic systems and how, from the knowledge of these differences, some principles on using the CO_2/hydrocarbon binary interaction parameters as tuning parameters could be deduced. Following the work developed by Jørgensen and Stenby (1993) and by use of the results of Coutinho et al. (1994), a tuning procedure based on the use of binary interaction parameters is presented to overcome the limitations of the proposed model for phase behavior predictions.

4.1. Crude oil boiling point

It has been shown previously that in some cases differences around 10% may occur in the crude oil boiling point calculations. This is clear in Fig. 5 for oil BSB. In spite of this error, a fair three-phase region prediction is obtained. The tuning parameter should correct the phase boundary between the Liquid and Liquid + Vapor regions but the three-phase region predictions should not be affected. For this purpose and following the previous works by Katz and Firoozabadi (1978) and Jørgensen and Stenby (1993), non zero binary interaction parameters between methane and the heavy fractions are used here:

$$K_{CH_4/C_{7+}} \neq 0 \tag{3}$$

Its use is physically acceptable due to the size difference between the molecules. The saturation pressure of the oil is used to assess the binary interaction parameters between methane and the heavy end. Good predictions of the entire phase diagram, three-phase region comprised, are obtained. The results of applying this idea to BSB and OILG are presented in Figs. 4 and 5. A small binary interaction parameter usually inferior to 0.05 is enough to correct the boiling point calculation and the phase boundary without destroying the three-phase region predictions.

4.2. Systems at temperatures higher than 314 K

As previously discussed, this behavior is related with a failure in the EOS temperature dependence. No attempt was made to correct the EOS, but a tuning procedure, able to overcome this difficulty, has been developed.

The easiest way of adjusting the temperature dependence of the equation of state is through the attractive term, namely on the temperature dependence of the a

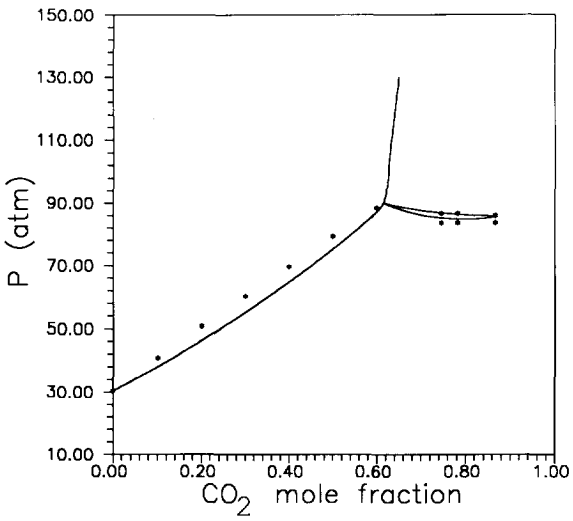

Fig. 9. JEMA oil: Experimental (*) and calculated (–) phase diagram by tuning of binary interaction parameters at 316.5 K.

parameter. A simple way of changing the parameter a value to emulate a temperature variation is acting on the binary interaction parameters. A good correlation of the three-phase region is easily achieved if the parameters in Eq. 1 are decreased, thus estimating lower values of the binary interaction parameters. The use of Eq. 1 in the tuning procedure is an easy and coherent form of tuning the binary interaction parameters, because the parameters for all components will change simultaneously and proportionally preventing the appearance of behaviors similar to that presented in Fig. 8. In spite of a physical meaning, the binary interaction parameters are semiempirical properties with a large deal of uncertainty associated with them, specially when dealing with complex mixtures such as crude oils. Aromatic and heavy aliphatic molecules have lower values of binary interaction parameters (Coutinho et al., 1994). In this way, reducing the value of the binary interaction parameters has an effect similar to that when dealing with a heavier oil.

This tuning procedure was applied to JEMA oil very successfully. The results using 0.9 and -0.04 as constants in Eq. 1 are presented in Fig. 9 and a good fit of experimental data is obtained. Similar results can be achieved for oil BSB three-phase region and other oils at temperatures above 314 K.

If the model is overtuned to fit experimental data, in some cases problems similar to those present in Fig. 8 may occur with prediction of four-phase regions.

5. Conclusions

A predictive model for the description of complex phase diagrams for CO_2–oil mixtures has been developed. The predictions obtained are good and adequate for use in reservoir simulators. The model uses a small number of pseudocomponents, thus reducing the computational time without loss in the predictive accuracy.

The model limitations have been identified. A tuning procedure based on the use of binary interaction parameters as tuning parameters was developed and applied to systems where the model was unable to give reasonable predictions. A good correlation of the data is easily achieved. For low temperatures only the saturation pressure of the oil, that can be easily measured, is needed to obtain a good representation of the experimental data. The binary interaction parameters are physically acceptable parameters to tune and no overtuning effects usually appear.

6. List of symbols

a equation of state parameter
b equation of state parameter
K_{ij} interaction parameter
Mw molecular weight
P pressure
Sg specific gravity
T temperature
V molar volume

Greek letters
ω acentric factor
Ω_a constant in the equation of state parameter a
Ω_b constant in the equation of state parameter b

Subscripts
c critical
i component i
j component j

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