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Predicting the Phase Equilibria of Synthetic Petroleum Fluids with the PPR78 Approach

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The PPR78 approach is a group contribution-based thermodynamic model which combines at constant packing fraction the Peng–Robinson equation of state and a Van Laar-type g^E model. This article demonstrates that, using classical mixing rules (linear on b *and quadratic on* a*), the PPR78 model may also be seen as a group contribution method for the estimation of the temperature-dependent* k_{ij} *of the widely used PR EoS. Our model is endowed of 15 groups and it is possible to predict the* k_{ij} *for any mixture containing alkanes, aromatics, naphthenes, CO_2, N_2, H_2S, and mercaptans. This study exhibits the capability of this approach to predict the phase behavior of synthetic petroleum fluids containing components of different volatilities. The many comparisons between calculated and experimental data on natural gases, crude oils, and gas condensates allow concluding that the PPR78 approach is a successful model for phase equilibria calculations of this kind of mixtures.* © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 3225–3235, 2010

Keywords: petroleum fluids, equation of state, vapor-liquid equilibrium, predictive model, binary interaction parameters

Introduction

Today, the synthesis design and optimization of the processes are carried out with the help of process simulators (ProSim, PRO/II, ASPEN, …). It is however well known that the accuracy of the simulated results mainly depends on the quality of the thermodynamic model. In most cases, the phase behavior of multicomponent systems for which nearly no data are available has to be known. The phase behavior can obviously be measured, but measurements are very time consuming. This is why modern process design requires models capable of (i) predicting the equilibrium properties without the preliminary use of experimental data (ii) yielding accurate results in both the subcritical and critical regions. Simultaneous fulfillment of these requirements is a very difficult and challenging task for a thermodynamic model. Dealing with petroleum fluids, many difficulties appear. Indeed, such mixtures contain a huge number of various compounds, such as paraffins, naphthenes, aromatics, gases (CO_2, H_2S, N_2, …), mercaptans and so on. A proper representation involves to accurately quantifying the interactions between each pair of molecules, which is obviously becoming increasingly difficult if not impossible as the number of molecules is growing. To avoid such a fastidious work, an alternative solution lies in using a predictive model, able to estimate the interactions from mere knowledge of the structure of molecules within the petroleum blend. To build such a model, we have combined at constant packing fraction the 1978 version of the Peng–Robinson[1] (PR) equation of state (EoS) and a Van Laar-type g^E function. The binary interaction parameters of the g^E model are calculated by a group contribution method (GCM) to make the model predictive.[2–14] As explained in this article, this approach may

Additional Supporting Information may be found in the online version of this article.

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equivalently be seen as a GCM to estimate the temperature-dependent k_{ij} of the widely used PR EoS working with classical mixing rules (linear on b and quadratic on a). This model has been called PPR78 (predictive, 1978 PR EoS). A cubic EoS has been chosen because in process design, due to their low complexity and their high accuracy for nonpolar compounds, such EoS allow for fast screening of a large number of design alternatives and preselection of the most favorable candidate structures. A GCM has been chosen to estimate the binary interaction parameters because we were aware that the group contribution concept could be useful to model complex processes like those involving supercritical fluids[15–17] and because the number of binary systems for which phase equilibrium data are available is at most several thousands while the number of the compounds used now by industry is estimated at around 100,000. It is thus necessary to be able to predict the binary interactions from the mere knowledge of the molecular structure. In product design, the availability of reliable methods for equilibrium property prediction is also important because fast screening of alternative chemical structures allows for reaching the specification requirements of the market before the competition, thus saving time, money and expert knowledge.

In this article, the theoretical basis of the PPR78 model is for the first time explained. In a second part, the capability of this approach to predict the phase behavior of synthetic petroleum fluids is exhibited. We thus can say that this article is the culmination of the project development of the predictive PPR78 model. We are indeed convinced that a model must always be tested on mixtures of industrial interest. This is the reason why, we selected in the open literature, hundreds of mixtures for which fluid–fluid equilibrium data were reported. A large diversity of petroleum fluids (natural gases, gas condensates and crude oils) containing from three to several dozens of components was considered. The properties of petroleum fluids, including classical bubble point or dew point pressures but also complex gas injection experiments like swelling test or slim tube test were predicted with the PPR78 model. This article thus gives a fair idea of the efficiency of our model.

The PPR78 Model

In 1976, Peng and Robinson[18] published their well-known equation of state, called in this article PR76. In 1978, the same authors[1] published an improved version of their equation of state, which yields more accurate vapor pressure predictions for the heavy hydrocarbons than those obtained by using PR76. This improved equation is called PR78 in this article. For a pure component, the PR78 EoS is:

$$P = \frac{RT}{v - b_i} - \frac{a_i(T)}{v(v + b_i) + b_i(v - b_i)} \tag{1}$$

with

$$\begin{cases} R = 8.314472\,\mathrm{J\,mol^{-1}\,K^{-1}} \\ X = \dfrac{-1+\sqrt[3]{6\sqrt{2}+8}-\sqrt[3]{6\sqrt{2}-8}}{3} \approx 0.253076587 \\ b_i = \Omega_b \dfrac{RT_{c,i}}{P_{c,i}} \quad \text{with} \quad \Omega_b = \dfrac{X}{X+3} \approx 0.0777960739 \\ a_i = \Omega_a \dfrac{R^2T_{c,i}^2}{P_{c,i}}\left[1 + m_i\left(1 - \sqrt{\dfrac{T}{T_{c,i}}}\right)\right]^2 \quad \text{with} \quad \Omega_a = \dfrac{8(5X+1)}{49-37X} \approx 0.457235529 \\ \text{if } \omega_i \le 0.491 \quad m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \\ \text{if } \omega_i > 0.491 \quad m_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3 \end{cases} \tag{2}$$

where P is the pressure, R the gas constant, T the temperature, a and b are EoS parameters, v the molar volume, T_c the critical temperature, P_c the critical pressure and ω the acentric factor. In this article, the PR78 EoS is used. To apply such an EoS to mixtures, mixing rules are necessary to calculate the values of a and b of the mixtures. In our approach and to define a predictive model, the binary interaction parameters appearing in the mixing rules are calculated by GCM. The methodology used i.e., the complete derivation of the PPR78 (Predictive Peng–Robinson 1978) model is given with many details in the Supporting Information.

To sum up, the PPR78 model may be seen as the coupling at constant packing fraction of the PR78 EoS and a Van Laar-type g^E function. The used mixing rules which combine at constant packing fraction a cubic EoS and a g^E model are based on the zeroth-order approximation of Guggenheim's quasi-reticular model[19] as initially proposed by Péneloux et al.[20] The PPR78 approach is thus a so-called EoS/g^E model.[21] The following equations are used:

$$\begin{cases} \dfrac{a(T,\mathbf{x})}{b(\mathbf{x})} = \displaystyle\sum_{i=1}^{N} x_i \frac{a_i(T)}{b_i} - \frac{g_{res}^E}{C} \\ b(\mathbf{x}) = \displaystyle\sum_{i=1}^{N} x_i b_i \end{cases} \tag{3}$$

with

$$\frac{g_{res}^E}{C} = \frac{1}{2} \times \frac{\sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_i b_j E_{ij}(T)}{\sum_{j=1}^{N} b_j x_j} \quad \text{and} \quad C = \frac{\sqrt{2}}{2}\ln(1+\sqrt{2}) \approx 0.6232 \tag{4}$$

x_i represents the mole fraction of component i and N the number of components in the mixture. g_{res}^E is the residual part of the molar excess Gibbs energy when the pressure goes to infinity.

To obtain a predictive model, and to completely define the PPR78 model, we developed, following the previous works of Kehiaian et al.[22] and of Abdoul et al.,[23] a GCM to estimate the interaction parameters $E_{ij}(T)$ in Eq. 4. The following equation was used:

$$E_{ij}(T) = -\frac{1}{2}\sum_{k=1}^{N_g}\sum_{l=1}^{N_g}(\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl})A_{kl} \times \left(\frac{298.15}{T/K}\right)^{\left(\frac{B_{kl}}{A_{kl}} - 1\right)} \tag{5}$$

In Eq. 5, T is the temperature. N_g is the number of different groups defined by the method (for the time being, 15

groups are defined and $N_g = 15$). α_{ik} is the fraction of molecule i occupied by group k (occurrence of group k in molecule i divided by the total number of groups present in molecule i). $A_{kl} = A_{lk}$ and $B_{kl} = B_{lk}$ (where k and l are two different groups) are constant parameters determined in our previous studies[2–9] ($A_{kk} = B_{kk} = 0$) by minimizing the deviations between calculated and experimental VLE data from an extended binary systems data base containing more than 65,000 experimental data points (bubble points, dew points, azeotropic points and mixture critical points). Most of the binary experimental data available in the open literature have been collected. The experimental data on petroleum fluids presented in this article have not been used in the parameter estimation. For the 15 groups available, a total of 204 parameters (expressed in MPa) were determined. They are summarized in Table 1.

The PPR78 model may also be seen as a GCM to estimate the temperature-dependent k_{ij} (see Eqs. 6 and 7) of the widely used PR78 EoS working with classical mixing rules (linear on b and quadratic on a):

$$\begin{cases} a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \sqrt{a_i a_j}\left[1 - k_{ij}(T)\right] \\ b = \sum_{i=1}^{N} x_i b_i \end{cases} \tag{6}$$

$$k_{ij}(T) = \frac{-\frac{1}{2}\left[\sum_{k=1}^{N_g}\sum_{l=1}^{N_g}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})A_{kl}\times\left(\frac{298.15}{T/K}\right)^{\left(\frac{B_{kl}}{A_{kl}}-1\right)}\right] - \left(\frac{\sqrt{a_i(T)}}{b_i}-\frac{\sqrt{a_j(T)}}{b_j}\right)^2}{2\frac{\sqrt{a_i(T)\cdot a_j(T)}}{b_i\cdot b_j}} \tag{7}$$

This second view is very useful for someone having commercial software working with the PR EoS. As shown in one of our previous studies,[2] working with hydrocarbon binary mixtures, Eq. 7 is able to predict the different k_{ij} trends commonly encountered. Indeed, the k_{ij} may increase, decrease or go through with a minimum with respect to temperature and chain length.

By establishing a relation between E_{ij} of the Van Laar model (Eq. 4) and k_{ij} of the classical mixing rules (Eq. 6), the PPR78 model allows to define a theoretical expression for the binary interaction parameters k_{ij} and to build a bridge between the classical mixing rules and the EoS/g^E models.

Capability of the PPR78 Model to Predict the Phase Behavior of Synthetic Petroleum Fluids

In this section the capability of the PPR78 model to predict the phase behavior of synthetic petroleum fluids including gas injection experiments is exhibited. We decided to work on synthetic petroleum fluids to avoid any characterization of the heavy fractions[24–31] which inevitably influences the results of the calculations. In other words, the composition of all the fluids studied in this article is perfectly known. In this section, to use the PPR78 model, we need to allocate to each pure component a critical temperature, a critical pressure and an acentric factor (the k_{ij} are predicted by our GCM). The pure fluid physical properties (T_c, P_c, and ω) used in this study originate preferentially from Poling et al.[32] However when these informations are missing, the DIPPR[33] data bank was used. By the end, for heavy molecules not present in this data bank, the three parameters were determined by the GCM developed by Constantinou and Gani.[34–35] We found many experimental data on synthetic petroleum fluids. For sake of clarity, the petroleum fluids were divided in three families: the natural gases, the gas condensates and the crude oils. The prediction of gas injection experiments (swelling tests and slim tube tests) will be discussed before "Conclusion" section.

Predicting the phase behavior of natural gases

Parikh et al.'s fluid. In 1984, Parikh et al.[36] measured 14 bubble-point pressures, 20 dew-point pressures and the critical coordinates of a natural gas containing 85.11 mol % of methane, 10.07 mol % of ethane and 4.82 mol % of propane. As shown in Figure 1, this system is very well predicted by the PPR78 model. The maximum deviations between calculated and experimental pressures are located in the vicinity of the cricondenbar. The average absolute deviation on the whole data (34 pressures) is only 0.93 bar (i.e., 2.1%). The PPR78 model slightly overestimates the critical temperature of 1.3 K (0.6%) and the critical pressure of 2.6 bar (i.e., 3.7%).

Haynes' fluids. In 1982, Haynes[37] measured 71 bubble-point pressures for 17 mixtures containing between 3 and 8 components (nitrogen, methane, ethane, propane, isobutane, *n*-butane, isopentane, *n*-pentane). The detailed composition of these mixtures is given in Supporting Information Table S1. We thus can see that they all contain more than 70 mol % of methane. The bubble-point pressures are measured at low temperature (T < 135 K). The (P,T) phase envelopes of these systems were predicted with the PPR78 model (Supporting Information Figure S1). The average absolute deviation on the bubble-point pressures is 0.05 bar i.e., 2.3%. We can thus conclude that despite the low temperatures, our model is able to perfectly predict these data.

Yarborough et al.'s fluids. In 1970, working on 45 different natural gases containing between 2 and 7 components (N_2, CO_2, methane, ethane, propane, *n*-butane, *n*-pentane), Yarborough et al.[38] measured 52 bubble and dew-point pressures. The composition of these natural gases is given in Supporting Information Table S2. The 45 (P,T) phase envelopes are not shown in this article but can be seen in Romain Privat's Ph.D. thesis manuscript.[39] The PPR78 model is able to predict these 52 pressures with an absolute average deviation of 2.0 bar (i.e., 3.2%) which is certainly close to the experimental uncertainty.

Davis et al.*'s fluids.* In their article from 1954, Davis et al.,[40] working on seven natural gases called A-1, A-2, A-3, A-4, AB-1, AB-2, and AB-3 measured 54 bubble and

Table 1. Group interaction parameters: ($A_{kl} = A_{lk}$)/MPa and ($B_{kl} = B_{lk}$)/MPa

	CH_3 (group 1)	CH_2 (group 2)	CH (group 3)	C (group 4)	CH_4 (group 5)	C_2H_6 (group 6)	CH_{aro} (group 7)	C_{aro} (group 8)	$C_{fused\ aromatic\ rings}$ (group 9)	$CH_{2,cyclic}$ (group 10)	CH_{cyclic} or C_{cyclic} (group 11)	CO_2 (group 12)	N_2 (group 13)	H_2S (group 14)	SH (group 15)
CH_3 (group 1)	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–
CH_2 (group 2)	$A_{12} = 74.81$ $B_{12} = 165.7$	0	–	–	–	–	–	–	–	–	–	–	–	–	–
CH (group 3)	$A_{13} = 261.5$ $B_{13} = 388.8$	$A_{23} = 51.47$ $B_{23} = 79.61$	0	–	–	–	–	–	–	–	–	–	–	–	–
C (group 4)	$A_{14} = 396.7$ $B_{14} = 804.3$	$A_{24} = 88.53$ $B_{24} = 315.0$	$A_{34} = -305.7$ $B_{34} = -250.8$	0	–	–	–	–	–	–	–	–	–	–	–
CH_4 (group 5)	$A_{15} = 32.94$ $B_{15} = -35.00$	$A_{25} = 36.72$ $B_{25} = 108.4$	$A_{35} = 145.2$ $B_{35} = 301.6$	$A_{45} = 263.9$ $B_{45} = 531.5$	0	–	–	–	–	–	–	–	–	–	–
C_2H_6 (group 6)	$A_{16} = 8.579$ $B_{16} = -29.51$	$A_{26} = 31.23$ $B_{26} = 84.76$	$A_{36} = 174.3$ $B_{36} = 352.1$	$A_{46} = 333.2$ $B_{46} = 203.8$	$A_{56} = 13.04$ $B_{56} = 6.863$	0	–	–	–	–	–	–	–	–	–
CH_{aro} (group 7)	$A_{17} = 90.25$ $B_{17} = 146.1$	$A_{27} = 29.78$ $B_{27} = 58.17$	$A_{37} = 103.3$ $B_{37} = 191.8$	$A_{47} = 158.9$ $B_{47} = 613.2$	$A_{57} = 67.26$ $B_{57} = 167.5$	$A_{67} = 41.18$ $B_{67} = 50.79$	0	–	–	–	–	–	–	–	–
C_{aro} (group 8)	$A_{18} = 62.80$ $B_{18} = 41.86$	$A_{28} = 3.775$ $B_{28} = 144.8$	$A_{38} = 6.177$ $B_{38} = -33.97$	$A_{48} = 79.61$ $B_{48} = -326.0$	$A_{58} = 139.3$ $B_{58} = 464.3$	$A_{68} = -3.088$ $B_{68} = 13.04$	$A_{78} = -13.38$ $B_{78} = 20.25$	0	–	–	–	–	–	–	–
$C_{fused\ aromatic\ rings}$ (group 9)	$A_{19} = 62.80$ $B_{19} = 41.86$	$A_{29} = 3.775$ $B_{29} = 144.8$	$A_{39} = 6.177$ $B_{39} = -33.97$	$A_{49} = 79.61$ $B_{49} = -326.0$	$A_{59} = 139.3$ $B_{59} = 464.3$	$A_{69} = -3.088$ $B_{69} = 13.04$	$A_{79} = -13.38$ $B_{79} = 20.25$	$A_{89} = 0.0$ $B_{89} = 0.0$	0	–	–	–	–	–	–
$CH_{2,cyclic}$ (group 10)	$A_{1-10} = 40.38$ $B_{1-10} = 95.90$	$A_{2-10} = 12.78$ $B_{2-10} = 28.37$	$A_{3-10} = 101.9$ $B_{3-10} = -90.93$	$A_{4-10} = 177.1$ $B_{4-10} = 601.9$	$A_{5-10} = 36.37$ $B_{5-10} = 26.42$	$A_{6-10} = 8.579$ $B_{6-10} = 76.86$	$A_{7-10} = 29.17$ $B_{7-10} = 69.32$	$A_{8-10} = 34.31$ $B_{8-10} = 95.39$	$A_{9-10} = 34.31$ $B_{9-10} = 95.39$	0	–	–	–	–	–
CH_{cyclic} or C_{cyclic} (group 11)	$A_{1-11} = 98.48$ $B_{1-11} = 231.6$	$A_{2-11} = -54.90$ $B_{2-11} = -319.5$	$A_{3-11} = -226.5$ $B_{3-11} = -51.47$	$A_{4-11} = 17.84$ $B_{4-11} = -109.5$	$A_{5-11} = 40.15$ $B_{5-11} = 255.3$	$A_{6-11} = 10.29$ $B_{6-11} = -52.84$	$A_{7-11} = -26.42$ $B_{7-11} = -789.2$	$A_{8-11} = -105.7$ $B_{8-11} = -286.5$	$A_{9-11} = -105.7$ $B_{9-11} = -286.5$	$A_{10-11} = -50.10$ $B_{10-11} = -891.1$	0	–	–	–	–
CO_2 (group 12)	$A_{1-12} = 164.0$ $B_{1-12} = 269.0$	$A_{2-12} = 136.9$ $B_{2-12} = 254.6$	$A_{3-12} = 184.3$ $B_{3-12} = 762.1$	$A_{4-12} = 287.9$ $B_{4-12} = 346.2$	$A_{5-12} = 137.3$ $B_{5-12} = 194.2$	$A_{6-12} = 135.5$ $B_{6-12} = 239.5$	$A_{7-12} = 102.6$ $B_{7-12} = 161.3$	$A_{8-12} = 110.1$ $B_{8-12} = 637.6$	$A_{9-12} = 267.3$ $B_{9-12} = 444.4$	$A_{10-12} = 130.1$ $B_{10-12} = 225.8$	$A_{11-12} = 91.28$ $B_{11-12} = 82.01$	0	–	–	–
N_2 (group 13)	$A_{1-13} = 52.74$ $B_{1-13} = 87.19$	$A_{2-13} = 82.28$ $B_{2-13} = 202.8$	$A_{3-13} = 365.4$ $B_{3-13} = 521.9$	$A_{4-13} = 263.9$ $B_{4-13} = 772.6$	$A_{5-13} = 37.90$ $B_{5-13} = 37.20$	$A_{6-13} = 61.59$ $B_{6-13} = 84.92$	$A_{7-13} = 185.2$ $B_{7-13} = 490.6$	$A_{8-13} = 284.0$ $B_{2-13} = 1892$	$A_{9-13} = 718.1$ $B_{9-13} = 1892$	$A_{10-13} = 179.5$ $B_{10-13} = 546.6$	$A_{11-13} = 100.9$ $B_{11-13} = 249.8$	$A_{12-13} = 98.42$ $B_{12-13} = 221.4$	0	–	–
H_2S (group 14)	$A_{1-14} = 158.4$ $B_{1-14} = 241.2$	$A_{2-14} = 134.6$ $B_{2-14} = 138.3$	$A_{3-14} = 193.9$ $B_{3-14} = 307.8$	$A_{4-14} = 305.1$ $B_{4-14} = -143.1$	$A_{5-14} = 181.2$ $B_{5-14} = 288.9$	$A_{6-14} = 157.2$ $B_{6-14} = 217.1$	$A_{7-14} = 21.96$ $B_{7-14} = 13.04$	$A_{8-14} = 1.029$ $B_{8-14} = -8.579$	$A_{9-14} = 1.029$ $B_{9-14} = -8.579$	$A_{10-14} = 120.8$ $B_{10-14} = 163.0$	$A_{11-14} = -16.13$ $B_{11-14} = -147.6$	$A_{12-14} = 134.9$ $B_{12-14} = 201.4$	$A_{13-14} = 319.5$ $B_{13-14} = 550.1$	0	–
SH (group 15)	$A_{1-15} = 799.9$ $B_{1-15} = 2109$	$A_{2-15} = 459.5$ $B_{2-15} = 627.3$	$A_{3-15} = 425.5$ $B_{3-15} = 514.7$	$A_{4-15} = 682.9$ $B_{4-15} = 1544$	$A_{5-15} = 706.0$ $B_{5-15} = 1483$	**N.A.**(*)	$A_{7-15} = 285.5$ $B_{7-15} = 392.0$	$A_{8-15} = 1072$ $B_{8-15} = 1094$	$A_{9-15} = 1072$ $B_{9-15} = 1094$	$A_{10-15} = 446.1$ $B_{10-15} = 549.0$	$A_{11-15} = 411.8$ $B_{11-15} = -308.8$	**N.A.**(*)	**N.A.**(*)	$A_{14-15} = -77.21$ $B_{14-15} = 156.1$	0

(*)NA, not available.

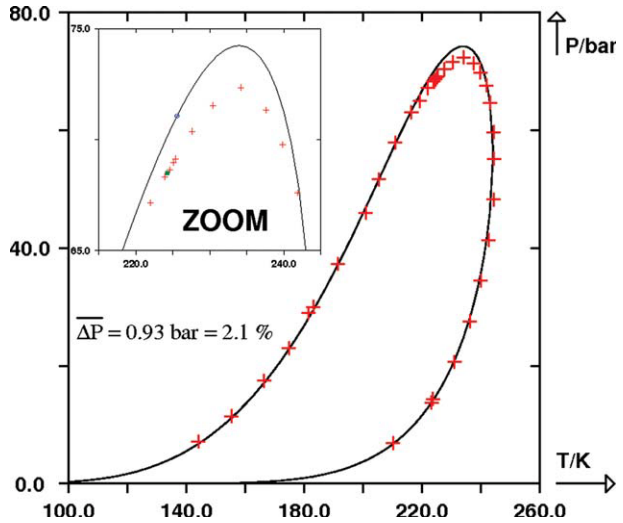

Figure 1. Solid line: (P,T) phase envelope of Parikh et al.'s synthetic natural gas predicted with the PPR78 model.

+: experimental dew and bubble-point pressures. ■: experimental critical point. ○: predicted critical point. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

upper dew point-pressures. These gases contain CO_2, N_2, alkanes up to n-C_6 and a very small amount (less than 0.2%) of an undefined C_7+ fraction. In this study, we decided to distribute this small quantity over the other components. Doing so, the compositions of the seven fluids are those given in Supporting Information Table S3. The average absolute deviation between experimental and predicted pressures is 1.7 bar, i.e., 3.3%. Supporting Information Figure S2 clearly demonstrates the high accuracy of the prediction.

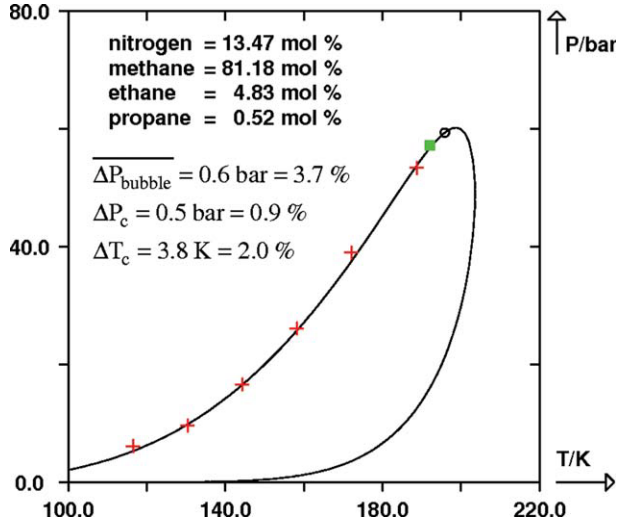

Figure 2. Solid line: (P,T) phase envelope of Oscarson and Saxey's fluid predicted with the PPR78 model.

+: experimental bubble-point pressures. ■: experimental critical point. ○: predicted critical point. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

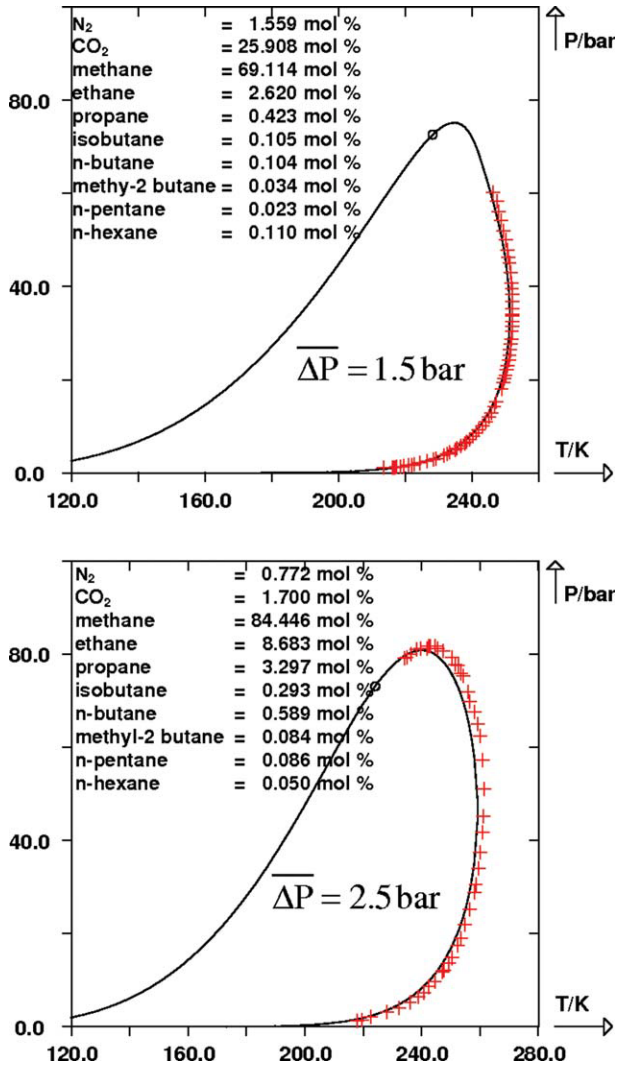

Figure 3. Solid line: (P,T) phase envelopes of Jarne et al.'s natural gases predicted with the PPR78 model.

+: experimental upper and lower dew-point pressures. ○: predicted critical point. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Oscarson and Saxey's fluid. Working for the Gas Processors Association, Oscarson and Saxey[41] measured in 1982 six bubble-point pressures and the critical coordinates of a natural gas the composition of which is given in Figure 2. This gas contains nitrogen, methane, ethane and propane. As shown in Figure 2, the PPR78 model is able to perfectly predict these data. In particular, the critical temperature is predicted with an average deviation of 2% and the deviation on the critical pressure is less than 1%.

Jarne et al.*'s fluids.* In 2004, Jarne et al.[42] measured 110 upper and lower dew-point pressures for two natural gases containing nitrogen, carbon dioxide and alkanes up to n-C_6. The composition of the fluids and the accuracy of the PPR78 model can be seen in Figure 3. The average deviation on these 110 pressures is only 2.0 bar. This is an extremely good result because many data points are located in the

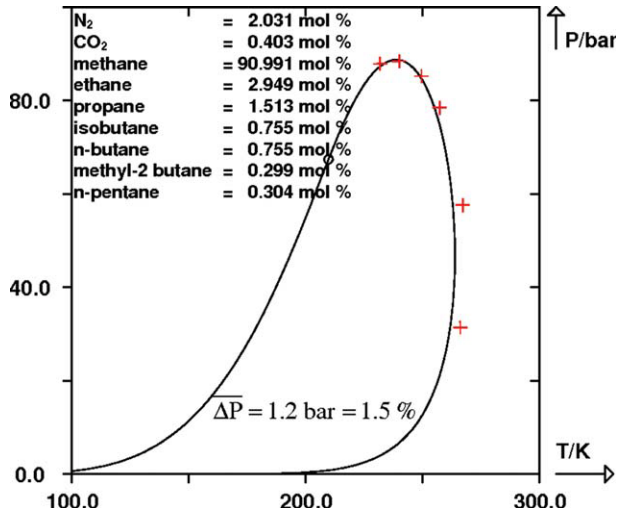

Figure 4. Solid line: (P,T) phase envelopes of Zhou et al.'s natural gas predicted with the PPR78 model.

+: experimental upper and lower dew-point pressures. ○: predicted critical point. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vicinity of the cricondentherm where the slope of the dew curve is very steep.

Zhou et al.*'s fluid.* In 2006, Zhou et al.[43] measured 6 dew point-pressures for a natural gas containing N_2, CO_2, and 7 alkanes. Figure 4 puts in evidence that with an average deviation lower than 1.2 bar (i.e., 1.5%), the PPR78 model is able to accurately predict these data.

Gonzalez and Lee's fluids. In 1968, Gonzalez and Lee[44] measured 146 bubble and dew-point pressures for six systems containing nitrogen and light *n*-alkanes. The composition of these six fluids is given in Supporting Information Table S4. The corresponding predicted phase envelopes can be seen in Supporting Information Figure S3. This figure outlines that fluids 1, 3, and 4 are predicted very accurately. Fluid 5 shows some deviations on the dew-point curve. However our model leads to poor results to predict the dew-point curve of fluids 2 and 6 (the bubble-point curve is predicted with accuracy). These 2 fluids (2 and 6) are the heaviest ones since they contain small amounts of *n*-hexane. The calculated dew-point pressures are much higher than the experimental values meaning that the fluid is too heavy. Values close to experimental data can be obtained by reducing the amount of *n*-hexane. As an example by reducing the amount of *n*-hexane from 2.3% to 0.65% in fluid 2, much better

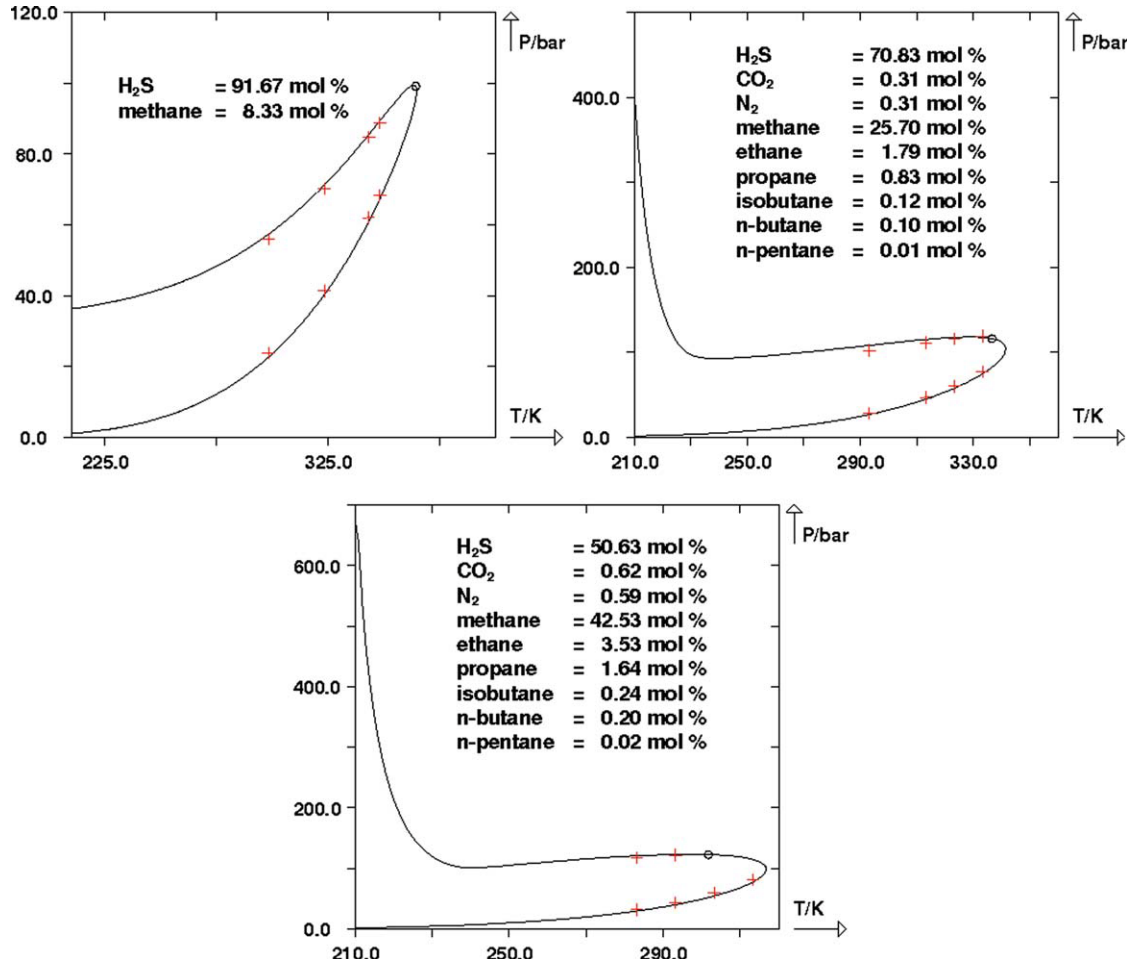

Figure 5. Solid line: (P,T) phase envelopes of Gu et al.'s natural gases predicted with the PPR78 model.

+: experimental bubble and dew-point pressures. ○: predicted critical point. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

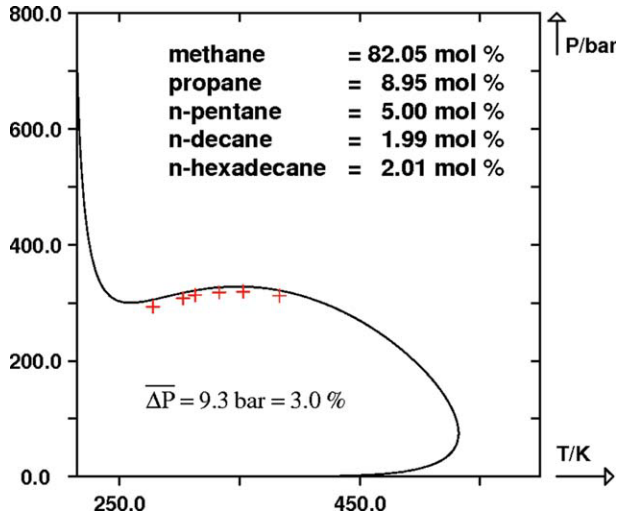

Figure 6. Solid line: (P,T) phase envelope of Gozalpour et al.'s gas condensates predicted with the PPR78 model.

+: experimental dew-point pressures. ○: predicted critical point. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

results are obtained (see the dashed curve in Supporting Information Figure S3).

Gu et al.'s fluids. In 1993, Gu et al.[45] measured 10 bubble-point pressures and 12 dew-point pressures for three mixtures. The first one is simply a methane + H_2S binary system but the two others are high H_2S-content natural gas mixtures. The prediction of these three systems with the PPR78 model along with the composition of the fluids can be seen in Figure 5. Once again, very accurate results are obtained with the PPR78 model. Indeed the average absolute deviation between experimental and predicted pressures is 2.3 bar (i.e., 3.6%).

Predicting the phase behavior of gas condensates

Jensen et al.'s fluids. In 2003, Jensen et al.[46] measured four bubble and 27 dew-point pressures for three synthetic gas condensates. These fluids have the same amount of methane, *n*-pentane, methyl-2 butane and *n*-hexane. These four components represent 99.5 mol % of the total composition. The remaining 0.5 mol % is pure tetracosane, pure naphthalene or a mixture of both. As shown in Supporting Information Figure S4, the addition of a small amount of a very heavy hydrocarbon makes drastically increase the dew-point pressures. Such data points are thus particularly difficult to predict. Although not able to predict very accurately these data, the PPR78 leads to an average deviation between experimental and predicted pressures of 15 bar (i.e. 7.7%) which is reasonable taking into account the difficulties to model such systems.

Gozalpour et al.*'s fluid.* In 2003, Gozalpour et al.[47] measured six dew point-pressures for a gas condensate containing five normal alkanes ranging from methane to *n*-hexadecane. Figure 6 puts in evidence that with an average deviation of 9.3 bar (i.e. 3.0%), the PPR78 model is able to accurately predict these data.

Predicting the phase behavior of crude oils

Fenghour et al.'s fluids. In 2001, Fenghour et al.[48,49] measured six bubble-point pressures for three ternary and for three quaternary systems containing *n*-alkanes ranging from methane to *n*-hexadecane. The six corresponding (*P*,*T*) phase envelopes predicted by the PPR78 model can be seen in Supporting Information Figure S5. From this figure, it is clear that the PPR78 model is able to perfectly predict these data. Indeed, the average deviation between calculated and experimental data is only 0.5 bar (1.8%).

Cramer and Swift's fluids. In 1985, Cramer and Swift[50] measured at T/K = 344, the bubble-point pressure for 22 multicomponent mixtures (the number of components varies between 2 and 5) containing between 58 and 78.2 mol % of CO_2. The other components are the *n*-butane, the *n*-decane, the *n*-butyl cyclohexane and the *n*-butyl benzene. The molar composition of these 22 fluids is given in Supporting Information Table S5. The 22 (*P*,*T*) phase envelopes are not shown in this article but can be seen in Romain Privat's Ph.D. thesis manuscript.[39] The PPR78 model is able to predict these 22 pressures with an absolute average deviation of 2.9 bar (i.e., 3.0%) which is promising.

The 32 fluids of Peng and Robinson. In 1977, Peng and Robinson[51] used their EoS to calculate the critical coordinates of 32 fluids for which the critical temperature and the critical pressure were known experimentally. The molar composition of these 32 fluids is given in Supporting Information Table S6. The corresponding (P,T) phase envelopes can be seen in Romain Privat's Ph.D. thesis manuscript.[39] In every instance the critical coordinates are accurately predicted with the PPR78 model. Indeed, the average deviations on the critical temperatures and pressures are:

$$\begin{cases} \overline{\Delta T_c} = 3.0\,\mathrm{K} = 0.91\% \\ \overline{\Delta P_c} = 1.8\,\mathrm{bar} = 2.2\% \end{cases}.$$

We can thus conclude that by using a cubic EoS and temperature-dependent k_{ij}, it is possible to calculate with accuracy the critical points of complex systems containing few-polar components.

Wiese et al.*'s fluids.* In 1970, Wiese et al.[52] measured 61 bubble-point pressures and 61 dew-point pressures on 122 ternary systems containing methane + propane + *n*-decane. Unfortunately, it is not always possible from the article of Wiese et al. to know whether the dew-point pressures are upper or lower dew-point pressures. Indeed, in the vicinity of the cricondentherm these two pressures can be extremely close. To avoid any mistake, only 54 dew-point pressures were predicted with the PPR78 model (those for which there was no ambiguity). 115 pressures were thus considered (61 bubble-point and 54 dew-point pressures). The composition of the corresponding 115 ternary systems is given in Supporting Information Table S7. The average deviation on the bubble-point pressures is 3.0 bar (i.e., 2.2%) which is very accurate. However, the average deviation on the dew-point pressures reaches 11 bar (i.e., 11%) which is not really satisfactory. The corresponding (P,T) phase envelopes can be seen in Romain Privat's Ph.D. thesis manuscript.[39]

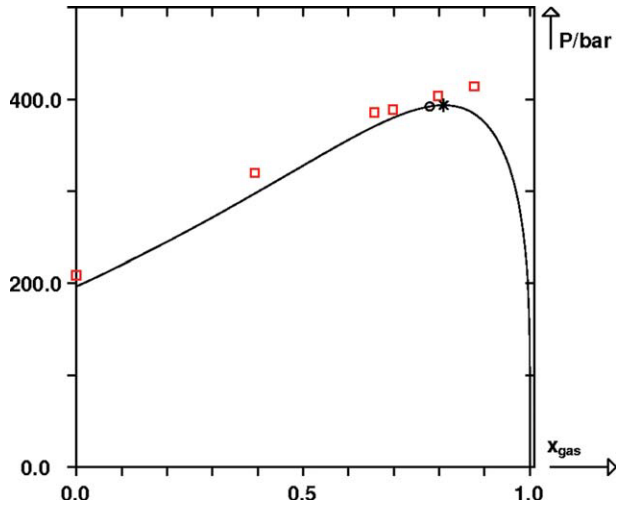

Figure 7. Solid line: variation of mixture saturation pressure with added gas to a crude oil (swelling test performed by Ruffier-Meray et al.) predicted with the PPR78 model (see Supporting Information Table S8).

□: experimental bubble-point and dew-point pressures. ○: predicted critical point. ∗: predicted FCMMP (first contact minimum miscibility pressure–top of the curve). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Predicting gas injection experiments

Swelling test performed by Ruffier-Meray et al. In 1998, Ruffier-Meray et al.[53] performed a swelling test[27] by injecting a lean gas in a synthetic crude oil. The composition of the two fluids is given in Supporting Information Table S8. In this kind of experiment, a known amount of oil is loaded into an equilibrium cell and the injection gas is progressively added to the oil stepwise. After each addition of the gas, the mixture saturation pressure is measured. Ruffier-Meray et al. indicate that the four first pressures they measured are bubble-point pressures and that the last two ones are dew-point pressures. As shown in Figure 7, this is exactly what predicts the PPR78 model. Moreover, our model is able to predict these pressures with an average deviation lower than 5% which is really enthusiastic for so complex systems. Indeed, the crude oil contains small amounts of very heavy components (n-C_{20}, n-C_{24} or squalane) and we know that the addition of small amounts of heavy molecules drastically changes the saturation pressure.

Swelling tests performed by Turek et al. In 1984, Turek et al.[54] performed swelling tests at two temperatures on a crude oil containing 10 n-alkanes ranging from methane to n-tetradecane. The injected gas is pure CO_2. 22 mixture saturation pressures were measured. The composition of the crude oil along with the accuracy of the PPR78 model to predict these data are shown in Figure 8. With an average deviation of 2.8 bar (i.e., 2.3%), we can conclude that our model is able to predict these data with high accuracy. It is here important to recall that no parameter is fitted on the experimental data.

Swelling test performed by Danesh et al. In 1991, Danesh et al.[55] measured four bubble-point pressures on four synthetic crude oils containing 25 components (mixtures of paraffins, naphthenes and aromatics). The composition of these four fluids is given in Supporting Information Table S9. As shown in Supporting Information Figure S6, the PPR78 model is able to predict these four pressures with an average deviation of 9.9 bar (i.e. 4.2%). This is promising since these fluids have a composition very close to real crude oils. Moreover, a swelling test has been conducted on the first crude oil. The composition of the injected gas is also given in Supporting Information Table S9. Six mixture saturation pressures were measured. They are predicted with an average deviation of 6.9 bar (i.e. 3.0%) (see Figure 9). Once again, we can consider this deviation as small.

Slim tube tests performed by Yang et al. In 2007, Yang et al.[56] performed slim tube tests at two temperatures to

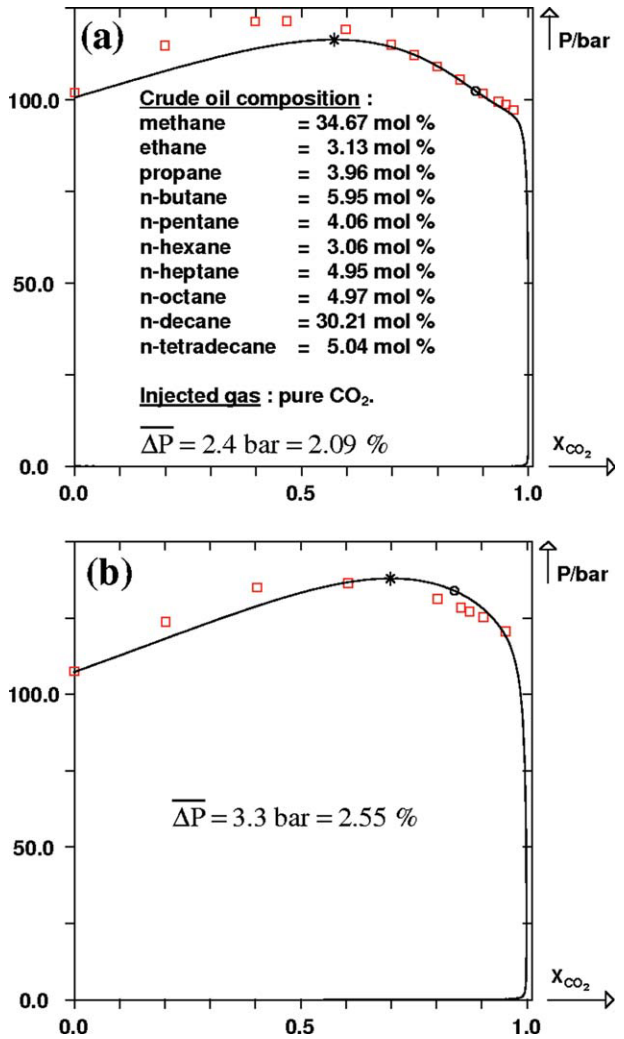

Figure 8. Solid line: variation of mixture saturation pressure with added CO_2 to a synthetic crude oil (swelling test performed by Turek et al.) predicted with the PPR78 model.

a) T/K = 322 and b) T/K = 338.7. □: experimental bubble-point and dew-point pressures. ○: predicted critical point. ∗: predicted FCMMP (first contact minimum miscibility pressure–top of the curve). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

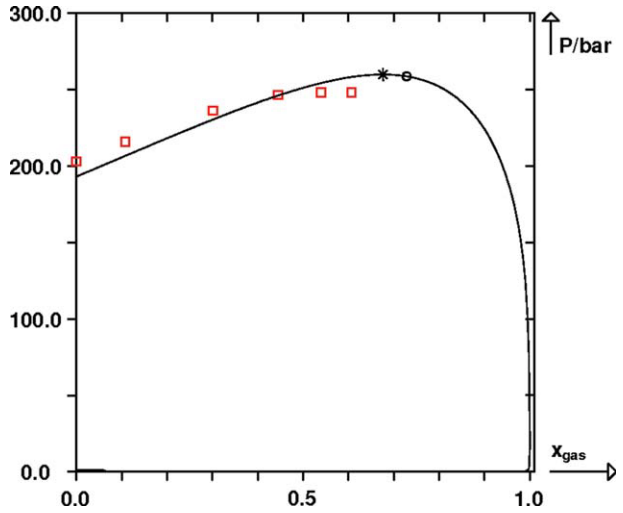

Figure 9. Solid line: variation of mixture saturation pressure with added gas to a crude oil (swelling test performed by Danesh et al.) predicted with the PPR78 model (see Supporting Information Table S9).

□: experimental bubble-point and dew-point pressures. ○: predicted critical point. ∗: predicted FCM MP (first contact minimum miscibility pressure–top of the curve). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

determine the minimum miscibility pressure[57–62] (MMP) when pure CO_2 is injected in a synthetic crude oil, the composition of which is: 43 mol % of *n*-pentane + 57 mol % of *n*-hexadecane. These two temperatures are $T_1 = 313.15$ K and $T_2 = 323.15$ K. The corresponding experimental values are:

$$\mathrm{MMP}_{\mathrm{exp}}(T_1) = 86.3 \text{ bar} \quad \text{and} \quad \mathrm{MMP}_{\mathrm{exp}}(T_2) = 104.8 \text{ bar}.$$

The predicted values with the PPR78 model are:

$$\mathrm{MMP}_{\mathrm{PPR78}}(T_1) = 82 \text{ bar} \quad \text{and} \quad \mathrm{MMP}_{\mathrm{PPR78}}(T_2) = 103 \text{ bar}.$$

As a consequence, the PPR78 model is able to predict these MMPs with high accuracy (4% deviation at T_1 and 0.7% deviation at T_2). This is extremely encouraging since we know that these critical pressures (MMPs) are particularly difficult to predict.

Conclusion

The PPR78 approach is a group contribution-based thermodynamic model which combines at constant packing fraction the Peng–Robinson (PR) equation of state (EoS) and a Van Laar-type g^E model. However, by using classical mixing rules (linear on *b* and quadratic on *a*), the PPR78 model may also be seen as a GCM for the estimation of the temperature-dependent k_{ij} of the widely used PR EoS.

For the time being, 15 groups are defined: CH_3, CH_2, CH, C, CH_4 (methane), C_2H_6 (ethane), CH_{aro}, C_{aro}, $C_{fused\ aromatic\ rings}$, $CH_{2,cyclic}$, CH_{cyclic} or C_{cyclic}, CO_2, N_2, H_2S, and SH. It is thus today possible to estimate the Van Laar parameters (E_{ij}) or the k_{ij} (involved with the classical Van der Waals's mixing rules) for any mixture containing alkanes, aromatics, naphthenes, CO_2, N_2, H_2S, and mercaptans whatever the temperature. Our model is thus ready to predict the properties of petroleum fluids.

In this article we have successfully applied the PPR78 model to mixtures of natural gases, gas condensates and crude oils. In most cases, good and even very good agreement is achieved for phase equilibrium properties when compared to experimental data.

In the open literature there however exists many EoS/g^E models, all derived by equating the excess Gibbs energy from a liquid phase activity coefficient model with the corresponding term from an EoS at a reference pressure. The most well known are those developed by Huron and Vidal,[21] MHV1,[63] MHV2,[64] PSRK,[65] Wong-Sandler,[66] LCVM,[67] VTPR,[68,69] UMR-PR.[70] It is not possible in this article to compare all these models with the proposed PPR78. We however can say that working with long chain alkanes, the PPR78 model leads to much better results than those obtained with the best EOS/g^E models (e.g., LCVM and MHV2). These comparisons can be found in our first article on PPR78.[2]

In conclusion, the PPR78 model is a simple, accurate, flexible and reliable thermodynamic model, appropriate for the prediction of the phase behavior of multicomponent systems. This is why it is today routinely used in petroleum companies like TOTAL and integrated in commercial simulators of industrial processes like PROSIM (the PPR78 model will be available in PRO/II in a few months).

Acknowledgments

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