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PPR78, a thermodynamic model for the prediction of petroleum fluid-phase behaviour

R. Privat and J.-N. Jaubert

ENSIC – LRGP (UPR CNRS 3349), 1 rue Grandville – BP20451 – 54001 Nancy Cedex - France

Abstract. Nowadays, design and optimization of chemical engineering processes are carried out using process simulators. However, the accuracy of the obtained results strongly depends on the choice of an appropriate thermodynamic model. In most of the cases, chemical engineers need information about phase equilibria of multicomponent systems for which few or no data are available. It is thus essential to dispose of a reliable thermodynamic model (i) predicting the equilibrium properties without the preliminary use of experimental data; (ii) yielding accurate results in both the sub-critical and critical regions. In order to meet these challenges, the predictive thermodynamic model PPR78 is developed since 2004. This equation of state combines the model proposed by Peng and Robinson in 1978 with classical Van der Waals mixing rules involving a temperature-dependent binary interaction parameter $k_{ij}(T)$. These k_{ij} coefficients are predicted by PPR78 from the mere knowledge of chemical structures of molecules within the mixture. Today, the PPR78 model is able to represent the fluid phase behaviour of any fluid containing alkanes, alkenes, aromatic compounds, cycloalkanes, permanent gases (CO_2, N_2, H_2S, H_2), mercaptans and water. In order to test the predictive capabilities of the PPR78 model, fluid phase behaviour of synthetic petroleum fluids including natural gases, gas condensate, crude oils etc. were predicted. In many cases, the PPR78 model allows a fine prediction of fluid phase behaviours with an accuracy close to the experimental uncertainty.

1 Introduction

Today, and still for a long time, petroleum mixtures are an essential raw material feeding most of chemical industries and daily impacting lives of people. Their thermodynamic description is an essential issue for the design and the simulation of several thousands processes. However, dealing with petroleum fluids, several 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 proposed a group-contribution method (GCM) to estimate the temperature-dependent k_{ij} of the widely used Peng-Robinson (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 non-polar compounds, such EoS allow for fast screening of a large number of design alternatives and pre-selection of the most favorable candidate structures. A GCM has been developed 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 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 paper, aimed at showing the predictive capacity of the PPR78 model, we considered a large diversity of petroleum fluids (natural gases, gas condensates and crude oils) containing from three to several dozens of components. 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 our model, thus giving a fair idea of its efficiency.

2 The PPR78 model

In 1976, Peng and Robinson [1] published their well-known equation of state, called in this paper PR76. In 1978, the same authors [2] 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 paper. For a pure component, the PR78 EoS writes:

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

with:

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

where P is the pressure, R the gas constant, T the temperature, a and b are EoS parameters, v is the molar volume, T_c the critical temperature, P_c the critical pressure and ω the acentric factor. In this paper, 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 in order to define a predictive model, the binary interaction parameters k_{ij} appearing in the mixing rules are calculated by a GCM.

More concretely, the PPR78 combines the widely used PR78 EoS with classical Van der Waals mixing rules:

$$\left\{\begin{array}{l} a = \displaystyle\sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \sqrt{a_i a_j} \left[1 - k_{ij}(T)\right] \\ b = \displaystyle\sum_{i=1}^{N} x_i b_i \end{array}\right. \tag{3}$$

with:

$$k_{ij}(T) = \frac{E_{ij} - \left(\dfrac{\sqrt{a_i(T)}}{b_i} - \dfrac{\sqrt{a_j(T)}}{b_j}\right)^2}{2\dfrac{\sqrt{a_i(T) \cdot a_j(T)}}{b_i \cdot b_j}}$$

$$with\ E_{ij} = -\frac{1}{2}\left[\sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \cdot \left(\frac{298.15}{T/K}\right)^{\left(\frac{B_{kl}}{A_{kl}} - 1\right)}\right] \tag{4}$$

In Eq. (4), T is the temperature. N_g is the number of different groups defined by the method (in this paper, the first fifteen groups are considered 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 ($A_{kk} = B_{kk} = 0$) by minimizing the deviations between calculated and experimental VLE data from an extended binary systems data base containing more than 65,000 azeotropic points and mixture critical points). These aspects are carefully explained by Jaubert et al. [3-5], Privat et al. [6-9] and Vitu et al. [10, 11].

Most of the binary experimental data available in the open literature have been collected. The experimental data on petroleum fluids presented in this paper have not been used in the parameter estimation. For the 15 groups available, a total of 204 parameters were thus determined.

3 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 in order to avoid any characterization of the heavy fractions which inevitably influences the results of the calculations. In other words, the composition of all the fluids studied in this paper is perfectly known. In this section, in order 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. [12]. However when such information is missing, the DIPPR data bank (Design Institute for Physical Property Data, DIADEM 2009) 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 et al. [13, 14]. 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.

2.1 Predicting the phase behavior of natural gases

2.1.1 Parikh et al.'s fluid

Parikh et al. [15] 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.a, 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 %).

2.1.2 Oscarson et al.'s fluid

Working for the Gas Processors Association, Oscarson et al. [16] measured six bubble-point pressures and the critical coordinates of a natural gas the composition of which is given in Figure 1.b. This gas contains nitrogen, methane, ethane and propane. As shown in Figure 1.b, 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 %.

2.1.3 Jarne et al.'s fluid

Jarne et al. [17] 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 one of these fluids and the accuracy of the PPR78 model can be seen in Figure 2.a. 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 vicinity of the cricondentherm where the slope of the dew curve is very steep.

2.1.4 Zhou et al.'s fluid

Zhou et al. [18] measured 6 dew point-pressures for a natural gas containing N_2, CO_2 and 7 alkanes. Figure 2.b 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.

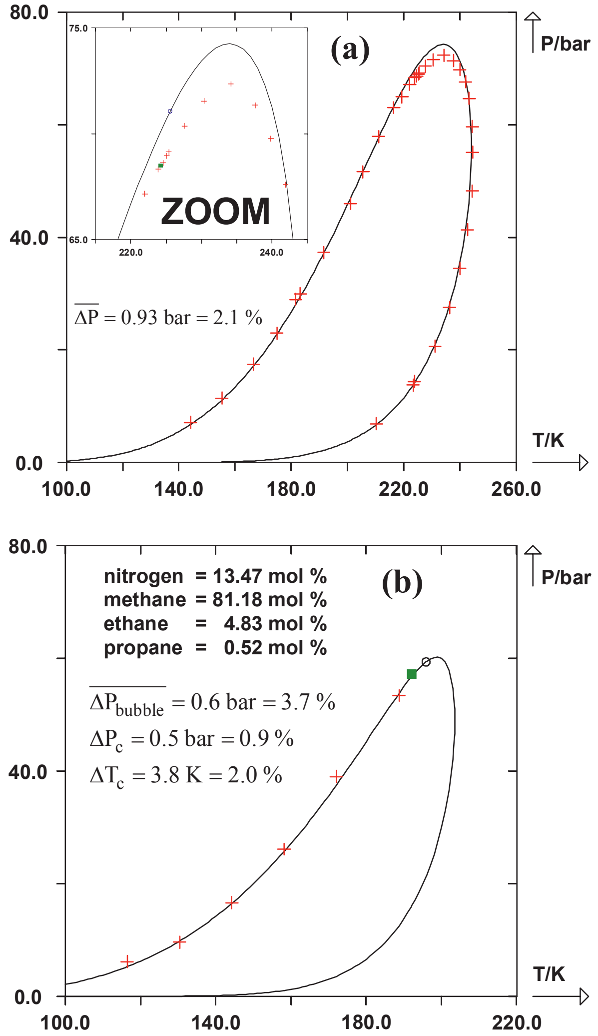

Fig. 1. +: experimental dew and bubble-point pressures. ■: experimental critical point. ○: predicted critical point. Solid line: phase envelope of synthetic natural gas predicted with the PPR78 model. (a) fluid of Parikh et al. (b) fluid of Oscarson et al.

2.2 Predicting the phase behavior of gas condensates

2.2.1 Gozalpour et al.'s fluid

Gozalpour et al. [19] measured 6 dew point-pressures for a gas condensate containing 5 normal alkanes ranging from methane to n-hexadecane. Figure 3 puts in evidence that with an average deviation of 3.0 %, the PPR78 model is able to accurately predict these data.

2.3 Predicting the phase behavior of crude oils

2.3.1 The 32 fluids of Peng and Robinson

Peng and Robinson [20] used their EoS to calculate the critical coordinates of 32 fluids for which the critical temperature and the critical pressure were known experimentally.

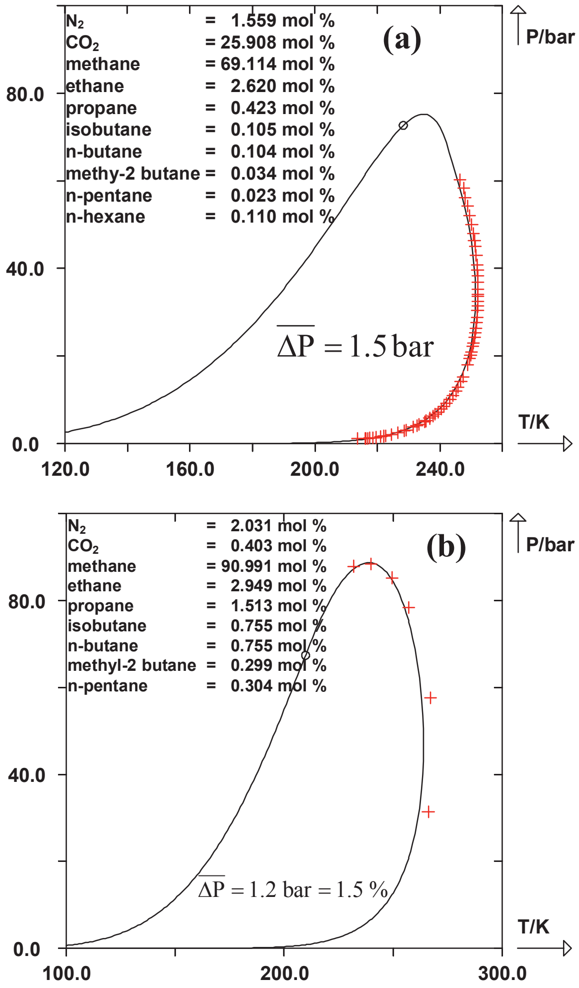

Fig. 2. +: experimental dew and bubble-point pressures. ○: predicted critical point. Solid line: (P,T) phase envelope of synthetic natural gas predicted with the PPR78 model (a) fluid of Jarne et al., (b) fluid of Zhou et al.

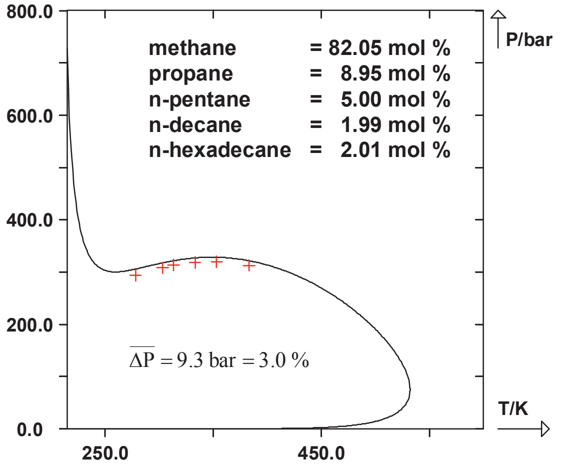

Fig. 3. Solid line: (P,T) phase envelope of Gozalpour et al.'s gas condensate predicted with the PPR78 model. +: experimental dew-point pressures.

The molar composition of these 32 fluids is given in their original paper. In every instance the critical coordinates are accurately predicted with the PPR78 model. Indeed, the average deviations on the critical temperatures and pressures are: $\left\{\begin{array}{l}\overline{\Delta T_c} = 3.0\ K = 0.91\ \% \\ \overline{\Delta P_c} = 1.8\ bar = 2.2\ \%\end{array}\right.$. We can thus conclude that by using a cubic EoS and temperature-dependent k_{ij}, it is possible to accurately calculate critical points of complex systems containing few-polar components.

2.4 Predicting gas injection experiments

2.4.1 Slim tube tests performed by Yang et al.

Yang et al. [21] performed slim tube tests at two temperatures in order to determine the minimum miscibility pressure (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: $MMP_{exp}(T_1) = 86.3$ bar and $MMP_{exp}(T_2) = 104.8$ bar. The predicted values with the PPR78 model are: $MMP_{PPR78}(T_1) = 82$ bar and $MMP_{PPR78}(T_2) = 103$ 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).

2.4.2 Swelling test performed by Ruffier-Meray et al.

Ruffier-Meray et al. [22] performed a swelling test by injecting a lean gas in a synthetic crude oil. The composition of the two fluids is given in their original paper. 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 2 ones are dew-point pressures. As shown in Figure 4.a, 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.

2.4.3 Swelling tests performed by Turek et al.

Turek et al. [23] 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 the data at 322 K are shown in Figure 4.b. 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 none parameter is fitted on the experimental data.

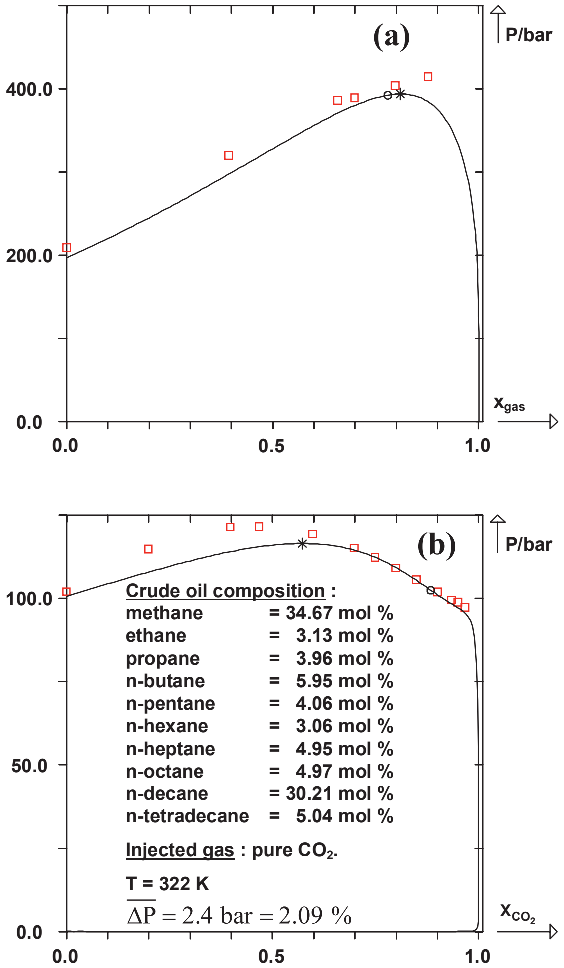

Fig. 4. □: experimental bubble-point and dew-point pressures. ○: predicted critical point. *: predicted first contact minimum miscibility pressure. Solid line: variation of mixture saturation pressure with added gas to a crude oil predicted with the PPR78 model. Swelling tests performed by (a) Ruffier-Meray et al. (b) Turek et al.

3 Conclusion

In this paper 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 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 or PRO/II

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