

# SOLUBILITY OF CO<sub>2</sub> IN BRANCHED ALKANES IN ORDER TO EXTEND THE PPR78 MODEL TO SUCH SYSTEMS

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## ABSTRACT

A high pressure, variable-volume visual cell was used to perform static measurements of phase equilibria involving carbon dioxide and four different alkanes: n-heptane, 2,2,4-trimethyl pentane (isooctane), 2,5-dimethyl hexane and 3-methyl pentane. Different temperatures ranging from 278.15 to 413.15 K were selected. The bubble point pressures, ranging from 12 to 134 bar were measured at carbon dioxide mole fractions between 0.23 and 0.91. The experimental data were compared with correlations obtained with a simplified version of the PPR78 model in which each molecule has been considered as a single group. Such a model is able to predict with quite high accuracy our data whatever the temperature.

## INTRODUCTION

In 2004, we started to develop a group contribution method aimed at predicting the binary interaction parameter  $k_{ij}$  for the widely used Peng-Robinson equation of state [1,2]. A key point in our approach is that the  $k_{ij}$  between two components  $i$  and  $j$  is a function of temperature ( $T$ ) and of the pure components critical temperatures ( $T_{ci}$ ,  $T_{cj}$ ), critical pressures ( $P_{ci}$ ,  $P_{cj}$ ) and acentric factors ( $\omega_i$ ,  $\omega_j$ ). This means that no additional properties besides those required by the equation of state (EOS) itself ( $T_c$ ,  $P_c$ ,  $\omega$ ) are needed. Because our model relies on the Peng-Robinson EOS as published by Peng and Robinson in 1978 and because the addition of a group contribution method to estimate the  $k_{ij}$  makes it predictive, we decided to call this new model PPR78 (predictive 1978, Peng Robinson EOS).

In our two first papers [1,2], six groups were defined: CH<sub>3</sub>, CH<sub>2</sub>, CH, CH<sub>aro</sub>, C, C<sub>aro</sub>, CH<sub>4</sub> (methane), and C<sub>2</sub>H<sub>6</sub> (ethane). Today, it is thus possible to estimate the  $k_{ij}$  for any mixture containing n-alkanes, branched alkanes and aromatic compounds whatever the temperature. At the moment, we are extending the PPR78 model to systems containing naphthenic molecules i.e. cyclic hydrocarbons. Two new groups, namely CH<sub>2,cyclic</sub> and CH<sub>cyclic</sub> will soon be added. After that, we plan to extend the PPR78 model to systems containing "permanent gases" like CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>S. Before adding a new group to our model it is necessary to build a huge data bank containing all the vapor liquid equilibrium (VLE) data for binary systems

containing the new group and the older ones. We were surprised to discover that very few VLE data were available for binary systems containing CO<sub>2</sub> and a branched alkane. It is thus more or less impossible to determine the interactions between the group "CO<sub>2</sub>" and the groups "CH" and "C". Indeed, in the PPR78 model, the  $k_{ij}$  is temperature dependent and we need experimental VLE data in a large temperature range in order to properly estimate the influence of the temperature. This is why, it was decided to measure bubble point pressures in a large temperature range for the four following binary systems: CO<sub>2</sub> + n-heptane, CO<sub>2</sub> + 2,2,4-trimethyl pentane, CO<sub>2</sub> + 2,5-dimethyl hexane and CO<sub>2</sub> + 3-methyl pentane. It is obvious that n-heptane is not a branched alkane. The solubility of CO<sub>2</sub> in this n-alkane was determined in order to test the accuracy of our apparatus and to make measurements at temperatures for which no VLE data are available in the literature.

Because the PPR78 model is not yet ready to predict the systems studied in this paper, the experimental data were compared with correlations obtained with a simplified version of the PPR78 model in which each molecule has been considered as a single group.

## I-EXPERIMENTAL SECTION

### Material

Carbon dioxide was supplied by Carboxyque Française and was of industrial grade (an average purity of 99.998 %). The four alkanes supplied from Aldrich had a stated purity higher than 99 %.

### Apparatus and procedure

Bubble point pressures of mixtures involving CO<sub>2</sub> and a given alkane were obtained using the static type apparatus described in previous papers [3-6].

### Experimental results

A total of 424 bubble point pressures were measured for the 4 binary systems investigated.

## II-CORRELATION OF THE DATA

### The thermodynamic model

A simplified version of the PPR78 model (in which each molecule has been considered as a single group) was used in order to correlate our data. For clarity, let us recall that the PPR78 model relies on the Peng-Robinson equation of state (PR-EOS) as published by Peng and Robinson in 1978 [7]. For a pure component, the PR78 EOS is:

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

with:

$$\left\{ \begin{array}{l} R = 8.314472 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ b_i = 0.0777960739 \frac{RT_{c,i}}{P_{c,i}} \\ a_i = 0.457235529 \frac{R^2 T_{c,i}^2}{P_{c,i}} \left[ 1 + m_i \left( 1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \\ \text{if } \omega_i \leq 0.491 \quad m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \\ \text{if } \omega_i > 0.491 \quad m_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3 \end{array} \right. \quad (2)$$

where P is the pressure, R the ideal gas constant, T the temperature, a and b are EOS parameters, v the molar volume, T<sub>c</sub> the critical temperature, P<sub>c</sub> the critical pressure and ω the acentric factor.

To apply such an EOS to mixtures, mixing rules are used to calculate the values of a and b of the mixtures. Classical mixing rules are used in the PPR78 model:

$$\left\{ \begin{array}{l} a = \sum_{i=1}^N \sum_{j=1}^N z_i z_j \sqrt{a_i a_j} (1 - k_{ij}(T)) \\ b = \sum_{i=1}^N z_i b_i \end{array} \right. \quad (3)$$

where z<sub>k</sub> represents the mole fraction of component "k" in a mixture, and N the number of components in the mixture. In Eq. (3), the summations are over all chemical species. k<sub>ij</sub>(T), whose choice is difficult even for the simplest systems, is the so-called binary interaction parameter characterizing molecular interactions between molecules "i" and "j". When i equals j, k<sub>ij</sub> is zero. In the PPR78 model, k<sub>ij</sub>, which depends on temperature, is calculated by a group contribution method [1,2] through the following expression:

$$k_{ij}(T) = \frac{-\frac{1}{2} \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \cdot \left( \frac{298.15}{T} \right)^{\left( \frac{B_{kl}-1}{A_{kl}} \right)} - \left( \frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)^2}{2 \frac{\sqrt{a_i(T) \cdot a_j(T)}}{b_i \cdot b_j}} \quad (4)$$

In Eq. (4), T is the temperature. a<sub>i</sub> and b<sub>i</sub> are simply calculated by Eq. (2). N<sub>g</sub> is the number of different groups defined by the method (for the time being, eight groups are defined and N<sub>g</sub> = 8). α<sub>ik</sub> 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<sub>kl</sub> = A<sub>lk</sub> and B<sub>kl</sub> = B<sub>lk</sub> (where k and l are two different groups) are constant parameters determined by Jaubert, Mutelet and co-workers [1,2] (A<sub>kk</sub> = B<sub>kk</sub> = 0). As can be seen, to calculate the k<sub>ij</sub> parameter between two molecules i and j at a selected temperature, it is necessary to know:

the critical temperature of both components ( $T_{ci}$ ,  $T_{cj}$ ), the critical pressure of both components ( $P_{ci}$ ,  $P_{cj}$ ), the acentric factor of each component ( $\omega_i$ ,  $\omega_j$ ) and the decomposition of each molecule into elementary groups ( $\alpha_{ik}$ ,  $\alpha_{jk}$ ).

Because the group "CO<sub>2</sub>" is not yet defined, it is not possible to use the PPR78 model to predict the VLE data measured in this study. It is however possible to use a simplified version of the PPR78 model in which each molecule is considered as a single group. Doing so, the temperature dependent  $k_{ij}$  is expressed by:

$$k_{12}(T) = \frac{A_{12} \cdot \left( \frac{298.15}{T} \right)^{\left( \frac{B_{12}-1}{A_{12}} \right)} - \left( \frac{\sqrt{a_1(T)}}{b_1} - \frac{\sqrt{a_2(T)}}{b_2} \right)^2}{2 \frac{\sqrt{a_1(T) \cdot a_2(T)}}{b_1 \cdot b_2}} \quad (5)$$

For a given binary system, it is thus enough to fit the two parameters  $A_{12}$  and  $B_{12}$  on the available experimental data. For the four binary systems investigated in this paper, these both parameters were determined in order to minimize the following objective function :

$$F_{obj} = 100 \sum_{i=1}^{n_{bubble}} 0.5 \left( \frac{|\Delta x|}{x_{1,exp}} + \frac{|\Delta x|}{x_{2,exp}} \right)_i \quad \text{with } |\Delta x| = |x_{1,exp} - x_{1,cal}| = |x_{2,exp} - x_{2,cal}| \quad (6)$$

$n_{bubble}$  is the number of experimentally determined bubble points for a given binary system.  $x_1$  is the mole fraction in the liquid phase of the most volatile component (CO<sub>2</sub>) and  $x_2$  the mole fraction of the heaviest component (it is obvious that  $x_2 = 1-x_1$ ).

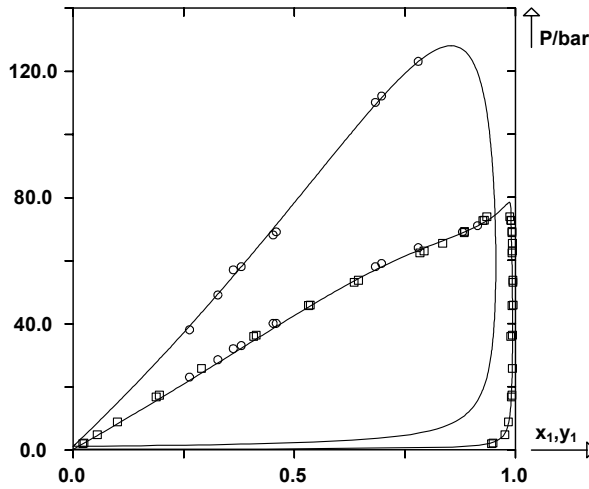
### III-RESULTS AND DISCUSSION

The CO<sub>2</sub> + n-heptane [8] and the CO<sub>2</sub> + 2,2,4-trimethyl pentane (isooctane) [9] systems have been previously studied by different authors. From our knowledge, the systems CO<sub>2</sub> + 2,5-dimethyl hexane and CO<sub>2</sub> + 3-methyl pentane are measured for the first time in this study. For the two first systems, our data are compared with those previously determined. Such a comparison may be seen in Figures 1 and 2. From these figures, it is possible to conclude that our apparatus gives bubble point pressures very close to those determined by other authors. In Figures 3 and 4 are shown the experimental data determined for the two last systems. In the four figures, our data were correlated with the simplified version of the PPR78 model: for each binary system, the fitted  $A_{12}$  and  $B_{12}$  parameters and the corresponding value of the objective function are given in Table 1.

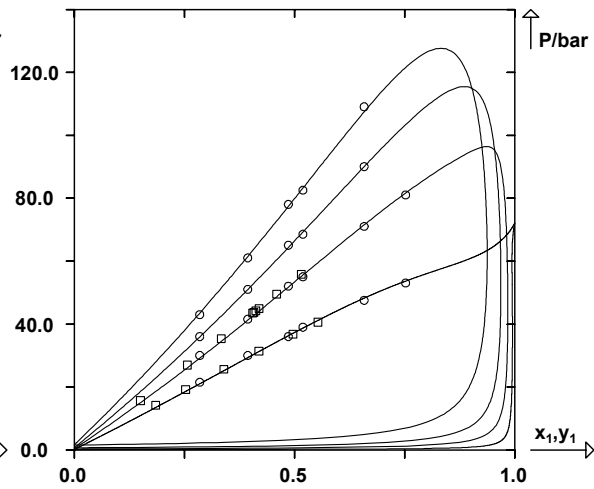
**Table 1:** Values of the fitted  $A_{12}$  and  $B_{12}$  parameters (Eq. 5) and value of the corresponding objective function (Eq. 6) for the four binary systems investigated in this study.

System: CO <sub>2</sub> +	$A_{12}$ /MPa	$B_{12}$ /MPa	$F_{obj}$ (%)
n-heptane	122.95	243.79	2.05
2,2,4-trimethyl pentane	129.95	298.82	1.29
2,5-dimethyl hexane	118.19	385.58	1.93
3-methyl pentane	101.86	236.56	0.92

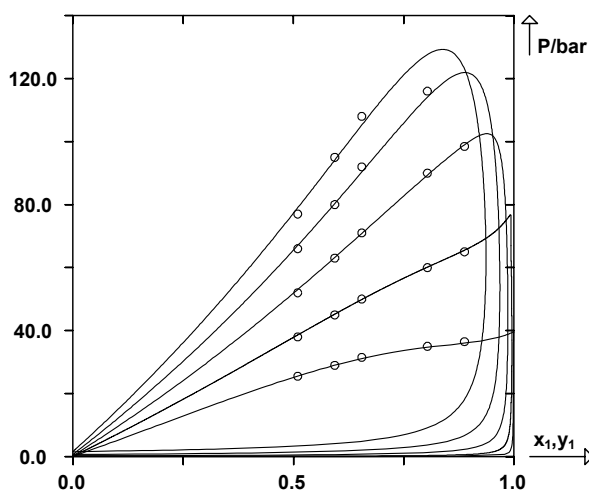
Because the objective function is always small (1.55% on average), the use of Eq. (5) is extremely useful to correlate VLE data.



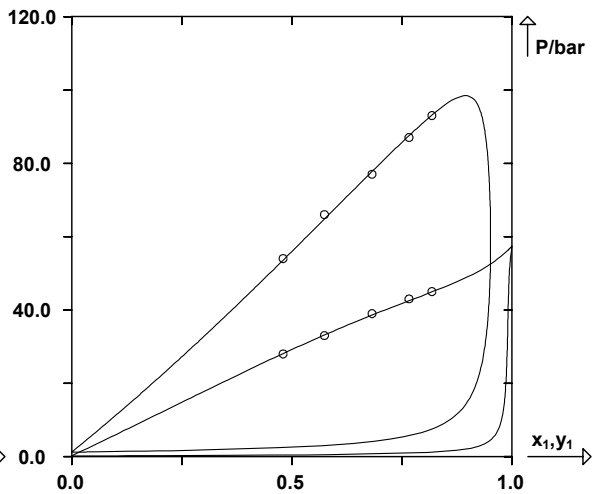
**Figure 1:** Experimental and calculated VLE for the CO<sub>2</sub> (1)+ n-heptane(2) system at T/K = 310.65 + 373.15  
 ○: bubble points measured in this study.  
 □: experimental data by Kalra et al. [8].  
 solid line : correlation results with a simplified version of the PPR78 model



**Figure 2:** Experimental and calculated VLE for the CO<sub>2</sub> (1) + 2,2,4-trimethyl pentane(2) system at T/K = 303.15 + 333.15 + 358.15 + 388.15  
 ○: bubble points measured in this study.  
 □: experimental data by Han et al. [9].  
 solid line : correlation results with a simplified version of the PPR78 model.



**Figure 3:** Experimental and calculated VLE for the CO<sub>2</sub> (1)+ 2,5-dimethyl hexane(2) system at T/K = 278.15 + 308.15 + 338.15 + 368.15 + 398.15.  
 ○: bubble points measured in this study.  
 solid line : correlation results with a simplified version of the PPR78 model.



**Figure 4:** Experimental and calculated VLE for the CO<sub>2</sub> (1)+ 3-methyl pentane(2) system at T/K = 293.5 + 343.15  
 ○: bubble points measured in this study.  
 solid line : correlation results with a simplified version of the PPR78 model.

## CONCLUSION

A high pressure, variable-volume view cell was used to perform static measurements of equilibria for four binary systems involving CO<sub>2</sub> and an alkane. Many temperatures ranging from 278.15 to 413.15 K were selected. For two systems, experimental data were previously published by other authors. Our measured bubble point pressures are in good agreement with these previously measured data.

Our data were compared with correlation obtained by using a simplified version of the PPR78 model recently described in the literature. By doing so, the  $k_{ij}$  is temperature dependent and more accurate results are obtained than by fitting a constant  $k_{ij}$  value.

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