A GROUP CONTRIBUTION METHOD TO PREDICT THE BINARY INTERACTION PARAMETERS (K_{IJ}) OF {CO_2 +HYDROCARBON} MIXTURES.

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SUMMARY

The scope of this study is to extend our recently developed group contribution method[1] allowing the estimation of the binary interaction parameters k_{ij} of the widely used Peng-Robinson equation of state (PPR78) to mixtures containing CO_2. In our approach, such parameters are temperature dependant in order to increase the accuracy of the proposed model. In this work, six groups are defined: CO_2, CH_3, CH_2, CH, C and CH_4, meaning that it is possible to estimate the k_{ij} for any mixture of saturated hydrocarbons with CO_2.

INTRODUCTION

It is well known that process synthesis as well as product design require information on the properties of pure components and mixtures. The needs have always been greater than the available experimental data, leading to the development of many property estimation methods. Generally, the simplest successful methods are based on the concept of additive group contributions. The major need in thermodynamic modeling of complex mixtures and especially of petroleum fluids is the calculation of high pressure vapor liquid equilibria. This is usually done by means of cubic equation of states (EOS). The most widely used is probably the Peng-Robinson[2] EOS which is implemented in many commercial simulation softwares. Nevertheless, this equation when applied to mixtures requires the knowledge of the critical temperature T_c, the critical pressure P_c, and the acentric factor ω of each pure component. Moreover molecular interactions are accounted for by means of a binary interaction parameter, the so-called k_{ij} whose choice is difficult even for the simplest systems. The common practice has been to fit k_{ij} so as to represent the vapor-liquid equilibrium data of the mixture under consideration.

Many methods suitable to estimate the properties (T_C, P_c, ω) of the pure components are described by Poling et al.[3]. However, to our knowledge there exists a unique group contribution method able to estimate the binary interaction parameters (bips) of a cubic equation of state. Such a method was developed by Péneloux and coworkers[4-5]. To be accurate, these authors developed an original mixing rule which combines at constant packing fraction a cubic equation of state and an excess Gibbs energy (g^E) model. However, if the selected g^E model is of the van Laar type (Eq. 1):

$$g^E(T,x) = \frac{1}{2}\frac{\sum_{i=1}^{p}\sum_{j=1}^{p} x_i x_j b_i b_j E_{ij}(T)}{\sum_{i=1}^{p} x_i b_i} \quad \text{with} \quad \begin{cases} E_{ij}(T) = E_{ji}(T) \\ E_{ii}(T) = 0.0 \end{cases} \qquad (1)$$

it is possible to demonstrate that the approach at constant packing fraction is equivalent to using classical mixing rules (linear on b and quadratic on a) with k_{ij}. Indeed, Péneloux et al.[4] established a simple relation between the binary interaction parameter E_{ij} of the van Laar function and the binary interaction parameter k_{ij} of the equation of state's attractive term. Such a relation is as follows:

$$k_{ij}(T) = \frac{E_{ij}(T) - \left(\delta_i - \delta_j\right)^2}{2\,\delta_i\,\delta_j} \qquad \text{with} \qquad \delta_i = \frac{\sqrt{a_i(T)}}{b_i} \qquad (2)$$

Moreover, Péneloux and coworkers[5] developed a group contribution method (GCM) to predict - as a function of temperature - the binary interaction parameter E_{ij} of the van Laar function. The equation of Redlich et al.[6] was used to express E_{ij} in terms of group contributions:

$$E_{ij}(T) = -\frac{1}{2}\sum_{k=1}^{ng}\sum_{l=1}^{ng}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})A_{kl}\cdot\left(\frac{298.15}{T}\right)^{\left(\frac{B_{kl}}{A_{kl}}-1\right)} \tag{3}$$

According to Eq. 2, their GCM may be used to predict k_{ij} values. Its main advantage comes from the k_{ij} being temperature dependant.

Even if very accurate, Péneloux's model[4,5] exhibits many disadvantages. Indeed, these authors did not use the original Peng-Robinson EOS but instead a "*translated PR type EOS*" in which the classical molar volume (v) and covolume (b) are replaced by the same translated quantities noted as $\tilde{v}$ and $\tilde{b}$. Moreover, in order to estimate the attractive parameter a(T) of their EOS, they defined two classes of pure compounds. For components which are likely to be encountered at very low pressure, the CRP a(T) correlation[7] which requires the knowledge of the normal boiling point was used. For other compounds, they used a Soave like expression[8] which is different from the one developed by Soave for the SRK EOS and different from the one developed by Peng and Robinson for their own equation. By the end, the decomposition in groups of the molecules is not so easy. For all these reasons, this very good model was never used by other research groups and never appeared in commercial process simulators.

The aim of this work is to extend our GCM allowing to estimating the k_{ij} for the widely used PR EOS to mixtures containing CO_2. To express k_{ij} in terms of group contributions, we used the same expression as the one proposed by Péneloux and coworkers[5]. This means that the k_{ij} are temperature dependant. In this work, six groups were defined: CO_2, CH_3, CH_2, CH, C and CH_4 meaning that it is possible to estimate the k_{ij} for any mixture of saturated hydrocarbons. The proposed decomposition in groups of the molecules is very easy. Very accurate results were obtained whatever the temperature and the nature of the hydrocarbons. Many new groups will soon be added.

THE THERMODYNAMIC MODEL

The equation of state used is the well known Peng-Robinson equation of state[2]:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{4}$$

with:

$$\begin{cases}
R = 8.314472\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}} \\
a = \sum_{i=1}^{n_{compd}}\sum_{j=1}^{n_{compd}} x_i x_j \sqrt{a_i a_j}\,(1-k_{ij}(T)) \\
b = \sum_{i=1}^{n_{compd}} x_i b_i \\
b_i = \Omega_b \frac{RT_{c,i}}{P_{c,i}} \\
\Omega_b = 0.0777960739 \\
a_i = \Omega_a \frac{R^2 T_{c,i}^2}{P_{c,i}}\left[1+m_i\left(1-\sqrt{\frac{T}{T_{c,i}}}\right)\right]^2 \\
\Omega_a = 0.457235529 \\
\text{if } \omega_i \le 0.491 \quad m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \\
\text{if } \omega_i > 0.491 \quad m_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.01666\omega_i^3
\end{cases}$$

(5-13)

According to the previous work of Péneloux et al.[5], k_{ij} is expressed in terms of group contributions, through the following expression (identical to Eqs. 2 and 3):

$$k_{ij}(T)=\frac{-\dfrac{1}{2}\sum_{k=1}^{ng}\sum_{l=1}^{ng}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})A_{kl}\cdot\left(\dfrac{298.15}{T}\right)^{\left(\frac{B_{kl}}{A_{kl}}-1\right)}-\left(\dfrac{\sqrt{a_i(T)}}{b_i}-\dfrac{\sqrt{a_j(T)}}{b_j}\right)^2}{2\dfrac{\sqrt{a_i(T)\cdot a_j(T)}}{b_i\cdot b_j}} \tag{14}$$

In Eq. 14, T is the temperature. a_i and b_i are simply calculated by Eqs. 10 and 8. ng is the number of different groups defined by the method (at the moment, six groups are defined and ng = 6). 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 this study ($A_{kk} = B_{kk} = 0$). As it can be seen, to calculate the k_{ij} parameter at a selected temperature between two molecules i and j, 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 (ω_i, ω_j) and the decomposition of each molecule in elementary groups (α_{ik}, α_{jk}).

RESULTS

As previously stated, only six groups were defined (group1 = CH_3, group2 = CH_2, group3 = CH, group4 = C, group5 = CH_4 i.e. methane, group6 = CO_2). The decomposition in groups of the hydrocarbons is as simple as possible. No substitution effects were considered. Indeed, the limitations of the PR EOS are well known and we are convinced it is not necessary to refine a lot a GCM suitable to estimate the bips because even with the best k_{ij} values, some systems will be poorly described.

For these 6 groups, we have to estimate 30 parameters (15A_{kl} and 15B_{kl}). These parameters were determined in order to minimize the deviations between calculated and experimental VLE data. In this study, about 7000 experimental data points were considered. The corresponding A_{kl} & B_{kl} values are summarized in Table 1 and some graphical results may be seen in figures 1 and 2.

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

	CH_3 (group 1)	CH_2 (group 2)	CH (group 3)	C (group 4)	CH_4 (group 5)	CO_2 (group 6)
CH_3 (group 1)	0	-	-	-	-	-
CH_2 (group 2)	$A_{12} = 74.81\times10^6$ $B_{12} = 165.7\times10^6$	0	-	-	-	-
CH (group 3)	$A_{13} = 261.5\times10^6$ $B_{13} = 388.8\times10^6$	$A_{23} = 51.47\times10^6$ $B_{23} = 79.61\times10^6$	0	-	-	-
C (group 4)	$A_{14} = 396.7\times10^6$ $B_{14} = 804.3\times10^6$	$A_{24} = 88.53\times10^6$ $B_{24} = 315.0\times10^6$	$A_{34} = -305.7\times10$ $B_{34} = -250.8\times10$	0	-	-
CH_4 (group 5)	$A_{15} = 32.94\times10^6$ $B_{15} = -35.00\times10^6$	$A_{25} = 36.72\times10^6$ $B_{25} = 108.4\times10^6$	$A_{35} = 145.2\times10^6$ $B_{35} = 301.6\times10^6$	$A_{45} = 263.9\times10^6$ $B_{45} = 531.5\times10^6$	0	-
CO_2 (group 6)	A_{16}=150.37×10^6 B_{16}=176.05×10^6	A_{26}=140.08×10^6 B_{26}=270.77×10^6	A_{36}=272.10×10^6 B_{36}=284.56×10^6	A_{46}=351.25×10^6 B_{46}=225.95×10^6	A_{56}=139.32×10^6 B_{56}=173.97×10^6	0

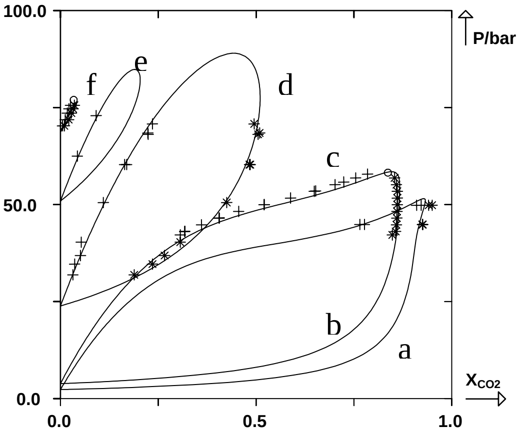

Figure 1. Prediction of isothermal dew and bubble curves for the binary systems {CH_4-CO_2}.
a: T/K = 199.82K, k_{ij}=0.079519;
b: T/K = 210.15K, k_{ij}=0.084000;
c: T/K =259.15, k_{ij}=0.106241;
d: T/K = 288.15, k_{ij}=0.119346;
e: T/K=301.00, k_{ij}=0.125419.

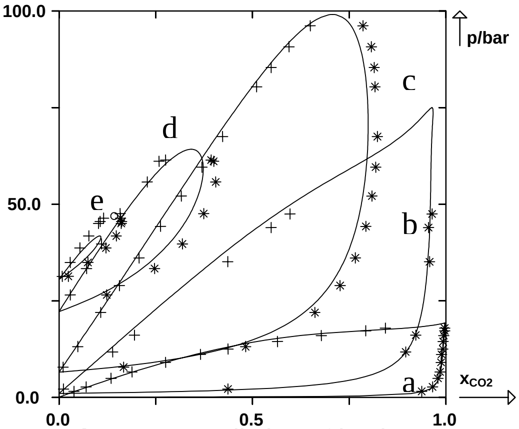

Figure 2. Prediction of isothermal dew and bubble curves for the binary systems {C_5H_{12}-CO_2}.
a: T/K = 252.67, k_{ij}=0.122490;
b: T/K = 310.40, k_{ij}=0.125394;
c: T/K = 377.71, k_{ij}=0.132710;
d: T/K=442.52, k_{ij}=0.142560;
e: T/K = 463.15, k_{ij}=0.146173.

REFERENCES

[1] Jaubert, J.-N., Mutelet, F. *Fluid Phase Equilib.*, **2004**, in press.

[2] Robinson, D.B.; Peng, D.Y. The characterization of the heptanes and heavier fractions for the GPA Peng-Robinson programs, Gas processors association, Research report RR-28, **1978**.

[3] Poling, B.E.; Prausnitz, J.M.; O'Connell, J.P. "The properties of gases and liquids", 5th edition, Mc Graw Hill, **2000**.

[4] Péneloux, A.; Abdoul, W.; Rauzy, E. *Fluid Phase Equilib.*, **1989**, 47, 115-132.

[5] Abdoul, W.; Rauzy, E.; Péneloux, A. *Fluid Phase Equilib.*, **1991**, 68, 47-102.

[6] Redlich, O.; Derr, E.L.; Pierotti, G.J. *J. Am. Chem. Soc.*, **1959**, 81, 2283-2285.

[7] Carrier, B.; Rogalski, M.; Péneloux, A. *Ind. Eng. Chem. Res.*, **1988**, 27(9), 1714-1721.

[8] Rauzy, E. Ph.D. Dissertation. The French University of Aix-Marseille II. **1982**.