Relationship between the binary interaction parameters (k_{ij}) of the Peng–Robinson and those of the Soave–Redlich–Kwong equations of state: Application to the definition of the PR2SRK model

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ABSTRACT

The purpose of this paper is to establish a relationship between the binary interaction parameters of the Peng–Robinson (PR) and those of the Soave–Redlich–Kwong (SRK) equations of state (EoS). This objective could be reached thanks to the rigorous equivalence between the classical mixing rules with temperature-dependent k_{ij} and the combination at constant packing fraction of a Van Laar-type excess Gibbs energy model with a cubic EoS. This equivalence makes it possible to find out a relationship between the $E_{ij}(T)$ parameters issued from the Van Laar function and the $k_{ij}(T)$ of the classical mixing rules. Our key idea was to make the hypothesis that the infinite pressure residual molar excess Gibbs energy ($g_{\mathrm{res}}^{E,\infty}$) was independent of the used EoS. Doing so, a simple relationship between the E_{ij} suitable for the PR-EoS (E_{ij}^{PR}) and those suitable for the SRK EoS (E_{ij}^{SRK}) can be obtained. Using this relationship and the one linking the k_{ij} and the E_{ij}, it was possible to find out a simple and general equation connecting the k_{ij} of a given EoS to the k_{ij} of any other EoS. This approach was then used to deduce k_{ij}^{SRK} from a known k_{ij}^{PR}. In a second step, using the previously mentioned mathematical equation relating k_{ij}^{PR} to k_{ij}^{SRK}, the PPR78 model which is a group contribution method for the estimation of the temperature-dependent BIPs of the PR-EoS was used to generate $k_{ij}(T)$ for the SRK EoS. It is shown how the group interaction parameters initially determined for the PR-EoS can be simply used to predict the temperature-dependent BIPs of the SRK EoS. This new predictive model has been called PR2SRK. As discussed in this paper, the accuracy of this model is similar to the accuracy of the PPR78 approach.

1. Introduction

Chemical engineers from petroleum companies widely use cubic equations of state (EoS) and especially the ones proposed by Peng and Robinson (Peng–Robinson EoS noted PR-EoS afterwards) [1] and by Soave (Soave–Redlich–Kwong EoS, noted SRK EoS afterwards) [2]. These equations of state directly stem from the Van der Waals theory and can be written for a given mixture under the general form:

$$P = \frac{RT}{v-b} - \frac{a}{Q(v)}$$

where P is the pressure, T, the absolute temperature and v, the molar volume of the fluid. $Q(v)$ is a second order polynomial in v. Classical Van der Waals mixing rules are frequently used to relate the a and b parameters of a mixture to the composition and to the a_i and b_i

parameters of the pure components i. Parameter a is taken to be a quadratic function of the mole fractions and parameter b, a linear function. A binary interaction parameter (BIP), classically noted k_{ij}, is usually involved in the a-parameter expression to provide more flexibility to the EoS. This k_{ij} parameter can be either chosen constant or temperature-dependent (a mole fraction dependence is more scarcely introduced in the k_{ij} expression). It is however important to note that numerical values of BIPs are specific (i) to the considered EoS, (ii) to the alpha-function (Soave, Twu, Mathias-Copeman, etc.) involved in the mathematical expression of the a_i parameter.

The key point when using such cubic EoS to describe complex mixtures like petroleum fluids is thus to give appropriate values to the binary interaction parameters. We however know by experience that the BIPs, suitable for the PR-EoS (k_{ij}^{PR}) cannot be used for the SRK EoS ($k_{ij}^{\mathrm{SRK}} \neq k_{ij}^{\mathrm{PR}}$). This assessment makes it impossible for petroleum engineers to mix the use of these two equations of state. Indeed, they usually have tables containing the numerical values of the BIPs only for the most widely used EoS in their company. To overcome this limitation, a relationship between the SRK BIP (k_{ij}^{SRK})

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and the PR BIP (k_{ij}^{PR}) is established in this paper. This relationship is then extended to relate the BIP of a given cubic EoS to the BIP of any other cubic EoS.

In addition, using the previously mentioned mathematical equation relating k_{ij}^{PR} and k_{ij}^{SRK}, the PPR78 model [3–16] which may be seen as a group contribution method for the estimation of the temperature-dependent BIPs of the widely spread PR-EoS, was used to generate k_{ij} for the SRK EoS. It is shown how the group interaction parameters initially determined for the PR-EoS [3–9] can be simply used to predict the temperature-dependent BIPs for the SRK EoS. This new predictive model has been called PR2SRK (here PR means predictive but also means Peng–Robinson since all the used parameters come from the PPR78 model).

2. Relationship between the binary interaction parameters of the Peng–Robinson and those of the SRK equations of state

2.1. Mathematical derivation

Following the zeroth-order approximation of Guggenheim's quasi-reticular model [17], Péneloux et al. [18] proposed to combine at constant packing fraction a cubic EoS and an expression for the molar excess Gibbs energy model (i.e. an activity coefficient model). The resulting mixing rules [11,18] are:

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

$g_{res}^{E,\infty}(T,\mathbf{x}) = \lim\limits_{P\to+\infty} g_{res}^{E}(T,P,\mathbf{x})$ is the residual part of the molar excess Gibbs energy calculated from the EoS when the pressure goes to infinity. a and b are EoS parameters. x_i represents the mole fraction of component i and N the number of components in the mixture. C_{EoS}, defined in the next section (see Eq. (29)), is a characteristic constant of the used EoS. For the PR and the SRK EoS, the following values are obtained: $C_{PR} = (\sqrt{2}/2)\ln(1+\sqrt{2}) \approx 0.6232$ and $C_{SRK} = \ln(2) \approx 0.6931$. In Eq. (1), in order to allow calculation of the $a(T,\mathbf{x})$ parameter, a mathematical expression must be assigned to $g_{res}^{E,\infty}(T,\mathbf{x})$. It may be chosen among the classical forms of molar excess Gibbs energy functions (Redlich-Kister, Margules, Wilson, Van Laar, NRTL, UNIQUAC, UNIFAC, . . .) which do not depend on pressure. In order to avoid confusion, we will write with a special font ($\mathcal{G}^E$) the selected activity coefficient model. We thus can write:

$$g_{res}^{E,\infty} = \mathcal{G}_{res}^{E} \tag{2}$$

When the $\mathcal{G}^E$ model per se contains a combinatorial (or athermal) part, essentially due to differences in size and shape of the molecules in the mixture, and a residual part, essentially due to energy interactions (e.g. the UNIQUAC and UNIFAC models), only the residual term ($\mathcal{G}_{res}^{E}$) of the $\mathcal{G}^E$ model must be introduced in Eq. (1). For other molar excess Gibbs energy models (Redlich–Kister, Margules, Wilson, Van Laar, NRTL), the complete $\mathcal{G}^E$ function is used

in Eq. (1) and we thus obtain:

$$g_{res}^{E,\infty} = \mathcal{G}^E \tag{3}$$

In this section, a Van Laar-type expression i.e. a *solely energetic* model is chosen for $g_{res}^{E,\infty}/C_{EoS}$. Using Eq. (3), we thus can write:

$$\frac{g_{res}^{E,\infty}}{C_{EoS}} = \frac{\mathcal{G}_{Van\ Laar}^{E}}{C_{EoS}} = \frac{1}{2}\frac{\displaystyle\sum_{i=1}^{N}\sum_{j=1}^{N} x_i \cdot x_j \cdot b_i \cdot b_j \cdot E_{ij}(T)}{\displaystyle\sum_{j=1}^{N} b_j x_j} \tag{4}$$

It now becomes possible to show that such mixing rules (combination at constant packing fraction of a Van Laar-type $\mathcal{G}^E$ model and a cubic EoS) are rigorously equivalent to the use of classical mixing rules with temperature-dependent k_{ij}, that is:

$$\begin{cases} a(T,\mathbf{x}) = \displaystyle\sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \sqrt{a_i a_j}\left[1 - k_{ij}(T)\right] \\ b(\mathbf{x}) = \displaystyle\sum_{i=1}^{N} x_i b_i \end{cases} \tag{5}$$

Indeed, by sending Eq. (5) in Eq. (1), one has:

$$\begin{aligned} \frac{g_{res}^{E,\infty}}{C_{EoS}} &= \sum_{i=1}^{N} x_i \frac{a_i(T)}{b_i} - \frac{a(T,\mathbf{x})}{b(\mathbf{x})} \\ &= \sum_{i=1}^{N} x_i \cdot \frac{a_i(T)}{b_i} - \frac{\displaystyle\sum_{i=1}^{N}\sum_{j=1}^{N} x_i \cdot x_j \sqrt{a_i \cdot a_j}\cdot\left[1-k_{ij}(T)\right]}{\displaystyle\sum_{j=1}^{N} x_j \cdot b_j} \\ &= \frac{\displaystyle\sum_{i=1}^{N} x_i \cdot \frac{a_i(T)}{b_i} \times \sum_{j=1}^{N} x_j \cdot b_j - \sum_{i=1}^{N}\sum_{j=1}^{N} x_i \cdot x_j \sqrt{a_i \cdot a_j}\cdot\left[1-k_{ij}(T)\right]}{\displaystyle\sum_{j=1}^{N} x_j \cdot b_j} \end{aligned} \tag{6}$$

We can write:

$$\begin{aligned} &\sum_{i=1}^{N} x_i \cdot \frac{a_i(T)}{b_i} \times \sum_{j=1}^{N} x_j \cdot b_j \\ &= \sum_{i=1}^{N}\sum_{j=1}^{N} x_i \cdot x_j \frac{a_i \cdot b_j}{b_i} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} x_i \cdot x_j \frac{a_i \cdot b_j}{b_i} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} x_i \cdot x_j \frac{a_j \cdot b_i}{b_j} \end{aligned} \tag{7}$$

Thus,

$$\frac{g_{res}^{E,\infty}}{C_{EoS}} = \frac{\displaystyle\sum_{i=1}^{N}\sum_{j=1}^{N} x_i \cdot x_j \left[\frac{1}{2}\frac{a_i \cdot b_j}{b_i} + \frac{1}{2}\frac{a_j \cdot b_i}{b_j} - \sqrt{a_i \cdot a_j}\cdot\left[1-k_{ij}(T)\right]\right]}{\displaystyle\sum_{j=1}^{N} x_j \cdot b_j} = \frac{\displaystyle\sum_{i=1}^{N}\sum_{j=1}^{N} x_i \cdot x_j \cdot b_i \cdot b_j \left[\frac{1}{2}\frac{a_i}{b_i^2} + \frac{1}{2}\frac{a_j}{b_j^2} - \frac{\sqrt{a_i}}{b_i}\frac{\sqrt{a_j}}{b_j}\cdot\left[1-k_{ij}(T)\right]\right]}{\displaystyle\sum_{j=1}^{N} x_j \cdot b_j} \tag{8}$$

At this step, we introduce for clarity:

$$\delta_i = \frac{\sqrt{a_i}}{b_i} \tag{9}$$

which has the Scatchard–Hildebrand solubility parameter feature, and we define the parameter E_{ij} by:

$$E_{ij} = \delta_i^2 + \delta_j^2 - 2\delta_i\delta_j\left[1 - k_{ij}(T)\right] \tag{10}$$

Eq. (8) thus writes:

$$\frac{g_{res}^{E,\infty}}{C_{EoS}} = \frac{1}{2} \cdot \frac{\displaystyle\sum_{i=1}^{N}\sum_{j=1}^{N} x_i \cdot x_j \cdot b_i \cdot b_j \cdot E_{ij}(T)}{\displaystyle\sum_{j=1}^{N} x_j \cdot b_j} \tag{11}$$

Eq. (11) is strictly identical to Eq. (4). We thus demonstrated that it is rigorously equivalent to combine at constant packing fraction a Van Laar-type $\mathcal{G}^E$ model with a cubic EoS and to use classical mixing rules with temperature-dependent k_{ij}. From Eq. (10) we have:

$$k_{ij}(T) = \frac{E_{ij}(T) - (\delta_i - \delta_j)^2}{2\delta_i\delta_j} \tag{12}$$

Eq. (12) thus establishes a connection between E_{ij} of the Van Laar-type $\mathcal{G}^E$ model and k_{ij} of the classical mixing rules.

In order to ascertain a relationship between the BIPs of the PR-EoS and those of the SRK EoS, our key idea was to make the hypothesis that $g_{res}^{E,\infty}$ was independent of the used EoS. A similar idea was originally used by Fransson et al. [19]. From Eq. (4), we thus obtain:

$$g_{res}^{E,\infty} = C_{PR}\frac{1}{2}\frac{\displaystyle\sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_i^{PR} b_j^{PR} E_{ij}^{PR}(T)}{\displaystyle\sum_{j=1}^{N} b_j^{PR} x_j}$$

$$= C_{SRK}\frac{1}{2}\frac{\displaystyle\sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_i^{SRK} b_j^{SRK} E_{ij}^{SRK}(T)}{\displaystyle\sum_{j=1}^{N} b_j^{SRK} x_j} \tag{13}$$

With:

$$\begin{cases} b_i^{PR} = \Omega_b^{PR}\dfrac{RT_{c,i}}{P_{c,i}}; \quad \Omega_b^{PR} = \dfrac{X}{X+3} \approx 0.07780 \text{ if} \\[2mm] X = \dfrac{-1 + \sqrt[3]{6\sqrt{2}+8} - \sqrt[3]{6\sqrt{2}-8}}{3} \\[2mm] b_i^{SRK} = \Omega_b^{SRK}\dfrac{RT_{c,i}}{P_{c,i}}; \quad \Omega_b^{SRK} = \dfrac{\sqrt[3]{2}-1}{3} \approx 0.08664 \end{cases} \tag{14}$$

Replacing in Eq. (13) b_i^{PR} by:

$$b_i^{PR} = \frac{\Omega_b^{PR}}{\Omega_b^{SRK}} b_i^{SRK} \tag{15}$$

one obtains:

$$C_{PR} \cdot \Omega_b^{PR} \cdot \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_i^{SRK} b_j^{SRK} E_{ij}^{PR}(T)$$

$$= C_{SRK} \cdot \Omega_b^{SRK} \cdot \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_i^{SRK} b_j^{SRK} E_{ij}^{SRK}(T) \tag{16}$$

Introducing : $\quad \xi = \dfrac{C_{PR} \cdot \Omega_b^{PR}}{C_{SRK} \cdot \Omega_b^{SRK}} \approx 0.807341 \tag{17}$

Eq. (16) writes:

$$\sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_i^{SRK} b_j^{SRK} \left[\xi \cdot E_{ij}^{PR}(T) - E_{ij}^{SRK}(T)\right] = 0 \tag{18}$$

For a binary system ($N=2$), remembering that $E_{11} = E_{22} = 0$ and $E_{21} = E_{12}$, Eq. (18) writes:

$$2x_1 x_2 b_1^{SRK} b_2^{SRK}\left[\xi \cdot E_{12}^{PR}(T) - E_{12}^{SRK}(T)\right] = 0 \tag{19}$$

That is:

$$E_{12}^{SRK}(T) = \xi \cdot E_{12}^{PR}(T) \tag{20}$$

For a binary system, equating the $g_{res}^{E,\infty}$ of the PR-EoS with that of the SRK EoS thus leads to a unique linear relationship between $E_{12}^{PR}(T)$ and $E_{12}^{SRK}(T)$.

For a multi-component system ($N > 2$), it would be possible to find many different mathematical relationships between $E_{ij}^{PR}(T)$ and $E_{ij}^{SRK}(T)$ so that Eq. (18) remains true. Among all of them, the one derived for a binary system, that is: $E_{ij}^{SRK}(T) = \xi \cdot E_{ij}^{PR}(T)$ can still apply when $N > 2$ (it verifies Eq. (18) whatever the number of components in the mixture). We however here work with binary interaction parameters: it means that a multi-component system must be considered as a system composed of different binary systems. It is thus essential that the relationship between $E_{ij}^{PR}(T)$ and $E_{ij}^{SRK}(T)$ which was established for binary systems, still persists for ternary systems, quaternary systems and so on (the binary relationship has to remain the same for any value of N). This is the reason why, the solution derived for a binary system which is acceptable whatever the number of components is the only one to be considered afterwards. The universal relationship between $E_{ij}^{PR}(T)$ and $E_{ij}^{SRK}(T)$ finally writes:

$$E_{ij}^{SRK}(T) = \xi \cdot E_{ij}^{PR}(T) \tag{21}$$

From Eq. (10), we can write:

$$E_{ij} = 2k_{ij}\delta_i\delta_j + \left(\delta_i - \delta_j\right)^2 \tag{22}$$

By combining Eqs. (21) and (22), we obtain:

$$2k_{ij}^{SRK}\delta_i^{SRK}\delta_j^{SRK} + \left(\delta_i^{SRK} - \delta_j^{SRK}\right)^2 = 2\xi k_{ij}^{PR}\delta_i^{PR}\delta_j^{PR} + \xi\left(\delta_i^{PR} - \delta_j^{PR}\right)^2 \tag{23}$$

The relation between k_{ij}^{SRK} and k_{ij}^{PR} is thus:

$$\boxed{k_{ij}^{SRK}(T) = \frac{2\xi k_{ij}^{PR}\delta_i^{PR}\delta_j^{PR} + \xi\left(\delta_i^{PR} - \delta_j^{PR}\right)^2 - \left(\delta_i^{SRK} - \delta_j^{SRK}\right)^2}{2\delta_i^{SRK}\delta_j^{SRK}}} \tag{24}$$

or conversely,

$$k_{ij}^{PR}(T) = \frac{2k_{ij}^{SRK}\delta_i^{SRK}\delta_j^{SRK} + \left(\delta_i^{SRK} - \delta_j^{SRK}\right)^2 - \xi\left(\delta_i^{PR} - \delta_j^{PR}\right)^2}{2\xi\delta_i^{PR}\delta_j^{PR}} \tag{25}$$

At this stage, two remarks can be made:

(1) From Eqs. (17) and (21), we can write:

$$C_{SRK} \cdot \Omega_b^{SRK} \cdot E_{ij}^{SRK}(T) = C_{PR} \cdot \Omega_b^{PR} \cdot E_{ij}^{PR}(T) \tag{26}$$

Introducing Eq. (22), we thus can say that by assuming that $g_{res}^{E,\infty}$ is independent of the used EoS, we state that the quantity:

$$C \cdot \Omega_b \cdot E_{ij} = C \cdot \Omega_b \left[2k_{ij}\delta_i\delta_j + \left(\delta_i - \delta_j\right)^2\right] \tag{27}$$

is independent of the used EoS.

(2) Using Eqs. (24) or (25), temperature-dependent k_{ij} will always be obtained. As an example, let us assume that a constant k_{ij} (independent of the temperature) is known for a given binary system and for the PR-EoS. By using Eq. (24), temperature-dependent k_{ij}, suitable for the SRK EoS, will be obtained.

Equation	r_1	r_2
Van der Waals (VdW)	0	0
Soave–Redlich–Kwong (SRK)	0	−1
Peng–Robinson (PR)	$-1+\sqrt{2}$	$-1-\sqrt{2}$

2.2. Generalization of the previous relationship to any couple of cubic equations of state

Cubic equations of state deriving from the Van der Waals equation take the general following form:

$$P(T,v) = \frac{RT}{v-b_i} - \frac{a_i(T)}{(v-r_1 b_i)(v-r_2 b_i)}$$

$$\text{with} \begin{cases} b_i = \Omega_b \dfrac{RT_{c,i}}{P_{c,i}} \\[2mm] a_i(T) = \Omega_a \dfrac{R^2 T_{c,i}^2}{P_{c,i}} \cdot \alpha_i(T, T_{c,i}, \omega_i) \end{cases} \quad (28)$$

The parameters r_1 and r_2 are specific to each equation. Table 1 reminds their values in the case of the most well-know models. The C_{EoS} constant defined by Eq. (1) can be calculated from r_1 and r_2 by:

$$C_{EoS} = \frac{1}{r_1 - r_2} \cdot \ln\left(\frac{1-r_2}{1-r_1}\right) \quad (29)$$

In the particular case where: $r_1 = r_2 = 0$, then $C_{EoS} = 1$.

Let us consider two cubic EoS, noted EoS1 and EoS2. Starting from Eq. (26), we can write:

$$C_{EoS1} \cdot \Omega_b^{EoS1} \cdot E_{ij}^{EoS1}(T) = C_{EoS2} \cdot \Omega_b^{EoS2} \cdot E_{ij}^{EoS2}(T) \quad (30)$$

That is:

$$E_{ij}^{EoS2}(T) = \xi_{1\to 2} \cdot E_{ij}^{EoS1}(T) \text{ with } \xi_{1\to 2} = \frac{C_{EoS1} \cdot \Omega_b^{EoS1}}{C_{EoS2} \cdot \Omega_b^{EoS2}} \quad (31)$$

By combining Eqs. (31) and (22), we obtain:

$$k_{ij}^{EoS2} = \frac{2\xi_{1\to 2}k_{ij}^{EoS1}\delta_i^{EoS1}\delta_j^{EoS1} + \xi_{1\to 2}\left(\delta_i^{EoS1} - \delta_j^{EoS1}\right)^2 - \left(\delta_i^{EoS2} - \delta_j^{EoS2}\right)^2}{2\delta_i^{EoS2}\delta_j^{EoS2}} \quad (32)$$

Using the previous equation, it is thus possible to calculate the k_{ij} for a desired cubic EoS (EoS2) knowing the corresponding value for another cubic EoS (EoS1).

Eq. (32) can also be used if we work with the same EoS (let us say the PR-EoS) but if we decide to only change the $a_i(T)$ function (e.g. we initially work with a Soave-type function [2] for which the k_{ij} are known and we decide to work with a Mathias and Copeman [20] function for which the k_{ij} are unknown). In this latter case, $\xi_{1\to 2} = 1$, but Eq. (32) in which the δ parameters depend on the $a(T)$ function will lead to a relationship between the k_{ij} to be used with the first $a(T)$ function and those to be used with the second one.

2.3. Check on an example of the validity of the hypothesis: $g_{res}^{E,\infty}$ independent of the used EoS

Eq. (24) which connects the k_{ij} for the SRK EoS (k_{ij}^{SRK}) and those for the PR-EoS (k_{ij}^{PR}) relies on the hypothesis that $g_{res}^{E,\infty}$ is independent of the used EoS. In order to check whether this hypothesis

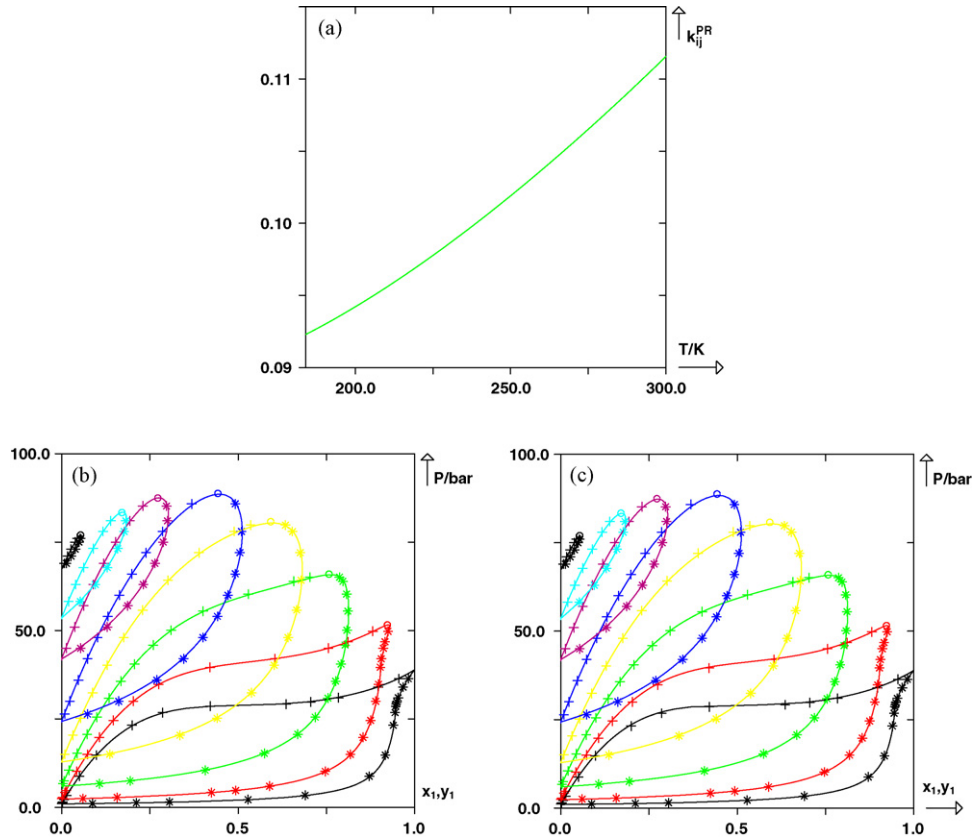**Fig. 1.** System methane(1) + CO_2(2). (a) k_{ij}^{PR} values used to generate the data. (b) +: pseudo experimental bubble points, *: pseudo experimental dew points. Isothermal dew and bubble curves calculated with the fitted k_{ij}^{SRK}. (c) +: pseudo experimental bubble points, *: pseudo experimental dew points. Isothermal dew and bubble curves calculated with the k_{ij}^{SRK} estimated from Eq. (24).

Table 2
Comparison between the k_{ij}^{SRK} fitted on pseudo experimental VLE data and the k_{ij}^{SRK} calculated from Eq. (24).

Temperature/K	Fitted k_{ij}^{SRK}	k_{ij}^{SRK} from Eq. (24)
185	0.089	0.092
200	0.092	0.094
220	0.097	0.098
240	0.103	0.102
260	0.109	0.107
280	0.115	0.112
290	0.118	0.115
300	0.122	0.118

is valid, it was decided to generate pseudo experimental VLE data using the PR-EoS and temperature-dependent k_{ij} for the system methane(1) + carbon dioxide(2). By this way, the numerical values of the k_{ij}^{PR} are perfectly known. In a second step, these pseudo experimental data were correlated with the SRK EoS. For each temperature, the k_{ij}^{SRK} was fitted in order to minimize the deviations between calculated and pseudo experimental data. Such k_{ij} can thus be compared to those calculated using Eq. (24). In this example, 181 pseudo experimental data (87 bubble points, 87 dew points, and 7 mixture critical points) were generated at eight temperatures ranging from 185 K to 300 K (T_1/K = 185, T_2/K = 200, T_3/K = 220, T_4/K = 240, T_5/K = 260, T_6/K = 280, T_7/K = 290 and T_8/K = 300). In Fig. 1a, the k_{ij}^{PR} used to generate the data are plotted with respect to the temperature. Such values originate from Vitu et al. [6]. The fitted k_{ij}^{SRK}, and the k_{ij}^{SRK} calculated from Eq. (24) are compared in Table 2. In Fig. 1b and c, the corresponding isothermal dew and bubble curves calculated either with the fitted k_{ij}^{SRK} or with the k_{ij}^{SRK} calculated from Eq. (24) are plotted. From Table 2, it clearly appears that the k_{ij}^{SRK} calculated using Eq. (24) are very close to the fitted k_{ij}^{SRK} (the average deviation between the two sets of k_{ij}^{SRK} values is only 2%). As a consequence, Fig. 1b and c are more or less undistinguishable. We can thus conclude (on this example) that the molar residual excess Gibbs energy at infinite pressure ($g_{res}^{E,\infty}$) is independent of the used EoS. The validity of this hypothesis is better evidenced in the next section.

3. From the PPR78 model to the PR2SRK model

3.1. Some reminders on the PPR78 model

In 1976, Peng and Robinson [21] published their well-known equation of state, called in this paper PR76. In 1978, the same authors published an improved version of their equation of state [1], which yields more accurate vapor pressure predictions for the heavy hydrocarbons than those obtained by using PR76. This improved equation, used in the PPR78 approach is noted PR78 in this paper. For a pure component, the PR78 EoS is:

$$P = \frac{RT}{v - b_i^{PR}} - \frac{a_i^{PR}(T)}{v(v + b_i^{PR}) + b_i^{PR}(v - b_i^{PR})} \tag{33}$$

with:

$$\begin{cases} R = 8.314472\,\text{J mol}^{-1}\,\text{K}^{-1} \\[4pt] \text{Noting}: X = \dfrac{-1 + \sqrt[3]{6\sqrt{2}+8} - \sqrt[3]{6\sqrt{2}-8}}{3} \approx 0.253076587, \text{ one has}: \\[8pt] b_i^{PR} = \Omega_b^{PR}\dfrac{RT_{c,i}}{P_{c,i}} \text{ with } \Omega_b^{PR} = \dfrac{X}{X+3} \approx 0.0777960739 \\[8pt] a_i^{PR} = \Omega_a^{PR}\dfrac{R^2 T_{c,i}^2}{P_{c,i}}\left[1 + m_i^{PR}\left(1 - \sqrt{\dfrac{T}{T_{c,i}}}\right)\right]^2 \\[8pt] \text{with } \Omega_a^{PR} = \dfrac{8(5X+1)}{49 - 37X} \approx 0.457235529 \\[4pt] \text{if } \omega_i \le 0.491\ m_i^{PR} = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \\[4pt] \text{if } \omega_i > 0.491\ m_i^{PR} = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3 \end{cases} \tag{34}$$

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 the PPR78 approach, classical mixing rules with k_{ij} [see Eq. (5)] or equivalently combination at constant packing fraction of a Van Laar-type $\mathcal{G}^E$ model with the PR78 EoS [see Eqs. (1) and (4)] are used. In order to obtain a predictive model, and to completely define the PPR78 model, we developed, following the previous works of Redlich et al. [22], Kehiaian et al. [23] and of Abdoul et al. [24], a group contribution method (GCM) to estimate indifferently the interaction parameters $E_{ij}(T)$ in Eq. (4) or the $k_{ij}(T)$ in Eq. (5). The following equations were used:

$$E_{ij}^{PR}(T) = -\frac{1}{2}\sum_{k=1}^{N_g}\sum_{l=1}^{N_g}(\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl})A_{kl}^{PR} \cdot \left(\frac{298.15}{T/K}\right)^{\left(\frac{B_{kl}^{PR}}{A_{kl}^{PR}} - 1\right)} \tag{35}$$

$$k_{ij}^{PR}(T) = \frac{-\frac{1}{2}\left[\sum_{k=1}^{N_g}\sum_{l=1}^{N_g}(\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl})A_{kl}^{PR} \cdot \left(\frac{298.15}{T/K}\right)^{\left(\frac{B_{kl}^{PR}}{A_{kl}^{PR}} - 1\right)}\right] - \left(\frac{\sqrt{a_i^{PR}(T)}}{b_i^{PR}} - \frac{\sqrt{a_j^{PR}(T)}}{b_j^{PR}}\right)^2}{2\frac{\sqrt{a_i^{PR}(T) \cdot a_j^{PR}(T)}}{b_i^{PR} \cdot b_j^{PR}}} \tag{36}$$

Let us recall that Eq. (36) is simply the coupling of Eqs. (9) (12) and (35).

In Eqs. (35) and (36), T is the temperature. N_g is the number of different groups defined by the method. 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 [3–9] ($A_{kk} = B_{kk} = 0$) by minimizing the deviations between calculated and experimental VLE data from an extended binary-system database containing 65,700 experimental data points (36,535 bubble points, 28,051 dew points, 58 azeotropic points and 1,056 mixture critical points). Most of the binary experimental data available in the open literature were collected. The detailed list of these experimental data is given in our previous papers [3–9]. For the 15 groups available, a total of 204 parameters (expressed in MPa) were determined. They are recalled in Table 3. With these groups, it is possible to predict the BIPs for any mixture containing alkanes, aromatics, naphthenes, CO_2, N_2, H_2S and mercaptans. As recently shown [11], such a model is perfectly able to predict the behavior of petroleum fluids. A GCM has been chosen to estimate the BIPs because we were aware that the group contribution concept could be useful to model complex processes like those involving supercritical fluids [25–27] 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.

Table 3

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

	CH$_3$ (group 1)	CH$_2$ (group 2)	CH (group 3)	C (group 4)	CH$_4$ (group 5)	C$_2$H$_6$ (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$_2$S (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$_2$H$_6$ (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_{39} = −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_{8-13} = 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$_2$S (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} = 411.18 B_{11-15} = −308.8	N.A.(*)	N.A.(*)	A_{14-15} = −77.21 B_{14-15} = 156.1	0

(*)N.A. = not available

Whatever the used method, an equation similar to Eq. (36) is obtained (it is enough to change the superscript PR in SRK):

$$k_{ij}^{SRK}(T) = \frac{-\frac{1}{2}\left[\sum_{k=1}^{N_g}\sum_{l=1}^{N_g}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})A_{kl}^{SRK}\cdot\left(\frac{298.15}{T/K}\right)^{\left(\frac{B_{kl}^{SRK}}{A_{kl}^{SRK}}-1\right)}\right] - \left(\frac{\sqrt{a_i^{SRK(T)}}}{b_i^{SRK}}-\frac{\sqrt{a_j^{SRK(T)}}}{b_j^{SRK}}\right)^2}{2\frac{\sqrt{a_i^{SRK(T)}\cdot a_j^{SRK(T)}}}{b_i^{SRK}\cdot b_j^{SRK}}} \tag{41}$$

3.2. Construction of the PR2SRK model

For a pure component, the SRK EoS [2] is:

$$P = \frac{RT}{v-b_i^{SRK}} - \frac{a_i^{SRK}(T)}{v(v+b_i^{SRK})} \tag{37}$$

with:

$$\begin{cases} R = 8.314472\,J\cdot mol^{-1}\cdot K^{-1} \\ b_i^{SRK} = \Omega_b^{SRK}\frac{RT_{c,i}}{P_{c,i}} \text{ with } \Omega_b^{SRK} = \frac{\sqrt[3]{2}-1}{3} \approx 0.08664 \\ a_i^{SRK} = \Omega_a^{SRK}\frac{R^2 T_{c,i}^2}{P_{c,i}}\left[1+m_i^{SRK}\left(1-\sqrt{\frac{T}{T_{c,i}}}\right)\right]^2 \text{ with } \Omega_a^{SRK} = \frac{1}{9(\sqrt[3]{2}-1)} \approx 0.42748 \\ m_i^{SRK} = 0.480 + 1.574\omega_i - 0.176\omega_i^2 \end{cases} \tag{38}$$

Classical mixing rules as defined by Eq. (5) or mixing rules defined by Eqs. (1) and (4) can obviously be used with the SRK EoS. However remembering that $E_{ij}^{SRK}(T) = \xi \cdot E_{ij}^{PR}(T)$ with $\xi \approx 0.807341$, it is noticeable from Eq. (35) that it is enough to multiply by ξ the A_{kl}^{PR} and B_{kl}^{PR} group interaction parameters to obtain the corresponding $E_{ij}^{SRK}(T)$ values for the SRK EoS. We thus can write:

$$\begin{cases} A_{kl}^{SRK} = \xi \cdot A_{kl}^{PR} \\ B_{kl}^{SRK} = \xi \cdot B_{kl}^{PR} \end{cases} \tag{39}$$

and

$$E_{ij}^{SRK}(T) = -\frac{1}{2}\sum_{k=1}^{N_g}\sum_{l=1}^{N_g}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})A_{kl}^{SRK}\cdot\left(\frac{298.15}{T/K}\right)^{\left(\frac{B_{kl}^{SRK}}{A_{kl}^{SRK}}-1\right)} \tag{40}$$

The $k_{ij}^{SRK}(T)$ values can now be obtained either by coupling Eq. (36) and Eq. (24) or by sending Eq. (40) in Eq. (12).

It is thus possible to use the GCM we developed for the PR-EoS to predict the temperature-dependent BIPs of the SRK EoS without having to re-estimate the parameters. Eqs. (5), (37), (38), (39) and (41) thus define a new predictive model based on the SRK EoS. It was decided to call this new model PR2SRK because it is predictive and because the group interaction parameters are those we developed for the PR-EoS.

3.3. Generalization of the previous methodology in order to estimate by a GCM, the k_{ij} for any cubic EoS using the GC parameters of the PPR78 model

Let us consider a cubic EoS as defined by Eq. (28) and noted EoS1. Let us define:

$$\xi_{PR\to EoS1} = \frac{C_{PR}\cdot\Omega_b^{PR}}{C_{EoS1}\cdot\Omega_b^{EoS1}} \tag{42}$$

Starting from Eqs. (39) and (41), we can write:

$$k_{ij}^{EoS1}(T) = \frac{-\frac{1}{2}\left[\sum_{k=1}^{N_g}\sum_{l=1}^{N_g}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})\xi_{PR\to EoS1}A_{kl}^{PR}\left(\frac{298.15}{T/K}\right)^{\left(\frac{B_{kl}^{PR}}{A_{kl}^{PR}}-1\right)}\right] - \left(\frac{\sqrt{a_i^{EoS1}(T)}}{b_i^{EoS1}}-\frac{\sqrt{a_j^{EoS1}(T)}}{b_j^{EoS1}}\right)^2}{2\left(\frac{\sqrt{a_i^{EoS1}(T)\cdot a_j^{EoS1}(T)}}{b_i^{EoS1}\cdot b_j^{EoS1}}\right)} \tag{43}$$

Using the previous equation, it is thus possible to calculate by GC, the temperature-dependent k_{ij} for any desired cubic EoS (EoS1), with any desired $a_i(T)$ function, using the group contribution parameters (A_{kl}^{PR} and B_{kl}^{PR}) we determined for the PPR78 model.

Eq. (43) can also be used if we work with the PR-EoS but with a different $a_i(T)$ function than the one defined by Eq. (34). In this latter case, $\xi_{PR\to EoS1} = 1$, but Eq. (43) will lead to k_{ij} values different of those obtained from the PPR78 model.

4. Results and discussion

The extended database, containing 65,700 data points, we previously built to develop the PPR78 model, was used in order to determine the accuracy of the PR2SRK model and thus to check the validity of the hypothesis we made ($g_{res}^{E,\infty}$ independent of the EoS). The following objective function was calculated:

$$F_{obj} = \frac{F_{obj,bubble} + F_{obj,dew} + F_{obj,crit.\,comp} + F_{obj,crit.\,pressure}}{n_{bubble} + n_{dew} + n_{crit} + n_{crit}} \tag{44}$$

$$\begin{cases} F_{obj,bubble} = 100\sum_{i=1}^{n_{bubble}} 0.5\left(\frac{|\Delta x|}{x_{1,exp}} + \frac{|\Delta x|}{x_{2,exp}}\right)_i \text{ with } |\Delta x| = |x_{1,exp}-x_{1,cal}| = |x_{2,exp}-x_{2,cal}| \\[2mm] F_{obj,dew} = 100\sum_{i=1}^{n_{dew}} 0.5\left(\frac{|\Delta y|}{y_{1,exp}} + \frac{|\Delta y|}{y_{2,exp}}\right)_i \text{ with } |\Delta y| = |y_{1,exp}-y_{1,cal}| = |y_{2,exp}-y_{2,cal}| \\[2mm] F_{obj,crit.\,comp} = 100\sum_{i=1}^{n_{crit}} 0.5\left(\frac{|\Delta x_c|}{x_{c1,exp}} + \frac{|\Delta x_c|}{x_{c2,exp}}\right)_i \text{ with } |\Delta x_c| = |x_{c1,exp}-x_{c1,cal}| = |x_{c2,exp}-x_{c2,cal}| \\[2mm] F_{obj,crit.\,pressure} = 100\sum_{i=1}^{n_{crit}}\left(\frac{|P_{cm,exp}-P_{cm,cal}|}{P_{cm,exp}}\right)_i \end{cases}$$

n_{bubble}, n_{dew} and n_{crit} are the number of bubble points, dew points and mixture critical points respectively. x_1 is the mole fraction in the liquid phase of the most volatile component and x_2 the mole fraction of the heaviest component (with $x_2 = 1 - x_1$). Similarly, y_1 is the mole fraction in the gas phase of the most volatile component and y_2 the mole fraction of the heaviest component (with $y_2 = 1 - y_1$). x_{c1} is the critical mole fraction of the most volatile component and x_{c2} the critical mole fraction of the heaviest component (with $x_{c2} = 1 - x_{c1}$). P_{cm} is the binary critical pressure.

For the 65,700 data points included in our database, the objective function defined by Eq. (44) is: $F_{obj} = 7.9\%$ (for the same database, the PPR78 model leads to: $F_{obj}^{PPR78} = 7.6\%$). The average overall deviation on the liquid phase composition is:

$$\begin{cases} \overline{\Delta x_1} = \overline{\Delta x_2} = \dfrac{\sum_{i=1}^{n_{bubble}} \left(\left| x_{1,\exp} - x_{1,cal} \right| \right)_i}{n_{bubble}} = 0.022 \\ \text{and} \\ \overline{\Delta x\%} = \dfrac{\overline{\Delta x_1\%} + \overline{\Delta x_2\%}}{2} = \dfrac{F_{obj,bubble}}{n_{bubble}} = 7.86\,\% \end{cases} .$$
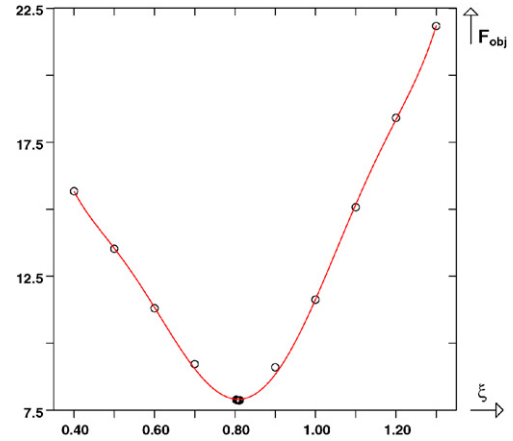

Fig. 2. Plot of the objective function defined by Eq. (44) as a function of the ξ parameter.
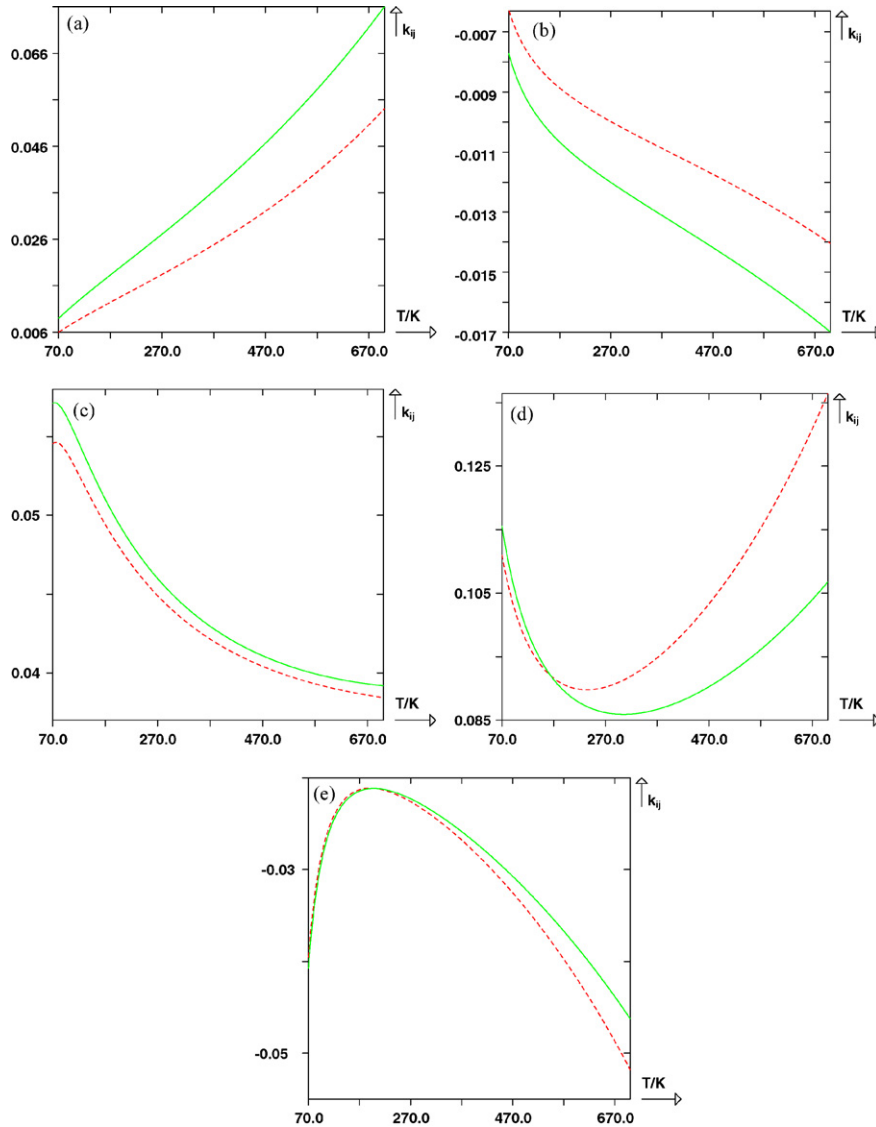

Fig. 3. Temperature dependence of estimated binary interaction parameters (k_{ij}) by means of Eqs. (36) and (41). Solid line: k_{ij} for the PR-EoS. Dashed line: k_{ij} for the SRK EoS. (a) System methane + cyclohexane. (b) System n-undecane + n-eicosane. (c) System propane + benzene. (d) System ethane + hydrogen sulfide. (e) System 2,2-dimethyl butane + 2,4-dimethyl pentane.
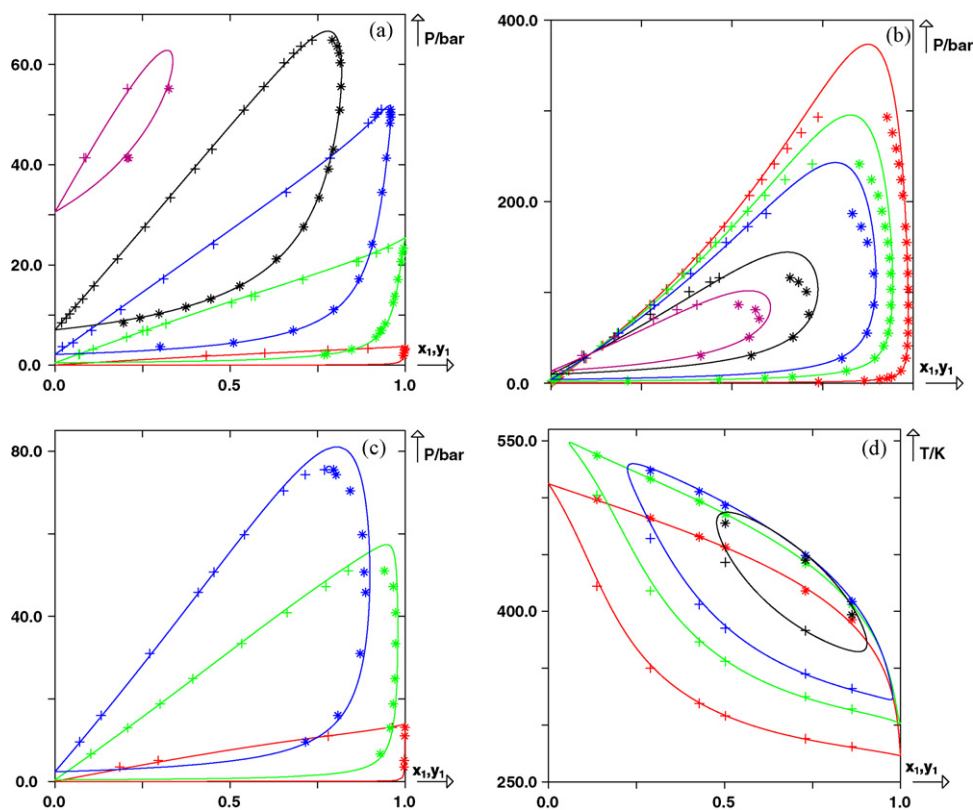
Fig. 4. Prediction of isothermal or isobaric dew and bubble curves for 4 binary systems using the PR2SRK model. Solid line: predicted curves with the PR2SRK model. +: experimental bubble points, *: experimental dew points. (a) system methane(1)/ethane(2) at 5 different temperatures: $T_1 = 130.37$ K ($k_{ij} = 0.00057$), $T_2 = 172.04$ K ($k_{ij} = 0.0012$), $T_3 = 199.93$ K ($k_{ij} = 0.0025$), $T_4 = 230.00$ K ($k_{ij} = 0.0040$), $T_5 = 283.15$ K ($k_{ij} = 0.0069$). (b) system methane(1)/decane(2) at 5 different temperatures: $T_1 = 410.93$ K ($k_{ij} = 0.046$), $T_2 = 477.59$ K ($k_{ij} = 0.059$), $T_3 = 510.95$ K ($k_{ij} = 0.068$), $T_4 = 563.25$ K ($k_{ij} = 0.086$), $T_5 = 583.05$ K ($k_{ij} = 0.095$). (c) system propane(1)/1,3,5-trimethyl benzene (2) at 3 different temperatures: $T_1 = 313.10$ K ($k_{ij} = 0.017$), $T_2 = 403.10$ K ($k_{ij} = 0.023$), $T_3 = 473.00$ K ($k_{ij} = 0.030$). (d) system ethane(1)/cyclohexane(2) at 4 different pressures: $P_1 = 24.1$ bar, $P_2 = 44.8$ bar, $P_3 = 58.6$ bar, $P_4 = 82.7$ bar.
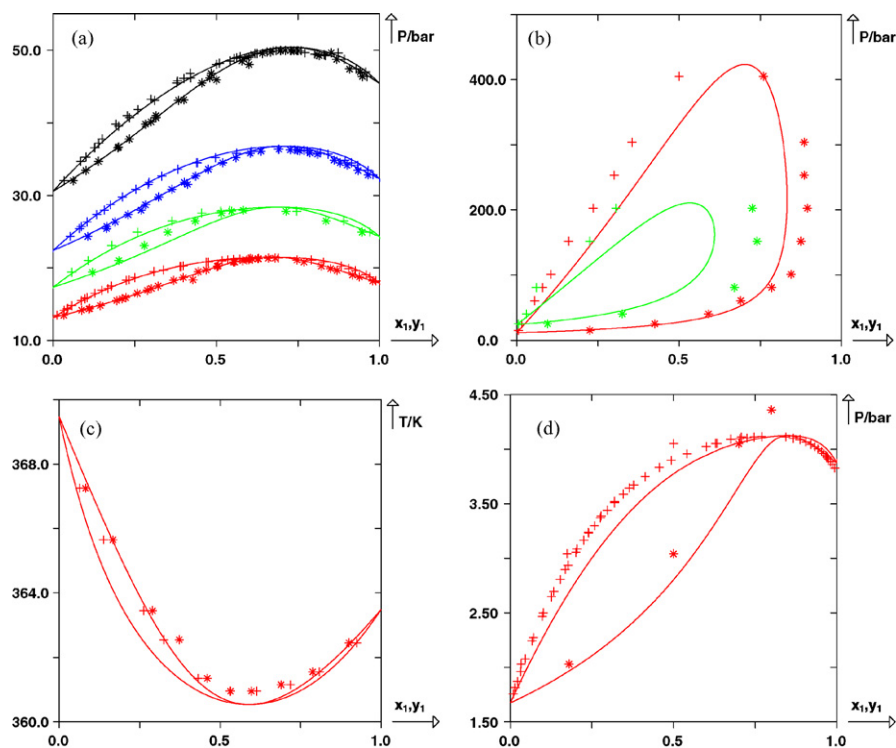

Fig. 5. Prediction of isothermal or isobaric dew and bubble curves for 4 binary systems using the PR2SRK model. Solid line: predicted curves with the PR2SRK model. +: experimental bubble points, *: experimental dew points. (a) System carbon dioxide(1)/ethane(2) at 4 different temperatures: $T_1 = 250.00$ K ($k_{ij} = 0.14$), $T_2 = 260.00$ K ($k_{ij} = 0.14$), $T_3 = 270.00$ K ($k_{ij} = 0.14$), $T_4 = 283.15$ K ($k_{ij} = 0.14$). (b) System nitrogen(1)/toluene(2) at 2 different temperatures: $T_1 = 498.15$ K ($k_{ij} = -0.23$), $T_2 = 548.15$ K ($k_{ij} = -0.31$). (c) System 2-methyl butane (1)/ethyl mercaptan (2) at $P_1 = 5.88$ bar. (d) System hydrogen sulfide(1)/propane(2) at $T = 243.2$ K ($k_{ij} = 0.062$).

Fig. 6. Prediction of the critical locus of various binary mixtures using the PR2SRK model. Solid line: predicted critical locus. Dashed line: pure component vaporization curve. +: pure component critical point. ○, □, ×, ■, *,♦,◇: experimental data. (a) Critical locus of ethane + n-alkane binary mixtures. (b) Critical locus of 6 binary systems containing aromatic compounds. (c) Critical locus of benzene + n-alkane binary mixtures. (d) Critical locus of 8 binary systems containing paraffinic, naphthenic and aromatic compounds.
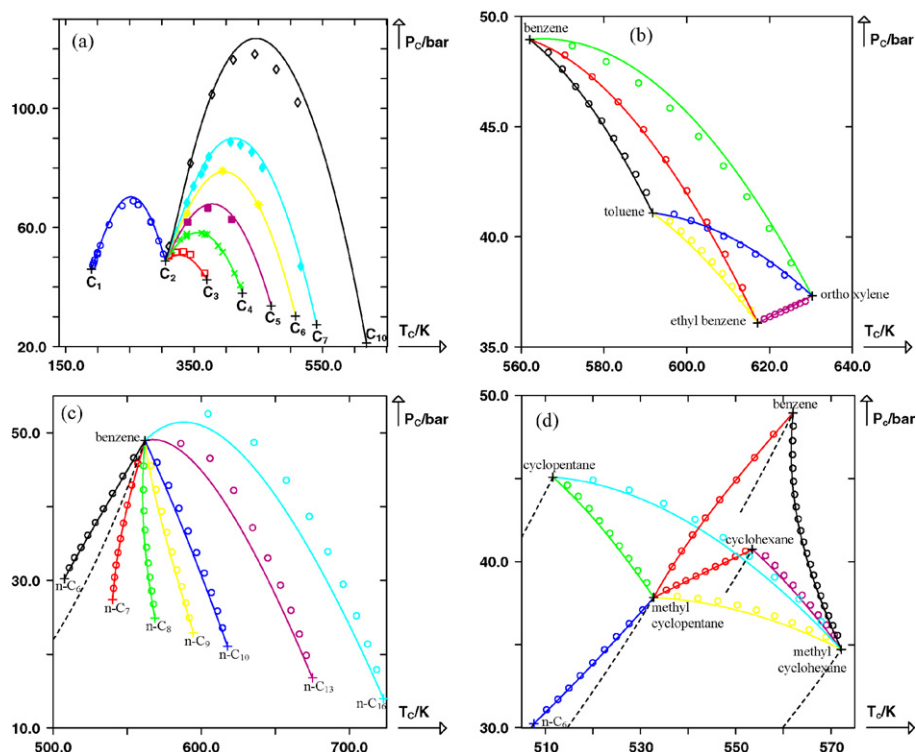

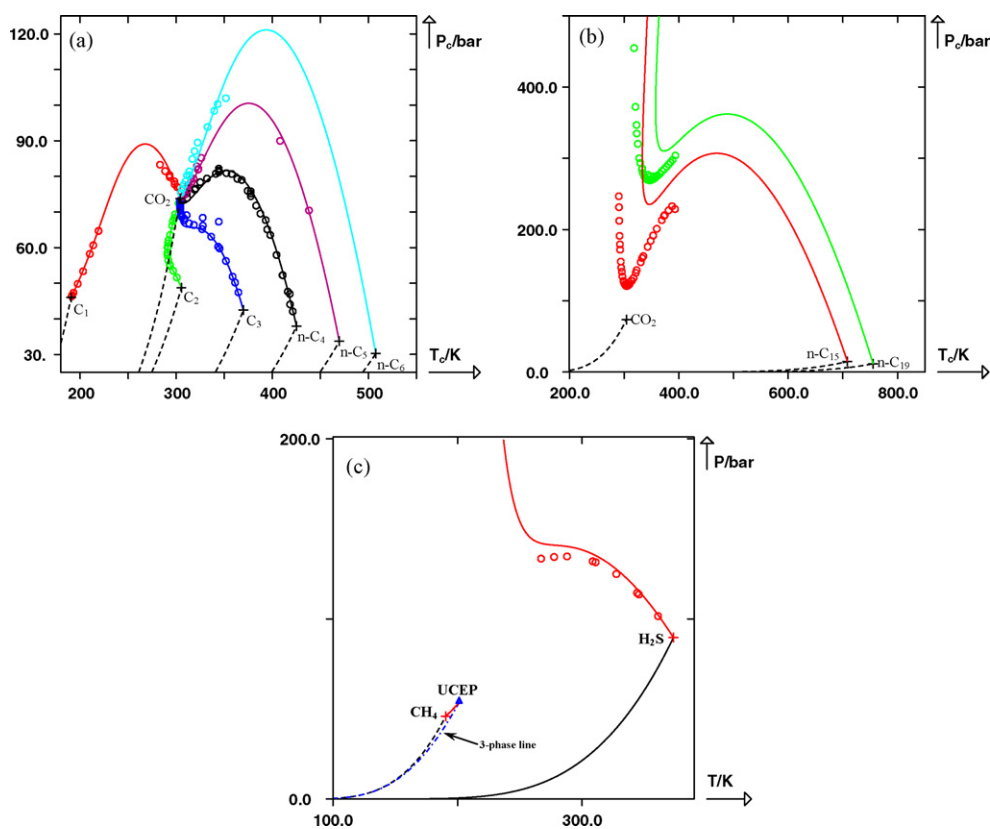**Fig. 7.** Prediction of the critical locus of various binary mixtures using the PR2SRK model. Solid line: predicted critical locus. Dashed line: pure component vaporization curve. +: pure component critical point. ○: experimental data. (a) Critical locus of 6 binary systems containing CO_2 and a n-alkane. (b) critical locus of 2 binary systems containing CO_2 and a n-alkane. (c) Critical locus of the methane + H_2S system.

The average overall deviation on the gas phase composition is:

$$
\begin{cases}
\overline{\Delta y_1} = \overline{\Delta y_2} = \dfrac{\displaystyle\sum_{i=1}^{n_{\text{dew}}} (|y_{1,\exp} - y_{1,\text{cal}}|)_i}{n_{\text{dew}}} = 0.014 \\
\text{and} \\
\overline{\Delta y\%} = \dfrac{\overline{\Delta y_1\%} + \overline{\Delta y_2\%}}{2} = \dfrac{F_{\text{obj,dew}}}{n_{\text{dew}}} = 8.09\,\%
\end{cases}.
$$

The average overall deviation on the critical composition is:

$$
\begin{cases}
\overline{\Delta x_{c1}} = \overline{\Delta x_{c2}} = \dfrac{\displaystyle\sum_{i=1}^{n_{\text{crit}}} (|x_{c1,\exp} - x_{c1,\text{cal}}|)_i}{n_{\text{crit}}} = 0.017 \\
\text{and} \\
\overline{\Delta x_c\%} = \dfrac{\overline{\Delta x_{c1}\%} + \overline{\Delta x_{c2}\%}}{2} = \dfrac{F_{\text{obj,crit.comp}}}{n_{\text{crit}}} = 6.57\,\%
\end{cases}.
$$

The average overall deviation on the binary critical pressure is:

$$
\begin{cases}
\overline{\Delta P_c} = \dfrac{\displaystyle\sum_{i=1}^{n_{\text{crit}}} (|P_{\text{cm,exp}} - P_{\text{cm,}cal}|)_i}{n_{\text{crit}}} = 6.39\,\text{bar} \\
\text{and} \\
\overline{\Delta P_c\%} = \dfrac{F_{\text{obj,crit. pressure}}}{n_{\text{crit}}} = 3.57\,\%
\end{cases}.
$$

These results clearly indicate that the PR2SRK model is really an accurate predictive model. The deviations are very similar to those obtained with the PPR78 approach: $\overline{\Delta x_1}$ and $\overline{\Delta y_1}$ are exactly the same for both these models. The critical compositions and the binary critical pressures are however slightly better predicted with the PPR78 model. We can thus conclude that the hypothesis we made ($g_{\text{res}}^{E,\infty}$ independent of the EoS) is pertinent. In order to strengthen this conclusion, it was decided to plot F_{obj} defined by Eq. (44) as a function of the ξ parameter. Our idea was to check whether the value of this parameter determined from Eq. (17), that is $\xi = 0.807$, was the optimized value. In this study, ξ was varied between 0.4 and 1.3 and the resulting curve smoothed with a sixth order polynomial may be seen in Fig. 2. From this figure, the ξ value minimizing the objective function is: $\xi_{\text{optimized}} = 0.808$ which is extremely close to the theoretical value ($\xi_{\text{theoretical}} = 0.807$) defined by Eq. (17). This result undeniably reinforces our conviction that $g_{\text{res}}^{E,\infty}$ is independent of the EoS.

At this step, it looks interesting to compare the numerical values of the k_{ij} for both the PR and the SRK EoS. Some typical illustrations, where the temperature varies between 70 and 700 K can be found in Fig. 3. From this figure it is possible to conclude that both EoS (PR and SRK) need different k_{ij} values. The difference between the two sets of k_{ij} is however not very large. Depending on the system, the k_{ij} for the PR-EoS may be larger or smaller than the k_{ij} for the SRK EoS. We can also conclude that the PPR78 and the PR2SRK models are able to predict the different k_{ij} trends commonly encountered. Indeed, the k_{ij} may increase, decrease or go through with an extremum with respect to temperature.

Figs. 4 and 5 illustrate for some typical binary systems the accuracy of the proposed PR2SRK model. From these figures, we can conclude that accurate results are obtained whatever the temperature and the pressure. However, as previously explained [7], systems containing nitrogen are difficult to predict with a cubic EoS.

The prediction of phase equilibria of binary mixtures in the critical region is an important problem because the shape of the critical locus gives necessary basic information about the topology of phase behavior. For this reason, it has been decided to predict the critical locus of various binary mixtures by using the PR2SRK equation of state. A comparison between theory and experiment is illustrated in Figs. 6 and 7. The overall quality of predictions obtained from the PR2SRK model are very good for type I phase diagrams in the classification scheme of Van Konynenburg and Scott [28]. Nevertheless, binary systems exhibiting type III phase behavior are more difficult to predict with accuracy.

5. Conclusion

A group contribution method allowing the estimation of the temperature-dependent binary interaction parameters ($k_{ij}(T)$) for the widely used Soave–Redlich–Kwong equation of state has been developed. This new model has been called PR2SRK. The group interaction parameters (A_{kl}^{SRK} and B_{kl}^{SRK}) used in this model are those previously determined for the PR-EoS multiplied by $\xi = 0.807$. It was thus not necessary to re-estimate the parameters for the SRK EoS. A very long, tedious and difficult job has thus been saved. In a paper to be published as soon as possible, it will be shown that by fitting the group interactions of the SRK EoS (A_{kl}^{SRK} and B_{kl}^{SRK}) directly on the 65,700 VLE data points used to elaborate the PPR78 model, only a small improvement of the SRK model can be obtained in comparison to the PR2SRK model developed in this study.

The key idea used in this paper was to assume that the residual molar excess Gibbs energy at infinite pressure ($g_{\text{res}}^{E,\infty}$) was independent of the EoS when one combines at constant packing fraction a Van Laar-type $\mathcal{G}^E$ function and a cubic EoS.

We have also shown that the mathematical equations derived for the SRK EoS are general and applicable to any cubic EoS. It is thus possible to calculate by GC, the temperature-dependent k_{ij} for any desired cubic EoS, with any desired $a_i(T)$ function, using the group-contribution parameters (A_{kl}^{PR} and B_{kl}^{PR}) we determined for the PR-EoS.

The most important conclusion is that the results obtained with the PR2SRK model are in many cases very accurate in both the sub-critical and critical regions. We can thus conclude that the hypothesis we made ($g_{\text{res}}^{E,\infty}$ independent of the EoS) is pertinent. The equations established for the SRK EoS only relies on this hypothesis. They are thus general and applicable to any cubic EoS. As a consequence, whatever the considered EoS, we can trust in the k_{ij} estimated by GCM from the PPR78 model.

List of symbols

$a(T)$	temperature-dependent function of the equation of state
A_{kl}, B_{kl}	group interaction parameters allowing the calculation of the BIPs
b	covolume
E_{ij}	binary interaction parameter of the Van Laar excess function
$\mathcal{G}^E$	expression for the molar excess Gibbs energy (i.e. activity coefficient model)
$\mathcal{G}_{\text{res}}^E$	residual term of an activity coefficient model
g_{res}^E	residual part of the molar excess Gibbs energy calculated from an EoS
$g_{\text{res}}^{E,\infty}$	residual part of the molar excess Gibbs energy under infinite pressure calculated from an EoS
k_{ij}	binary interaction parameter
m	shape parameter
P	pressure
P_c	critical pressure
R	gas constant
T	temperature
T_c	critical temperature
v	volume
x_i, y_i, z_i	mole fraction

Greek letters

ω acentric factor

α_{ik} fraction occupied by group k in the molecule i

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