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## Letter to the editor

### SAFT and cubic EoS: type of deviation from ideality naturally predicted in the absence of BIPs. Application to the modelling of athermal mixtures.

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Recently, in a paper that arose our interest, Tassin et al. [1] addressed the modelling of nearly athermal mixtures by cubic equations of state (CEoS), 15 years after the publication of exciting and controversial papers [2,3] on the same topic. The authors concluded that the well-established Soave-Redlich-Kwong (SRK) [4] and Peng-Robinson (PR) [5,6] EoS totally fail in describing the non-ideality of size-asymmetric athermal systems (like those composed of a light and a heavy n-alkane) when they are combined with classical Van der Waals one-fluid (VdW1f) mixing rules [7] and zero binary interaction parameters (BIPs) values. Indeed, with such mixing rules (MR) the SRK and PR EoS predict positive deviations from ideality while experimental measurements show exactly the opposite, i.e., negative excess Gibbs energy values ( $g^E < 0$ ).

On the contrary, the non-associating terms of the PC-SAFT EoS (with no binary interaction parameters) can represent such solutions since they predict negative  $g^E$  values. Since this EoS involves 3 parameters ( $m$ ,  $\sigma$ ,  $\varepsilon/k$ ) to describe each pure species, Tassin et al. [1] conclude that CEoS like the SRK or PR EoS that encompass 2 parameters (the T-dependent attractive parameter  $\tilde{\varepsilon}$  and the covolume  $b$ ) are not sophisticated enough and that only an *augmented* version of CEoS involving also 3 parameters ( $\tilde{\varepsilon}$ ,  $b$  and a third one), could represent this type of systems properly. We do not share such conclusions even if at first sight, they seem to be supported by the data. Our purpose is to take another look and shed new light on the modelling of athermal systems and on the consequence of using null  $k_{ij}$  values. We thus decided to take the opportunity of a *letter to the editor* to open a scientific debate on these issues. It is believed that essentially two points deserve discussion:

- Following Tassin et al., we are convinced that the number of parameters involved in EoS is a key factor when comparing their performances. However, we do not share the way they used to count the parameters of CEoS. We will explain why we believe preferable to classify the classical SRK and PR CEoS as 3-parameter models instead of 2-parameter models. Following our approach, the RK-PR EoS is actually a 4-parameter model. In addition, considering at first the case of pure components, we will discuss why we believe that the forth parameter of this latter model is likely to improve density predictions but not phase-equilibrium predictions. Our view on the extension to

mixtures will also be discussed and will entail inevitably a debate on the conclusions proposed by the authors in terms of EoS performances.

- In the same spirit, it is believed appropriate to debate on the physical interpretation of the binary interaction parameter (BIP, denoted  $k_{ij}$  generally) involved in CEoS using classical mixing rules. Following what Tassin et al. presuppose, we defend the idea that BIP of CEoS govern enthalpic (or residual) contribution to non-ideality in binary systems. However, we will show that a null  $k_{ij}$  does not cancel the residual contribution. As a consequence, modelling an athermal system with CEoS using a null- $k_{ij}$  seems inappropriate and doomed to fail. By the way, we will highlight that the  $k_{ij}$  involved in the combination rule of the PC-SAFT EoS also plays a central role: under infinite pressure, no matter the values of the parameters of the pure compounds, the use of a null- $k_{ij}$  for modelling a binary system leads inevitably to negative deviations from ideality. As previous, these observations direct us to debate on the conclusions proposed by Tassin et al.

### **1. Definition of a so-called 2 or 3-parameter EoS.**

First of all, we believe it necessary to initiate the debate by clarifying the definition of what is called a 2-parameter or a 3-parameter EoS. In our opinion, the number of parameters must refer to the corresponding-states principle (CSP) on which the EoS relies. In other words, this number must identify the number of component-dependent parameters required by the EoS. As a first example, the VdW EoS follows the 2-parameter CSP and requires the knowledge of  $T_{c,\text{exp}}$  and  $P_{c,\text{exp}}$ , i.e., of 2 input properties for describing a pure component. As a second example, the PC-SAFT EoS requires the specification of 3 input properties for a given pure compound ( $m$ ,  $\sigma$ ,  $\varepsilon/k$ ) and must be classified as a 3-parameter EoS. Unlike Tassin et al., we claim that the PR and SRK EoS are also 3-parameter EoS since both of them rely on Pitzer's 3-parameter CSP for which the 3 properties are  $T_{c,\text{exp}}$ ,  $P_{c,\text{exp}}$  and  $\omega_{\text{exp}}$ . We even believe that the 3 input parameters embedded in PC-SAFT and in a CEoS like PR or SRK have comparable physical meaning. The segment number  $m$  is, somehow, the molecular equivalent of the acentric factor  $\omega$ ; it explicitly considers the chain length or non-sphericity of the molecules. Likewise,  $\sigma$ , the segment diameter is clearly related to the covolume  $b$ , which is proportional to the molecular volume. Lastly,  $\varepsilon$ , an energy parameter is the molecular equivalent of  $a_c$ , the critical value of the attractive parameter. Consequently, we do not share the view of Tassin et al. when they explain that comparing the PR and the PC-SAFT EoS would amount to comparing a race between a car and an airplane. Our recent comparison between these 2 EoS [8] makes it possible to conclude that they show actually very similar performances.

What can be said about the RK-PR EoS developed by Cismondi and Mollerup [9]? First, let us state that this EoS is a variant of that proposed by Schmidt and Wenzel in

1980 [10]. For a clear presentation, let us recall that in a generalized form, CEoS can be expressed as:

$$P(T, v) = \frac{RT}{v-b} - \frac{a(T)}{v^2 + ubv + wb^2} \quad (1)$$

The constants  $u$  and  $w$  are either universal real numbers (the same values apply to all compounds) or substance-dependent quantities. By considering  $u$  and  $w$  as universal (component-independent) constants, the critical compressibility factor engendered by the EoS ( $z_c^{EoS}$ ) is the same for all components so that the predicted saturated liquid densities, and particularly those in the critical region, will inevitably deviate from their experimental values. Indeed, known experimental values of  $Z_c$  range between 0.0144 (for magnesium oxide) and 0.637 (for triethyl phosphate). One option to make  $u$  and  $w$  component-dependent is to correlate them to a readily available property like the acentric factor or the experimental critical compressibility factor  $z_c^{\text{exp}}$ .

To come back to the 3-parameter SRK and PR EoS, they are characterized by universal ( $u, w$ ) pairs; the SRK EoS corresponds to  $u=1$  and  $w=0$  so that the corresponding critical compressibility factor is:  $z_c^{SRK} = 1/3$ . In 1976, Peng and Robinson selected  $u=2$  and  $w=-1$ ; they thus obtained a critical compressibility factor equal to 0.3074. We immediately notice that all these authors (and some others [11]) assumed that  $u$  and  $w$  are subject to the constraint  $u+w=1$  without a clear explanation or theoretical foundations.

In 1980, in order to improve the prediction of liquid densities in the critical region, i.e., to make the  $z_c^{EoS}$  value component-dependent, Schmidt and Wenzel decided to consider component-dependent values for  $u$  and  $w$ . They noticed that the SRK EoS better described liquid molar volumes of spherical molecules like methane (for which  $\omega=0$ ) than the PR EoS while, conversely, the PR EoS yielded better results for n-hexane (the acentric factor of which is about 0.33) than the SRK EoS. Schmidt and Wenzel thus decided to keep the relationship  $u+w=1$  that applies to both EoS and in order to find back the SRK EoS ( $w=0$ ) when  $\omega=0$  and the PR ( $w=-1$ ) EoS when  $\omega \approx 0.33$ , they set:  $w = -3\omega$ . This led them to the following expression:

$$P(T, v) = \frac{RT}{v-b} - \frac{a_c \cdot \alpha(T)}{v^2 + (c+1)bv - cb^2} \quad \text{with: } c = 3\omega \quad (2)$$

Such an EoS, which makes it possible to switch from the volumetric dependence of the RK ( $c=0$  for small molecules) EoS to that of the PR ( $c=1$  for intermediate-size molecules) EoS is exactly the *RK-PR* EoS [9] in which  $c$ , however, is not correlated to the acentric factor but determined component by component in order that the critical compressibility factor returned by the EoS is 1.168 time the experimental value. The RK-PR is thus a 4-parameter CEoS and the 4 macroscopic properties are:  $T_{c,\text{exp}}$  and  $P_{c,\text{exp}}$  (to determine  $a_c$  and  $b$ ), the acentric factor  $\omega$  (to determine the unique parameter  $k$  involved in the  $\alpha(T)$  function) and  $z_c^{\text{exp}}$  to determine  $c$ . By comparing the PC-SAFT and the RK-PR EoS, an advantage is thus given to the RK-PR EoS since it has one more parameter.

As reported by Twu et al. [12] and by Le Guennec et al. [13], the ability for a CEoS to predict vapor pressure and vapor-liquid equilibrium (VLE) data requires the

selection of an appropriate  $\alpha$ -function while the accuracy of the predicted volumetric properties is governed by the volume function of the attractive term. To support these conclusions, Table 1 reports – for hundreds of pure compounds – the mean average percent error (MAPE) between calculated and experimental data on vapor pressures ( $P^{sat}$ ), enthalpies of vaporization ( $\Delta_{vap}H$ ), liquid heat capacities ( $c_{P,L}^{sat}$ ) and liquid molar volumes ( $v_L^{sat}$ ) for the PR and the RK EoS, both armed with a consistent [14,15] Twu  $\alpha$ -function [16]. As expected, these two CEoS, that only differ by the volume function of the attractive term exhibit very similar deviations on VLE data ( $P^{sat}$ ,  $\Delta_{vap}H$  and  $c_{P,L}^{sat}$ ) but extremely different deviations on liquid densities.

**Table 1.** MAPE on  $P^{sat}$ ,  $\Delta_{vap}H$ ,  $c_{P,L}^{sat}$  and  $v_L^{sat}$  as predicted by the PR and RK EoS armed with a Twu  $\alpha$ -function.

| EoS | MAPE on $P^{sat}$<br>(980 compounds) | MAPE on $\Delta_{vap}H$<br>(805 compounds) | MAPE on $c_{P,L}^{sat}$<br>(529 compounds) | MAPE on $v_L^{sat}$ ( $T_r \leq 0.9$ )<br>(997 compounds) |
|-----|--------------------------------------|--|--|---|
| PR  | <b>0.9 %</b>                         | <b>2.0 %</b>                               | <b>2.0 %</b>                               | <b>7.4 %</b>  |
| RK  | <b>1.1 %</b>                         | <b>2.1 %</b>                               | <b>2.2 %</b>                               | <b>17.3 %</b>   |

Consequently, by focusing on pure components, the use of the RK-PR EoS instead of the original RK or PR EoS only significantly improves the deviations between experimental and calculated liquid densities. The impact on pure-component phase equilibrium calculations is so small that we can certainly anticipate that when working with binary systems – the impact on  $g^E$  values should also be weak if appropriate mixing rules are selected. This point is debated in the next section.

As stated by Tassin et al., the introduction of the fourth parameter  $C$  is not mathematically equivalent to translate the EoS [17–19] but as demonstrated by Piña-Martinez et al. [20], both modifications of the original PR or RK EoS (addition of a 4<sup>th</sup> parameter that only modifies the volume function or addition of a Pénélox volume shift) have a similar impact on their accuracy. Unlike the addition of a fourth parameter, the volume-translation concept does not affect the VLE calculations at all but as previously stated since such a fourth parameter only alters the volumetric dependence of the CEoS, it only slightly modifies VLE results.

## 2. Discussion on the modelling of athermal mixtures and on the consequence of using zero $k_{ij}$ values

To continue the debate, let us now clarify:

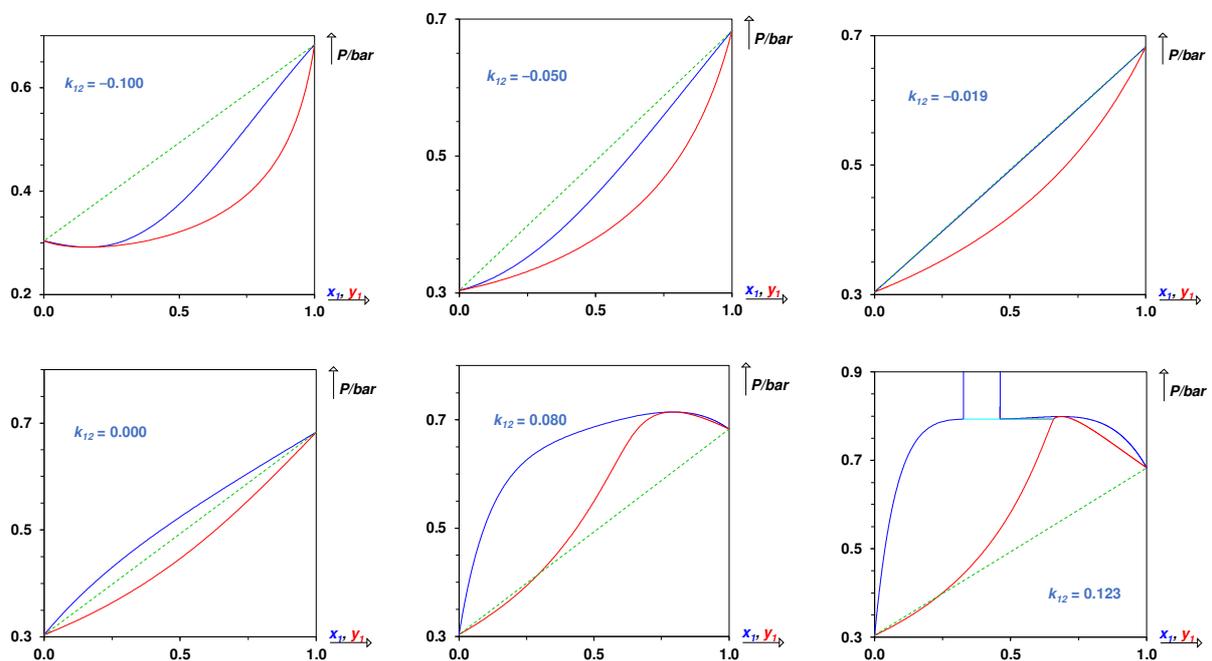
- whether the failure in modelling activity coefficients in nearly athermal mixtures of n-alkanes is due to the lack of a fourth parameter in a CEoS like SRK or PR or to the mixing rules used by Tassin et al.
- the possible reason of the success observed with the PC-SAFT EoS.

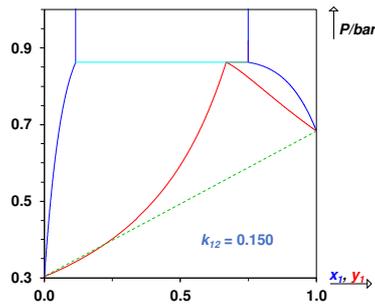
### 2.1. Influence of the $k_{ij}$ value in CEoS like SRK or PR armed with classical VdW1f mixing rules

To demonstrate the failure of CEoS like SRK or PR, Tassin et al. selected the classical VdW1f mixing rules but it is believed that the weak point of their calculations

is the choice of null  $k_{ij}$  values. We indeed know by experience that by varying  $k_{ij}$ , the highly flexible VdW1f MR can reproduce all the phase-equilibrium behaviors observed in binary systems. To illustrate this point, and highlight the huge influence of the  $k_{ij}$  value on fluid-phase equilibrium calculation, it was decided to plot – using the PR EoS and classical VdW1f MR – the isothermal phase diagram for the n-pentane (1) + acetone (2) system at  $T = 298.15\text{ K}$  giving different values to  $k_{12}$ . Results, visible in Fig. 1, show that:

1. for  $k_{12} = -0.10$ , the system exhibits a negative homogeneous azeotrope
2. for  $k_{12} = -0.05$ , the system still shows negative deviations from ideality but the azeotrope does not exist any more
3. for  $k_{12} = -0.019$ , the bubble curve is a straight line so that the system can be considered as ideal
4. for  $k_{12} = 0.0$ , the system shows positive deviations from ideality
5. for  $k_{12} = 0.08$ , the system exhibits a positive homogeneous azeotrope
6. for  $k_{12} = 0.123$ , the system simultaneously exhibits a positive homogeneous azeotrope and liquid-phase splitting giving birth to a three-phase line
7. for  $k_{12} = 0.15$ , the system exhibits a heterogeneous azeotrope.





**Figure 1.** Influence of  $k_{12}$  on the calculated isothermal phase diagram using the PR EoS and classical VdW1f MR for the n-pentane (1) + acetone (2) system at  $T/K = 298.15$ . The dashed line is Raoult's line.

Experimental VLE data on such a system [21] make it possible to conclude that deviations from ideality stem from enthalpic effects so that the excess entropy is negligible when compared to the excess enthalpy. Following Scatchard [22] and Hildebrand [23], the n-pentane + acetone binary system is thus a so-called *regular* solution. Using the terminology employed with activity coefficient models, we can assert that for such a system, the *combinatorial* (also called *entropic* or *athermal solution*) contribution to the excess Gibbs energy is close to zero ( $g^{E,comb} \approx 0$ ). Reciprocally, the *residual* (also called *enthalpic* or *energetic* or *regular solution*) contribution to the excess Gibbs energy is close to 100% so that for such a system:  $g^E \approx g^{E,res} \approx h^E$ . Coming back to Fig. 1, and comparing the relative positions of Raoult's lines and bubble curves (it is recalled that these relative positions reveal the sign of the deviations from ideality), it is thus now possible to draw the 2 following conclusions:

1.  $k_{12} = 0.0$  does not cancel  $g^{E,res}$ ; in other words,  $k_{12} = 0.0$  does not induce an ideal solution behavior for the considered *regular* system. Indeed, with  $k_{12} = 0.0$ , the system shows positive deviations from ideality and  $g^{E,res} > 0$ . It is believed that some scientific papers sometimes state that  $k_{12} = 0.0$  implies  $g^{E,res} = 0$  because by cancelling the binary interaction parameters of activity-coefficient models (Wilson, UNIQUAC ...), we systematically cancel the *residual* contribution to  $g^E$ .
2. a negative  $k_{12}$  value is necessary to cancel  $g^{E,res}$  and to get an ideal solution with the considered *regular* system.

As demonstrated below, these 2 important features, brought to light on an example are in fact completely general.

## 2.2. Consequence of using zero $k_{ij}$ value in CEoS like SRK or PR armed with classical VdW1f MR. Application to the modelling of athermal mixtures

In conclusion of the previous section, we do not think that the inability of the PR EoS, with classical Van der Waals mixing rules and null  $k_{ij}$  value to correlate athermal systems should be ascribed to the lack of a 4<sup>th</sup> EoS parameter but instead

to an inadequate choice of the  $k_{ij}$  value. To start our argumentation, let us recall that size-asymmetric athermal systems like those composed of a light and a heavy n-alkane are characterized by excess enthalpy values close to zero so that  $g^{E,res} \approx 0$  and consequently:  $g^E \approx g^{E,comb} \approx -Ts^E < 0$ . To accurately correlate such systems, a thermodynamic model thus needs to satisfy 2 constraints:

- The mathematical expression of  $g^{E,comb}$  must be able to accurately describe deviations from ideality of entropic nature
- The calculated value of  $g^{E,res}$  must be close to zero.

Regarding the first constraint, it is worth recalling that the *combinatorial* contribution to  $g^E$  (or to the excess Helmholtz energy  $a^E$  if excess volume effects are neglected) stemming from a 3-parameter CEoS like the SRK or the PR EoS is similar to a Flory-Huggins [24–27] expression:

$$a_{SRK \text{ or } PR}^{E,comb} = \underbrace{RT \sum_{j=1}^{n_c} x_j \ln \left( \frac{v_j - b_j}{v - b} \right)}_{\substack{\text{Flory-Huggins expression} \\ \text{(here in form of free-volume rather than volume)}}} \quad (3)$$

Such an equation is acknowledged to be particularly suitable to describe deviations from ideality attributed to size and shape differences of the components. It thus should be particularly suitable to satisfy the first constraint.

To discuss the fulfilment of the second constraint and justify the failure of the mixing rules selected by Tassin et al. to describe athermal systems, we are going to demonstrate that, at least under infinite pressure:

1. null  $k_{ij}$  values always lead to positive values of  $g^{E,res}$
2. only negative  $k_{ij}$  values make it possible to obtain  $g^{E,res} = 0$ . With such negative  $k_{ij}$  values, CEoS like SRK or PR can represent asymmetric athermal systems very accurately.

Our demonstration of these 2 points starts by recalling that by selecting a linear mixing rule for the covolume:

$$b_m(x) = \sum_{j=1}^{n_c} x_j b_j \quad (4)$$

the *residual* part of the excess Gibbs energy calculated from a 3-parameter CEoS like the SRK or the PR EoS when the pressure goes to infinity is given by the rigorous equation:

$$\frac{g^{E,res,EoS,\infty P}}{\Lambda_{EoS}} = \sum_{j=1}^{n_c} x_j \frac{a_j(T)}{b_j} - \frac{a_m(T,x)}{b_m(x)} \quad (5)$$

$\Lambda_{EoS}$  is a positive constant, the value of which only depends on  $\mathcal{L}$  and  $\mathcal{W}$ . To avoid confusion, let us recall that Eq. (5) only applies to CEoS in which  $\mathcal{L}$  and  $\mathcal{W}$  are universal constants (i.e., component independent). Therefore, it cannot be used for

the RK-PR EoS.  $g^{E, \text{res}, \text{EoS}}$  is calculated under infinite pressure in order to reason on a simple expression such as Eq. (5). The latter has many similarities with the equation established many years ago by Huron and Vidal [28] during the derivation of their famous advanced mixing rules and we refer the reader to their original paper [28] or to the book by Kontogeorgis and Folas [29] if more details are required.

By combining Eq. (5) with the classical VdW1f mixing rules recalled in Eq. (6), one obtains (after some algebraic derivation) the mathematical expressions shown in Eq. (7) [30–33]:

$$\left\{ \begin{array}{l} \text{Classical VdW1f mixing rules :} \\ b_m(x) = \sum_{j=1}^{n_c} x_j b_j \\ a_m(T, x) = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} x_i x_j a_{ij} \\ \text{The Berthelot combining rule is used, so that:} \\ a_{ij} = \sqrt{a_i(T) a_j(T)} \cdot [1 - k_{ij}(T)] \end{array} \right. \quad (6)$$

$$\left\{ \begin{array}{l} \updownarrow \\ \frac{g^{E, \text{res}, \text{EoS}, \infty P}}{\Lambda_{\text{EoS}}} = \frac{\sum_{i=1}^{n_c} \sum_{j=1}^{n_c} x_i x_j \cdot b_i b_j \cdot E_{ij}(T)}{2b_m(x)} \\ E_{ij}(T) = (\delta_i - \delta_j)^2 + 2\delta_i \delta_j k_{ij}(T) \\ \text{with: } \delta_i = \frac{\sqrt{a_i(T)}}{b_i} \end{array} \right. \quad (7)$$

We immediately notice that in Eq. (7),  $g^{E, \text{res}, \text{EoS}, \infty P}$  has the mathematical expression of a solely energetic Van Laar-type model. As previously discussed, in order to describe size-asymmetric athermal systems, it is necessary to impose  $g^{E, \text{res}} = 0$ , i.e., to impose  $E_{ij}(T) = 0$ . By doing so, we immediately get from Eq. (7) :

$$k_{ij}(T) = \frac{-(\delta_i - \delta_j)^2}{2\delta_i \delta_j} < 0 \quad (8)$$

It is thus possible to conclude that the only way to describe athermal systems using a classical 3-parameter CCoS with VdW1f mixing rules is to consider negative values of the BIPs ( $k_{ij} < 0$ ). Using a null  $k_{ij}$  with the SRK or PR EoS is definitively unsuitable for such systems.

The negative  $k_{ij}$  values calculated with Eq. (8) make vanish  $g^{E, \text{res}, \text{EoS}, \infty P}$  so that the corresponding mixing rules stemming from Eqs. (4) and (5), simply write:

$$\left\{ \begin{array}{l} b_m(x) = \sum_{j=1}^{n_c} x_j b_j \\ \frac{a_m(T, x)}{b_m(x)} = \sum_j x_j \frac{a_j(T)}{b_j} \end{array} \right. \quad (9)$$

We can thus conclude that the so-called “a/b mixing rules” depicted in Eq. (9) are only a particular case of the classical VdW1f mixing rules in which the  $k_{ij}$  obey Eq. (8). Although Kontogeorgis and Coutsikos [3] clearly demonstrated that such mixing rules accurately correlated size-asymmetric athermal systems, it was decided to calculate the activity coefficients of n-hexane infinitively diluted in heavier n-alkanes using the PR EoS with VdW1f MR and the negative  $k_{ij}$  values engendered by Eq. (8). Experimental values of the critical temperature ( $T_{c,exp}$ ), critical pressure ( $P_{c,exp}$ ) and acentric factor ( $\omega_{exp}$ ) are from the DIPPR database and the calculated  $\gamma_{n-C_6}^\infty$  values are confronted to experimental data in Table 2. From this table, it is clear that a very good agreement is obtained between the experimental and predicted activity coefficients at infinite dilution: the average deviation between both quantities is lower than 5%. This small deviation also makes it possible to conclude that the derivation of Eq. (8), although performed under infinite pressure, remains valid at lower pressures. This last result agrees with the observations made with the use of the mixing rules developed by Huron and Vidal: they were derived at infinite pressure but can be applied under ambient conditions.

**Table 2.** Experimental and predicted activity coefficients of n-hexane infinitively diluted in heavy n-alkanes ( $\gamma_1^\infty$ ) using the PR EoS with VdW1f MR and the negative  $k_{ij}$  values returned by Eq. (8)

| System 1+2                           | T/K    | Exp. $\gamma_1^\infty$ | $k_{12}$ from Eq. (8) | Calculated $\gamma_1^\infty$ with PR + VdW1f MR | Deviation     |
|--------------------------------------|--------|------------------------|-----------------------|---|---------------|
| n-C <sub>6</sub> + n-C <sub>16</sub> | 303.15 | 0.904 [34]             | -0.014                | 0.863   | 4.57%         |
| n-C <sub>6</sub> + n-C <sub>18</sub> | 308.15 | 0.877 [34]             | -0.017                | 0.838   | 4.40%         |
| n-C <sub>6</sub> + n-C <sub>20</sub> | 353.15 | 0.872 [35]             | -0.020                | 0.840   | 3.63%         |
| n-C <sub>6</sub> + n-C <sub>22</sub> | 373.15 | 0.859 [35]             | -0.026                | 0.815   | 5.13%         |
| n-C <sub>6</sub> + n-C <sub>24</sub> | 373.15 | 0.801 [35]             | -0.028                | 0.804   | 0.39%         |
| n-C <sub>6</sub> + n-C <sub>28</sub> | 373.15 | 0.736 [35]             | -0.035                | 0.766   | 4.14%         |
| n-C <sub>6</sub> + n-C <sub>32</sub> | 373.15 | 0.689 [35]             | -0.043                | 0.729   | 5.81%         |
| n-C <sub>6</sub> + n-C <sub>36</sub> | 373.15 | 0.639 [35]             | -0.048                | 0.708   | 10.79%        |
|                                      |        |                        |                       | <b>Average:</b>                                 | <b>4.86 %</b> |

We have thus given proof that the VdW1f mixing rules do not fail in describing athermal systems at all. Selection of more complex mixing rules is unnecessary. Addition of a 4<sup>th</sup> component-dependent parameter in the formulation of the EoS is unnecessary. However, appropriate negative  $k_{ij}$  values have to be selected.

Reciprocally, Eq. (7) shows that by using a null  $k_{ij}$  value as made by Tassin et al., a positive value of the *residual* excess Gibbs energy is obtained with a 3-parameter CEoS like SRK or PR:

$$k_{ij}(T) = 0 \Leftrightarrow \begin{cases} E_{ij}(T) = (\delta_i - \delta_j)^2 \\ \frac{g^{E, \text{res}, \text{EoS}, \infty P}}{\Lambda_{\text{EoS}}} > 0 \end{cases} \quad (10)$$

In other words,  $k_{ij} = 0$  will lead to *residual* activity coefficients greater than unity ( $\gamma_i^{\text{res}} > 1$ ). A null  $k_{ij}$  value is thus inappropriate to model athermal systems in which the *residual* contribution to  $g^E$  is expected to be negligible. Eq. (10) also highlights that even with *combinatorial* activity coefficients lower than unity, it is possible to get positive deviations from ideality, i.e.,  $\ln \gamma_i = \left( \underbrace{\ln \gamma_i^{\text{comb}}}_{<0} + \underbrace{\ln \gamma_i^{\text{res}}}_{>0} \right) > 0$ , when modelling athermal systems, if  $k_{ij} = 0$  is selected. This is the behavior observed by Tassin et al. However, neither the EoS nor the VdW1f mixing rules are guilty. The drawback of false positive deviations from ideality only comes from an inappropriate  $k_{ij}$ -value selection.

To conclude this section and avoid any ambiguity, we believe it is important to state that we are convinced by the high accuracy of the RK-PR cubic EoS. Indeed, as clearly demonstrated in several papers [36–38], the addition of a fourth parameter makes it possible to improve the accuracy of both the PR and SRK CEoS. As an example, the average 5% deviation reported in Table 1 is still more than twice the deviations obtained from predictions with the RK-PR EoS (2.3 %). The purpose of this section was to discuss the role and the influence of such a fourth parameter.

### 2.3. Consequence of using zero $k_{ij}$ value in the PC-SAFT EoS. Application to the modelling of athermal mixtures

When modelling athermal systems, Tassin et al. emphasized that by selecting  $k_{ij} = 0$ , the PC-SAFT EoS leads – as experimentally observed – to negative deviations from ideality.

For clarity, let's recall that the number of segments of a mixture is given by a linear mixing rule:

$$m(x) = \sum_{j=1}^{n_c} x_j m_j \quad (11)$$

In the same way as for cubic equations of state, it is necessary to define combining rules for the crossover parameters of the parameters  $\sigma$  and  $\epsilon$ . The Lorentz [39]-Berthelot [40] combining rules (CR) are generally used:

$$\begin{cases} \text{Lorentz CR: } \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \\ \text{Berthelot CR: } \epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}} (1 - k_{ij}) \end{cases} \quad (12)$$

where  $i$  and  $j$  denote two segments belonging to molecules  $i$  and  $j$  respectively.

Working with CEoS we were able to demonstrate that – at least under infinite pressure – a null  $k_{ij}$  value systematically led to positive value of the *residual* excess Gibbs. We thus now wonder if the negative deviations from ideality observed when modelling athermal systems with the PC-SAFT EoS and null  $k_{ij}$  value persist whatever the system. To answer this question, we found necessary to determine the mathematical expression of  $g^E$  stemming from the PC-SAFT EoS armed with zero  $k_{ij}$  value and to study its sign. From classical thermodynamics:

$$\frac{g^E}{RT} = \sum_{j=1}^{n_c} x_j \ln \left( \frac{\varphi_j}{\varphi_j^{pure}} \right) \quad (13)$$

where  $\varphi_j$  is the fugacity coefficient of component  $j$  in the mixture and  $\varphi_j^{pure}$  that of pure component  $j$  at the same temperature, pressure and aggregation state as the mixture. The mathematical expression of  $\varphi_j$  and  $\varphi_j^{pure}$ , available in the open literature for the PC-SAFT EoS, contain a high number of terms. For simplicity, it was decided to establish the expression of  $g^{E,PC-SAFT,k_{ij}=0}$  under infinite pressure, i.e., when the reduced densities of both the mixture and each pure component approach 1 ( $\eta$  and  $\eta_j^{pure} \rightarrow 1$ ). However, even in such a simplified case the resulting mathematical expression of  $g^{E,PC-SAFT,\infty P,k_{ij}=0}$  is very complex and takes the form of a development in the variable  $\eta$ . Keeping only the leading term of such a development, one obtains:

$$\left\{ \begin{array}{l} \frac{g^{E,PC-SAFT,\infty P,k_{ij}=0}}{RT} \approx - \frac{2m_1m_2x_1x_2[x_1m_1d_1^3 \cdot f(d_1,d_2) + x_2m_2d_2^3 \cdot f(d_2,d_1)]}{(1-\eta)^3 \left( \sum_{j=1}^2 x_j m_j d_j^3 \right)^2} \\ \text{with: } \begin{cases} d_j(T) = \sigma_j \left[ 1 - 0.12 \exp \left( -\frac{3\varepsilon_j}{k_B T} \right) \right] \\ f(x,y) = x^3 - 3xy^2 + 2y^3 \quad (> 0 \text{ when } x \text{ and } y \text{ are } > 0) \end{cases} \end{array} \right. \quad (14)$$

It is possible to demonstrate that  $f(x,y) = x^3 - 3xy^2 + 2y^3$  is always positive when the variables  $X$  and  $y$  are also positive. Since  $d_1$  and  $d_2$  are always positive, one can assert that:

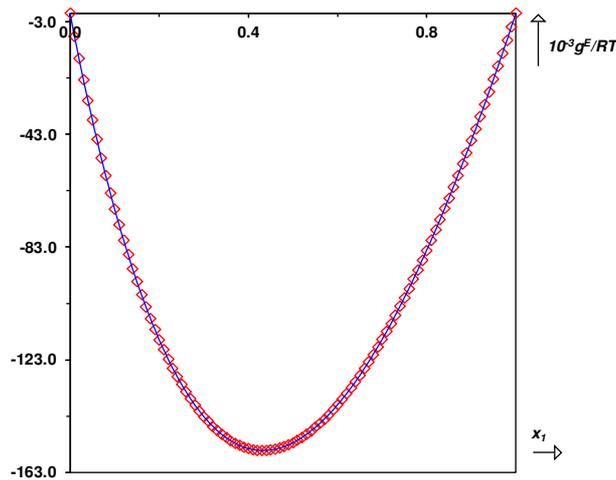
$$\boxed{g^{E,PC-SAFT,\infty P,k_{ij}=0} < 0} \quad (15)$$

Thus, under infinite pressure, no matter the values of the parameters of the pure compounds, the PC-SAFT EoS systematically predicts negative deviations from ideality in the absence of  $k_{ij}$ . It is believed this result was never mentioned before.

To validate, the mathematical expression depicted in Eq. (14), it was decided to plot for the system ethane(1) + CO<sub>2</sub>(2), the rigorous mathematical expression of

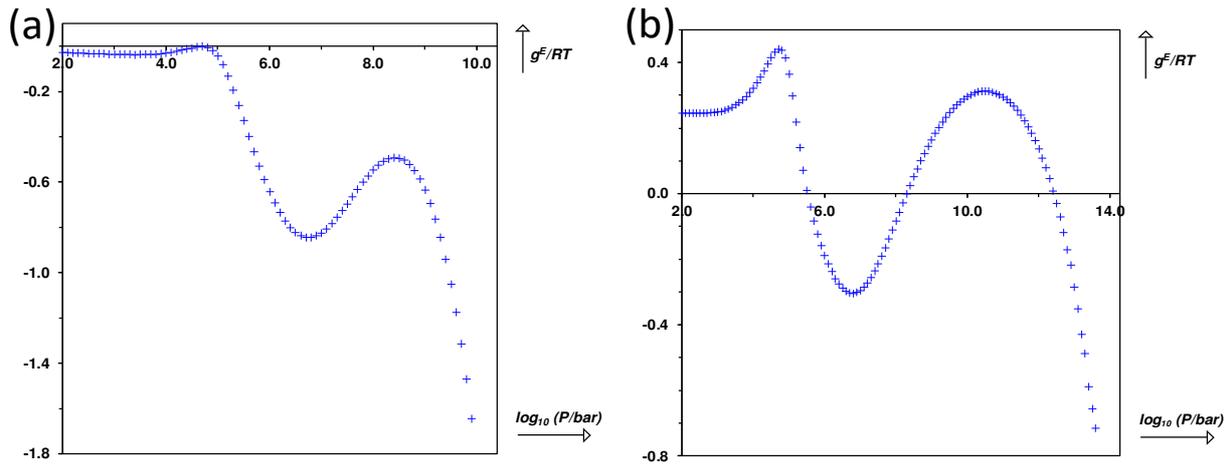
$\frac{g^E(T = 300 \text{ K}, \eta = 0.99, k_{12} = 0)}{RT}$  stemming from the PC-SAFT EoS as a function of  $x_1$

and to superimpose the obtained curve with values returned by Eq. (14). When  $g^E$  was rigorously calculated with the PC-SAFT EoS, the infinite pressure was approximated by imposing  $\eta = 0.99$  and the pure-component parameters were extracted from the paper by Gross and Sadowski [41]. The 2 curves, visible in Fig. 2, are indistinguishable what makes it possible to conclude that Eq. (14) is an excellent approximation of  $g^{E,PC-SAFT,\infty P,k_{ij}=0}$ .



**Figure 2.** Validation of the mathematical expression depicted in Eq. (14). Full line:  $\frac{g^E}{RT}(T = 300 \text{ K}, \eta = 0.99, k_{12} = 0)$  as a function of  $x_1$  for the system ethane(1) + CO<sub>2</sub>(2) as rigorously calculated by the PC-SAFT EoS. Symbols: values returned by Eq. (14).

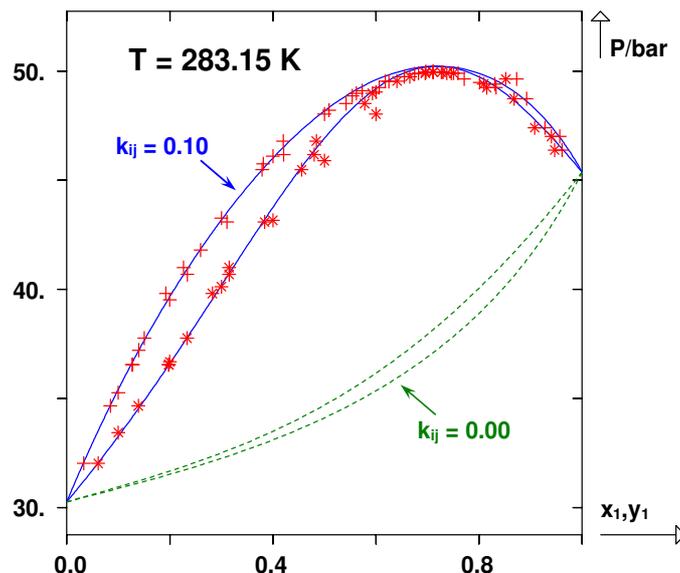
At this point, we thought it would be interesting to study the influence of the pressure on the sign of  $g^E$  predicted by the PC-SAFT EoS. For this reason, two binary systems that experimentally exhibit positive deviations from ideality were selected. These 2 systems are ethane(1) + CO<sub>2</sub> and water(1) + ethanol (2). The pure-component parameters were extracted from the paper by Gross and Sadowski [41] for ethane and CO<sub>2</sub> and from the database available in *Aspen Plus* for water and ethanol. For each binary system, the pressure was varied between 10 MPa and 10<sup>13</sup> MPa and for each pressure  $g^E$  was calculated at  $T = 300 \text{ K}$  for an equimolar mixture ( $x_1 = 0.5$ ) with the PC-SAFT EoS. The results are summarized in Fig. 3.



**Figure 3.** Influence of the pressure on the sign of  $g^E$  predicted by the PC-SAFT EoS and null  $k_{ij}$ .  $g^E$  is plotted at  $T = 300 \text{ K}$  for an equimolar mixture ( $x_1 = 0.5$ ). (a) system ethane(1) + CO<sub>2</sub>(2). (b) system water(1) + ethanol(2).

In both cases the resulting curve has the shape of a “double wave” and, as expected, at infinite pressure,  $g^E$  is negative whatever the system. It is however noticeable that  $g^E$  remains negative whatever the pressure for the system ethane + CO<sub>2</sub> while experimental data show exactly the opposite. On the contrary, for the system water(1) + ethanol(2), the PC-SAFT EoS with null  $k_{ij}$  predicts positive deviations from ideality until pressures as high as 10<sup>4</sup> MPa.  $g^E$  becomes negative only at extremely pressures.

For illustration and to emphasize the magnitude of the negative deviations observed with the ethane + CO<sub>2</sub> binary system, the isothermal phase diagram of such a system was calculated at 283.15 K with the non-associating PC-SAFT EoS armed with null BIPs. It is recalled that such a system is known to exhibit absolute positive azeotropy. It is thus characterized by positive deviations from ideality whatever the temperature. The results of the calculations are shown in Fig. 4 and speak by themselves: as expected with  $k_{ij} = 0$ , large negative deviations from ideality are observed demonstrating that the PC-SAFT EoS with zero  $k_{ij}$  value totally fails in describing the non-ideality of such a system. In order to reproduce the experimentally observed positive deviations from ideality, the absolutely necessity to insert a large positive  $k_{ij}$  value in the Berthelot combining rule (see Eq. (12)) appears clearly in Fig. 4.



**Figure 4.** Modeling of the system CO<sub>2</sub>(1) + ethane(2) at  $T/K = 283.15$  by the PC-SAFT equation (without association or polarity terms) by using a zero and a positive  $k_{ij}$  value.

### 3. Conclusion

The major conclusion of this letter is that CEoS like SRK and PR can represent athermal systems very accurately with the VdW1f MR provided that a suitable negative  $k_{ij}$  value is used. Therefore, it is not necessary to turn to more complex mixing rules or to more complex EoS by adding, e.g., a 4<sup>th</sup> parameter. This negative  $k_{ij}$  value has the property to cancel the infinite pressure *residual* contribution to the excess Gibbs energy ( $g^{E,res,CEoS,\infty P} = 0$ ,  $\gamma_i^{res} = 1$ ) stemming from the EoS which is the expectation for modelling athermal solutions. In addition, it has been demonstrated that the use of such a negative  $k_{ij}$  value is equivalent to using the so-called a/b mixing rules.

It has often been reported that a CEoS cannot adequately represent asymmetric systems. We here gave proof that, in fact, it was not the case and that this improper drawback is only the consequence of using a null  $k_{ij}$  value in the VdW1f MR. Neither the functional form of the 3-parameter CEoS nor the VdW1f MR have to be incriminated.

Another key conclusion of this letter is that the use of a zero  $k_{ij}$  value in the Berthelot combining rule (see Eqs. (6) and (12)) leads – under infinite pressure – to positive values of  $g^{E,res}$  when a 3-parameter CEoS is used but instead leads to negative deviations from ideality with the PC-SAFT EoS. This last result explains why – in the absence of BIPS – the PC-SAFT EoS is turned naturally to accurately correlate athermal systems while the opposite occurs with CEoS like SRK or PR.

### 4. Take-home message

We believe that the debate about the modelling of athermal mixtures originates from a vocabulary ambiguity: what is called *binary interaction parameters* covers

totally different quantities in activity coefficient ( $g^E$ ) models and in EoS. However, in both cases, the BIPs are used to model the enthalpic effects (they appear in the residual part of  $g^E$  models and in the attractive part of CEOs).

The key point is that by introducing BIP values equal to zero in activity coefficient models like UNIQUAC, WILSON or NRTL, the *residual* part of such models is rigorously cancelled so that they immediately can be used to describe athermal solution (in the case the  $g^E$  model contains a combinatorial part). Working with a 3-parameter CEOs and VdW1f MR, this is not the case and the situation is very different. Under infinite pressure, the use of a null  $k_{ij}$  value in the SRK or PR EoS does not cancel but instead makes positive the *residual* contribution to  $g^E$  ( $\gamma_i^{res} > 1$ ) so that the resulting model is inappropriate to correlate athermal systems. According to Eq. (8), a possibility to cancel  $g^{E,res,EoS,\infty P}$  when  $k_{ij} = 0$  would be to redefine the BIP by introducing the following combining rule in the VdW1f MR:

$$a_{ij} = \sqrt{a_i(T)a_j(T)} \cdot \left[ 1 - \frac{\overbrace{(\delta_i - \delta_j)^2}^{\text{BIP as defined by VdW}}}{-2\delta_i\delta_j} \left[ 1 - k_{ij}^{NEW}(T) \right] \right] \quad (16)$$

where the new BIP is denoted  $k_{ij}^{NEW}$ .

The key message of this paper is that the BIP that appears in the Berthelot combining rule for both the PC-SAFT and a 3-parameter CEOs is in fact a central parameter that needs to be considered absolutely. It should no longer be regarded as a side parameter the value of which is fixed arbitrarily or at least without deep reflection in order to improve the correlation of VLE data. We indeed demonstrated that (under infinite pressure) some deviations from ideality could be modeled only with specific  $k_{ij}$  values.

In the first part as this letter, proof was given that negative  $k_{ij}$  values in CEOs were absolutely necessary to model systems that exhibit negative deviations from ideality (systems for which  $g^{E,res} \leq 0$ ). As an example, it was discussed at length that the use of zero  $k_{ij}$  value could not model athermal systems.

Similarly, positive  $k_{ij}$  values are absolutely necessary to correlate systems that exhibit positive deviations from ideality with the PC-SAFT EoS. As an example, also discussed at length in this letter, a null  $k_{ij}$  is unable to reproduce the experimentally observed positive azeotrope on the binary system CO<sub>2</sub> + ethane.

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