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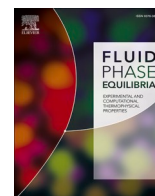
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# The state of the art of cubic equations of state with temperature-dependent binary interaction coefficients: From correlation to prediction

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## ABSTRACT

Cubic equations of state (CEoSs) are extensively used in academia and industry for their consistency, reliability, even under extrapolation conditions, and capacity to predict phase-equilibrium and energetic properties with acceptable accuracy. The optimal parametrization of a pure-component CEoS, a prerequisite for the development of any CEoS for mixtures, is discussed first. The binary interaction parameter (BIP) involved in the Van der Waals mixing rules of CEoSs is introduced with special attention to the temperature-dependent functions used to express it. The following questions are addressed: what is the physical meaning of the BIP? How does this parameter reveal deviations from ideal mixtures? What are the connections between Van der Waals and advanced (EoS/ $g^E$ ) mixing rules? What are the best methods to correlate this parameter? How can we predict it? In conclusion, the limitations and performances of models involving Van der Waals mixing rules, including BIPs, are examined and compared to the CEoSs based on advanced mixing rules.

## 1. Introduction

Thermodynamic models for fluids are the cornerstone of the simulation and conception of chemical engineering and energy conversion processes. These models can be used to calculate the thermodynamic properties involved in energy, mass and momentum balances, as well as the *equilibrium state* which is the borderline case of any energy and mass transfer kinetics. Therefore, an enlightened selection of these models is an important prerequisite for the success of any calculation related to process simulation and design. Two types of thermodynamic models are mainly used in practice: the activity coefficient models, which are formulated as pressure-independent functions and, therefore, are usable at low pressure only, and the equations of state (EoSs), the application range of which can be extended to high pressures, including the sub- and supercritical states.

In this panorama, cubic equations of state (CEoSs) have a special place. Historically, this class of EoSs derives from the seminal Van der Waals EoS proposed in 1873 [1], which reconciled gaseous and liquid states through the prediction of vapour-liquid equilibria and critical phenomena. As shown in the fascinating book by Levelt Sengers entitled “*How fluids unmix*” [2], this EoS was capable of many other feats, including the prediction of critical phenomena, of two-phase equilibria

in binaries involving two liquid phases or one supercritical phase, and even of gas-gas equilibria. Although the existence of these gas-gas equilibria was suspected by Van Laar from advanced calculations based on the Van der Waals EoS, they were demonstrated experimentally only some decades later.

During the 20th century, multiple versions of the CEoSs have been proposed and used for industrial and commercial applications, such as oil exploitation, production and processing.

The need for always increasing accuracy has led CEoS developers to propose continuous refinements to their formulation until the introduction of a very important coefficient to Van der Waals mixing rules (MRs), i.e., the *binary interaction parameter* (BIP) of the attractive term, often denoted  $k_{ij}$  for a binary system  $i + j$ . While extremely popular but considered empirical and nonphysically based, this coefficient is absent, or almost, in some major books on thermodynamics from the 2nd part of the 20th century (see, e.g., [3,4]). However, in a paper devoted to “the legacy of Otto Redlich”, Prof. John Prausnitz explains in detail the origins of the introduction of this coefficient [5]: “*Prior to 1953, it was customary to write mixing rules in terms of pure component parameters only. It is hard to believe now, but it was not until about 30 years ago that binary parameters were introduced into mixing rules. To my best knowledge, it was Benedict at MIT and Kobe at Texas who first recommended that a small empirical adjustment in a cross coefficient could be used to improve*

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**Nomenclature and abbreviations***Latin letters*

$a$	cohesive parameter [Pa·m <sup>6</sup> ·mol <sup>-2</sup> ]
$A_{k\prime}$	group-interaction parameter between groups $k$ and $\prime$ involved in the expression of the Van Laar parameter $E_{ij}$ by GC [Pa]
ARP	GC CEoS proposed by Abdoul, Rauzy and Pénélox
$b$	(molar) covolume [m <sup>3</sup> ·mol <sup>-1</sup> ]
$B_{k\prime}$	group-interaction parameter between groups $k$ and $\prime$ involved in the expression of the Van Laar parameter $E_{ij}$ [Pa]
BIP	binary interaction parameter
CEoS	acronym for <i>cubic equation of state</i>
$c$	(molar) volume translation parameter [m <sup>3</sup> ·mol <sup>-1</sup> ]
$c_p$	molar heat capacity [J·mol <sup>-1</sup> ·K <sup>-1</sup> ]
$E$	Van Laar excess function [J·mol <sup>-1</sup> ]
$E_{ij}$	Van Laar parameter [J·m <sup>-3</sup> ]
EoS	acronym for <i>equation of state</i>
$g$	molar Gibbs energy [J·mol <sup>-1</sup> ]
GC	group contribution
G-BIP	group-binary-interaction parameter
GPED	global phase equilibrium diagram
$k_{ij}$	binary interaction parameter for the cohesive parameter [dimensionless]
LLE	liquid-liquid equilibrium
$\prime_{ij}$	cross-covolume binary interaction parameter [dimensionless]
MR	mixing rule
$P$	pressure [Pa]

$P_i^{sat}$	vapour pressure of pure component $i$ [Pa]
PNA	paraffins, naphthenes, aromatics
PPR78	predictive Peng-Robinson 1978 EoS
$R$	gas constant [J·mol <sup>-1</sup> ·K <sup>-1</sup> ]
$T$	temperature [K]
$T_r$	reduced temperature $T/T_c$ [dimensionless]
$u$	universal constant of the CEoS [dimensionless]
$v$	molar volume [m <sup>3</sup> ·mol <sup>-1</sup> ]
VLE	vapour-liquid equilibrium
$w$	universal constant of the CEoS [dimensionless]
$z$	composition vector (containing the molar fractions of mixture components) [dimensionless]

*Greek symbols*

$\delta$	Scatchard-Hildebrand solubility parameter [J <sup>1/2</sup> ·m <sup>-3/2</sup> ]
$\Delta_{vap}H$	molar vapourization enthalpy [J·mol <sup>-1</sup> ]
$\rho$	molar density [mol·m <sup>-3</sup> ]
$\omega$	acentric factor [dimensionless]

*Indices and superscripts*

$c$	critical point
$E$	excess property
$E, \gamma$	excess property issued from an activity-coefficient model from the literature
exp	experimental data
$i$	related to a given pure component $i$ ,
liq	liquid phase
$m$	related to a mixture
$P \rightarrow \infty$	property under infinite pressure
sat	saturation point

significantly agreement between calculated and experimental results". He added: "When I came to Berkeley in 1955, almost all chemical engineers accepted the geometric mean without question. Robert Gunn and Ping Chueh were amongst the first to use the expression" [of Van der Waals mixing rules embedding a  $k_{ij}$  parameter].

This article focuses on temperature-dependent BIPs involved in CEoSs, with special attention given to predictive methods enabling their estimation from the mere knowledge of molecular structures. The first part of the article is devoted to the parametrization of pure-component CEoSs, a prerequisite to the development of CEoSs for mixtures. A methodology for obtaining EoS parameters is proposed leading to optimal performances concerning the correlation of vapour-liquid equilibria and energetic properties.

Then, the binary parameters involved in Van der Waals mixing rules are introduced, namely, parameter  $k_{ij}$ . The physical meaning of  $k_{ij}$  is discussed in detail. It is attempted to convince the reader that although  $k_{ij}$  brings flexibility into the EoS for fitting multiple phase behaviours in multicomponent systems, this parameter is certainly more than this, on closer inspection. The main methods used for estimating this parameter are presented, from the most basic and specific methods to the more general ones. Special attention is given to the CEoSs using group contribution-based methods for  $k_{ij}$  prediction. The Abdoul, Rauzy and Pénélox (ARP), Predictive Peng-Robinson 1978 (PPR78) and Enhanced ( $E$ )-PPR78 models relying on this type of approach are introduced and compared in terms of formulation and performance. In conclusion, the strengths and limitations of  $k_{ij}$ -based CEoSs are discussed.

## 2. What is the optimal form of a pure-component CEoS?

As mentioned earlier, the construction of a CEoS for a mixture first requires the development of a CEoS for the pure species (the transition

from the pure-component CEoS to mixture CEoS being reached through the application of adequate mixing and combining rules in the framework of the Van der Waals 1-fluid theory).

For a given pure component  $i$ , most CEoSs are written in the general following form:

$$P(T, v) = \frac{RT}{v - b_i} - \frac{a_i}{v^2 + u \cdot b_i \cdot v + w \cdot b_i^2} \quad (1)$$

In this model, to accurately reproduce the volumetric and non-volumetric properties of pure species, three different types of parameters playing dissociated roles in terms of the EoS capacity can be identified:

- (1) The cohesive parameter  $a_i$  involved in the attractive term of the EoS is known to govern the reproduction of nonvolumetric properties, such as vapour pressure, but also derived properties, including the  $\Delta_{vap}H_i$ ,  $c_{p,i,liq}^{sat}$ , enthalpy and heat capacity in the sub- and supercritical domains [6–8]. This temperature-dependent function is generally expressed as the product of the critical value of  $a_i$ , denoted  $a_{c,i}$ , and a dimensionless alpha function  $\alpha_i(T)$  revealing the temperature dependency of  $a_i$ . A large number of alpha functions have been proposed in the literature involving various numbers of physical or fitted parameters, as highlighted, for example, in review papers by Valderrama [9] and Lopez-Echeverry et al. [10].
- (2) The covolume  $b_i$ , which is a volumetric parameter, has a large influence on the estimation of liquid density. In most CEoSs,  $b_i$  is considered a constant. The expressions for constants  $a_{c,i}$  and  $b_i$  are generally chosen to ensure an exact reproduction [11,12] of the experimental critical temperature  $T_{c,i,exp}$  and pressure  $P_{c,i,exp}$ . Eq.

(2) provides the exact expressions of  $a_{c,i}$  and  $b_i$  with respect to properties  $T_{c,i,exp}$  and  $P_{c,i,exp}$ :

$$\begin{cases} K = \frac{1}{2} \left[ 4(u+2)(u+w+1) + 4\sqrt{(u^2-4w)(u+w+1)^2} \right]^{1/3} \\ x = K + K^{-1} \cdot (u+w+1) + 1 \\ \Omega_b = (3x+u-1)^{-1} \\ \Omega_a = \Omega_b^2 (x^2 + ux + w)(2x+u)(x-1)^{-1} \\ a_{c,i} = \Omega_a R^2 T_{c,i,exp}^2 / P_{c,i,exp} \\ b_i = \Omega_b R T_{c,i,exp} / P_{c,i,exp} \end{cases} \quad (2)$$

Note that the  $x$  quantity in Eq. (2) denotes the component-independent ratio  $v_{c,i}/b_i$ . In cases where experimental values of  $T_c$  and  $P_c$  are not available, these properties can be straightforwardly estimated by specifically developed group contribution methods [13–15], which considerably extend the scope of the CEoS.

Another volumetric parameter is sometimes added to the CEoS when a *volume translation* is applied, as suggested by P eneloux et al. [16,17]. This process consists simply of translating molar volumes of the CEoS by a value  $c_i$ , which is generally kept constant, to improve the description of the liquid density. In doing so, the covolume (i.e., the volume corresponding to an infinite fluid pressure) is mechanically translated by the same quantity. The molar volume and covolume obtained after translation are shown in Eq. (3).

$$\begin{cases} v_{translated} = v - c_i \\ b_{translated} = b_i - c_i \end{cases} \quad (3)$$

(3) Constants  $u$  and  $w$  are called *universal* because they are not component specific. The Redlich-Kwong CEoS [18], modified by Soave [19], is obtained for ( $u = 1, w = 0$ ) and the Peng-Robinson CEoS [20] for ( $u = 2, w = -1$ ). Although some authors have modified universal constants to improve CEoS performance in recent decades (e.g., [21,22]), how they are likely to influence CEoS performance is not obvious and is discussed later.

Through fruitful and exciting recent collaborations (in particular with Prof. Din-Yu Peng, Dr. Paul Mathias and Dr. Giorgio Soave), we have studied in depth the best way to generate optimal versions of pure-component CEoSs and examined how to optimize each of the three kinds of CEoS parameters introduced above. In this section, our main results are presented.

### 2.1. Optimal selection of the cohesive parameter

Through a series of papers devoted specifically to this parameter, we investigated how to optimally select the mathematical expression for the alpha function [6–8] with the particular aim of ensuring the following:

- Maximum precision in the description of the nonvolumetric equilibrium properties like vapour pressure, enthalpy of vapourization, and heat capacity of saturated-liquid phase;
- Physical consistency (i.e., physically sound behaviour) of derivative properties, including enthalpy, entropy and heat capacity;
- Safe extrapolation of the alpha function in the supercritical domain. Most often, alpha functions are selected, and their parameters are fitted to obtain accurate vapour-liquid equilibrium (VLE) properties; supercritical properties are rarely considered in the development

process of alpha functions, and their use in the supercritical domain can be considered to be an extrapolation.

These research studies have led us to propose a *consistency test for alpha functions*, enabling us to satisfy the goals mentioned above. For nonquantum fluids, this test is described by Eq. (4)

$$\begin{cases} \alpha(T_c) = 1 \\ \alpha(T) > 0 \text{ and } \alpha(T) \text{ continuous for all } T \\ \left(\frac{d\alpha}{dT}\right) < 0 \text{ and } \frac{d\alpha}{dT} \text{ continuous for all } T \\ \left(\frac{d^2\alpha}{dT^2}\right) > 0 \text{ and } \frac{d^2\alpha}{dT^2} \text{ continuous for all } T \\ \left(\frac{d^3\alpha}{dT^3}\right) < 0 \text{ for all } T \end{cases} \quad (4)$$

Note that for quantum fluids such as  $H_2$  and He, there are specific alpha function requirements [23,7]. That is, the alpha function is expected to exhibit the shape of a *bell*: it is increasing and concave below  $\approx 50$  K and is decreasing, convex, with a negative third derivative at higher temperature.

A deep analysis of alpha functions frequently used in CEoSs [7] highlight that most of them fail the consistency test, including the classical famous Soave function (see Eq. (6)), which exhibits an increasing behaviour with temperature at high temperatures, above the critical temperature. It is important to acknowledge that this inconsistent behaviour is far enough from the reasonable temperature domains of applications to be ignored, and consequently, the Soave function is still considered to be one of the most efficient alpha functions currently available. In a recent work [24], the  $m(\omega)$  function involved in the Soave alpha function (see Eq. (6)) was redetermined for both the Peng-Robinson and Soave CEoSs to improve the modelling of heavy compounds (showing high  $\omega$  values). This has led to the following updated functions:

$$\begin{cases} \text{Soave EoS} : m = 0.4810 + 1.5963\omega - 0.2963\omega^2 + 0.1223\omega^3 \\ \text{Peng - Robinson EoS} : m = 0.3919 + 1.4996\omega - 0.2721\omega^2 + 0.1063\omega^3 \end{cases} \quad (5)$$

A slight disadvantage of the Soave alpha function is its limited flexibility, as it only includes one parameter ( $m$ ) correlated to the acentric factor ( $\omega$ ), which results in less satisfactory performance for some polar and associating compounds (e.g., alcohols, glycols) [23,25]. The so-called ‘‘Twu 91’’ function [25] (see Eq. (6)) is a rare alpha function that is fully consistent provided that the 3 adjustable parameters it contains (i.e.,  $L, M$ , and  $N$ ) obey specific constraints (see Eqs. (A.3), (A.10) and (A.13) in [8]).

$$\begin{cases} \text{Soave} : \alpha(T_r) = \left[ 1 + m(\omega_{exp}) \cdot \left( 1 - \sqrt{T_r} \right) \right]^2 \text{ with } :T_r = T/T_{c,exp} \\ \text{Twu91} : \alpha(T_r) = T_r^{N(M-1)} e^{L(1-T_r^{MN})} \end{cases} \quad (6)$$

Note that consistent values for the ( $L, M, N$ ) parameters can be found for 1800 pure compounds in the supporting information of a recent paper [26]. In the body of the same article, generalized correlations are proposed for these three parameters making it possible to deduce them from the mere knowledge of the acentric factor  $\omega_{exp}$ :

$$\begin{cases} L = 0.0544 + 0.7536\omega_{exp} + 0.0297\omega_{exp}^2 \\ M = 0.8678 - 0.1785\omega_{exp} + 0.1401\omega_{exp}^2 \\ N = 2 \end{cases} \quad (7)$$

### 2.2. Liquid-density improvement strategy and optimal selection of the covolume

Liquid density is often considered to be the bane of CEoSs for several

reasons. First, CEoSs are unable to reproduce the pressure-volume behaviour near the critical point. Note, however, that this limitation is due to the incapacity of the EoSs, relying on the mean-field theory approximation, to account for density fluctuations and is shared by all EoS types, without exception. Second, the saturated liquid densities at temperatures well below the critical region ( $T_r \leq 0.9$ ) are not accurately reproduced; the mean deviations over the liquid density are generally higher than 5% for CEoSs that do not embed a volume translation. Eventually, CEoSs cannot easily reproduce the experimental behaviour of isotherms in the pressure-volume plane, thus revealing an imperfect description of the coefficient of compressibility  $\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T$ . Annihilating the defaults of CEoSs in the critical density region seems illusory. However, simple techniques can be considered to mitigate the limitations appearing outside this domain.

As a preliminary consideration, the capacity of a CEoS to describe the density behaviour strongly depends on the universal constant values ( $u, w$ ). As a proof, the mean deviation over the liquid density data for the SRK EoS ( $u = 1, w = 0$ ) is approximately 17%, while for the Peng-Robinson EoS ( $u = 2, w = -1$ ), it is approximately 7% (see Table 3 in [27]; values presented in this table were calculated by averaging the results over 1000 compounds). Regarding the nonvolumetric properties, both models are equivalent (see Table 6 in [27]). As a first conclusion, the PR CEoS can be considered an improved version of the SRK CEoS in terms of liquid density estimation.

This observation gives a first part of the answer concerning the influence of universal constants on EoS performance. The remainder of the discussion regarding universal constants can be found in Section 1.3.

Another way to improve the liquid density is to modify the covolume. In particular, some authors decided to make this parameter temperature dependent (e.g., [28,29]). Doing so can dramatically improve the description of the saturated-liquid density, but it entails the generation of highly undesirable counterparts:

- The appearance of isotherm crossings under high pressure in the pressure-volume plane [30].
- The necessary appearance of an infinitely negative isochoric heat capacity at infinite pressure ( $\lim_{P \rightarrow \infty} c_v = -\infty$ ) [31] which breaks the thermal stability criterion that states that the isochoric heat capacity  $c_v$  must remain positive.

For this reason, it seems undesirable to make the covolume temperature dependent. However, nothing prevents switching all the molar volumes, including the covolume, by a constant component-specific value; this is the spirit of the *volume translation* technique proposed by P eneloux et al. [16] (see Eq. (3)). This modification originates from a simple observation: when experimental molar volumes are compared to the values calculated from the SRK EoS in the pressure-molar volume plane, it appears that they are systematically overestimated. The use of a negative molar volume shift greatly improves the estimation of molar volumes (or equivalently, of densities). With the Peng-Robinson CEoS, molar volumes are either overestimated or underestimated, and thus, the volume correction can be either negative or positive. In its original formulation, the volume correction was chosen as temperature independent and component specific. The leading idea was to correct liquid volumes without changing nonvolumetric phase-equilibrium properties. P eneloux et al. explained that this correction “*is founded on the property that certain translations along the volume axis may be effected such that the predicted equilibrium conditions ( $T, P, x_i$ ) remain unchanged*” [16]. An extensive list of expressions for volume translation parameters used with the Peng-Robinson EoS can be found in the review by Lopez-Echeverry et al. (see Table 3 of [10]); it can be observed that these parameters are sometimes expressed as temperature functions.

Making the volume-translation parameter  $c_i$  temperature dependent entails the same issues as those observed when the covolume is temperature-dependent and consequently, this modification cannot be

envisaged. How the use of a temperature-independent and a temperature-dependent  $c_i$  affects EoS properties (not specifically a CEoS but any volume-translated EoS) is described in detail in [17]. The application of a volume translation to the SRK EoS makes it possible to decrease the deviations in liquid density from  $\approx 17\%$  to  $\approx 4\%$ . For the PR EoS, these deviations pass from  $\approx 7\%$  to  $\approx 3\%$  (see Table 3 in [27]). Note that these results were obtained by selecting a volume translation parameter such that the experimental liquid density at  $T_r = 0.8$  is exactly reproduced by the EoS and that deviations were calculated from liquid-density data at  $T_r \leq 0.9$  (the critical region was excluded from the evaluation for the reason mentioned earlier).

In conclusion, the application of a volume translation technique on the CEoS leads to a remarkable improvement in terms of liquid density estimation and preserves the physical consistency of EoS provided that covolume and volume correction parameters are kept temperature independent.

### 2.3. Selection of optimal universal constants

As discussed in Section 1.2, universal constants ( $u, w$ ) have an important effect on the capacity of the CEoS to reproduce the liquid density data. This effect deserves, however, to be discussed more in depth depending on whether a volume translation is imbedded in the CEoS.

In a recent study exploring the actual role played by universal constants on CEoS performances [32], the following conclusions were reached:

- If the CEoS is used in its basic formulation, i.e., without volume translation, then there are optimal values of ( $u, w$ ), making it possible to minimize a criterion accounting for deviations in the vapour pressure, enthalpy of vapourization and liquid molar volume. This optimum is found to be ( $u_{opt} = 2.10, w_{opt} = -0.75$ ) and is very close to Peng-Robinson EoS values ( $u = 2, w = -1$ ); the reader is referred to Fig. 5 and Eq. (24) in [32]. Remembering that the values of ( $u_{opt}, w_{opt}$ ), determined by minimizing an objective function formed from experimental data, have an uncertainty, it can be concluded that the Peng-Robinson CEoS is an optimized version of the nonvolume-translated CEoS.
- If the CEoS is used with a volume translation, then an infinite number of optimal value sets ( $u_{opt}, w_{opt}$ ) enable us to obtain the least deviations with respect to the vapour pressure, enthalpy of vapourization and liquid molar volumes. Actually, the optimal region is defined by the relation  $w_{opt} = 0.14u_{opt}^2 - 0.47(u_{opt} + 1)$  (see Fig. 6, Eqs. (25) and (32) in [32]). By selecting  $u = 2$  and  $w = -1$ , Peng and Robinson made a very good choice since these two values are extremely close to the optimal region. The Van der Waals ( $u = w = 0$ ) and the Soave EoSs, both armed with a Soave-type  $\alpha$ -function, are a close neighbour of this optimal region. The component-dependent volume shift to be used with the VdW CEoS is substantial, but deviations as low as 4% are obtained for liquid molar volumes with such a simple equation.

### 2.4. General recommendations

In light of the recent results presented above, one can conclude the following:

- The PR CEoS is definitively an optimal version of the CEoS for pure species, regardless of whether a volume translation is embedded. When coupled with a Soave-type  $\alpha$ -function, low deviations in vapour pressures ( $\approx 1.5\%$  on average for  $\approx 1500$  species [32]) and derived properties are obtained. Meanwhile, deviations in liquid densities are acceptable.

- If a volume translation is used, then the capacity to reproduce saturated-liquid density data becomes excellent and comparable to the best EoS currently available ( $\approx 1.9\%$  on average for  $\approx 1500$  species [32] if the critical region is excluded).
- In terms of the parametrization strategy, it is strongly advised to use a temperature-independent covolume and volume-translation parameter to preserve the physical consistency of EoS predictions. The use of the simple Soave alpha function is an acceptable option, although it does not satisfy the consistency test for the alpha function at a (very) high temperature and can lead to significant deviations in vapour pressure for associating compounds. On the other hand, sophisticated alpha functions (such as the one developed by Twu in 1991 [25]) that do not break the *alpha function consistency test* can be used to obtain a highly accurate estimation of vapour pressure and derived properties of species, including polar and associating compounds. The parameters involved in such sophisticated  $\alpha$ -functions have to be fitted to the experimental data by enforcing that the resulting  $\alpha$ -function obeys the constraints given by Eq. (4). As an example, the *tc-PR* EoS [27], where *tc* stands for *translated and consistent*, which combines the PR EoS with a component-dependent volume shift aimed at exactly reproducing the liquid molar volume at  $T_r = 0.8$  and embeds the consistent Twu 91  $\alpha$ -function, can correlate the vapour pressures and liquid densities of 1800 fluids with an average deviation of 1% and 2.1%, respectively. Moreover, the enthalpies of vapourization (over 1536 fluids) and liquid heat capacities (of 890 fluids) are correlated with average deviations of 1.9 and 2.5%, respectively. Such small deviations led Piña-Martinez et al. [26] to write that the *tc-PR* EoS is "probably not only the safest (the consistent character of the  $\alpha$ -function of such an EoS ensures safe property predictions in both subcritical and supercritical domains) but also the most accurate cubic EoS available".

### 3. Presentation of the family of CEoSs with temperature-dependent binary interaction parameters

Following the Van der Waals 1-fluid theory, a CEoS for a mixture can be deduced from a pure-component CEoS by replacing the component-specific EoS parameters with mixture parameters (characterized by the subscript  $m$ ):

$$P(T, v, \mathbf{z}) = \frac{RT}{v - b_m(\mathbf{z})} - \frac{a_m(T, \mathbf{z})}{v^2 + u \cdot b_m(\mathbf{z}) \cdot v + w \cdot b_m^2(\mathbf{z})} \quad (8)$$

These parameters are now dependent on a composition variable  $\mathbf{z}$ . Eq. (8) describes a mixture CEoS in its basic version (without volume translation). If the EoS is volume translated, then the corresponding parameter  $c_m$  becomes composition dependent. Let us analyse one by one the possible expressions for the 3 parameters ( $a_m$ ,  $b_m$  and  $c_m$ ) present in the CEoS for mixtures with temperature-dependent BIPs.

#### 3.1. The covolume parameter for mixtures

In this class of models, the covolume parameter is assumed to obey Van der Waals' mixing rules (MRs); i.e., its expression is a quadratic function of mole fractions, as introduced in Eq. (9).

$$b_m(\mathbf{z}) = \sum_{i=1}^N \sum_{j=1}^N z_i \cdot z_j \cdot b_{ij} \quad (9)$$

where  $N$  denotes the total number of components in the mixture. There are essentially two types of combining rules proposed for  $b_{ij}$ . The first one expresses  $b_{ij}$  as the arithmetic mean of the pure-component covolumes and involves a cross-covolume interaction parameter ( $\ell_{ij}$ ) to account for nonlinear effects:

$$b_{ij} = \frac{1}{2}(b_i + b_j)(1 - \ell_{ij}) \quad (10)$$

In most CEoSs (e.g., PSRK [33], LCVM [34], and PPR78 [35], as well as in most EoS versions implemented in commercial simulation software), the  $\ell_{ij}$  parameter is considered null. In such cases, the quadratic MR on  $b_m$  becomes a simple linear MR of mole fractions  $z_i$  weighted by the covolumes of corresponding species  $b_i$ :

$$b_{ij} = \frac{1}{2}(b_i + b_j) \Rightarrow b_m(\mathbf{z}) = \sum_{i=1}^N z_i b_i \quad (11)$$

Since the same causes have the same effects,  $\ell_{ij}$  must be chosen to be temperature independent to keep the covolume temperature independent and avoid the unphysical behaviours mentioned above (isotherm crossings in the  $P$ - $v$  plane and negative heat capacities).

With some exceptions, the precise role played by the  $\ell_{ij}$  parameter is rarely discussed in the literature. This parameter was ignored for a long time for the simple reason that it was considered unnecessary since the so-called  $k_{ij}$  binary interaction coefficient involved in Van der Waals MR for  $a_m$  was enough to efficiently correlate VLE mixture data. It is, however, worthwhile to cite the work by Polishuk et al. [36] that advises plotting the global phase diagram, i.e., the map of phase behaviour that a particular EoS can predict for a particular binary system in the  $k_{12} - \ell_{12}$  plane. Here,  $k_{12}$  and  $\ell_{12}$  are the BIPs for the cohesive parameter  $a_m$  (see next section) and the covolume  $b_m$ , respectively. It thus becomes possible to investigate the predictive abilities of the EoS and to discuss the influence of each BIP. These authors concluded that "*parameter  $k_{12}$  has a strong influence on Type-III phase diagrams with high immiscibility, whereas parameter  $\ell_{12}$  influences Type-V or Type-I behaviour that shows high miscibility and becomes important when cross-attraction becomes significant*".

In recent articles [37,38], Kontogeorgis et al. discussed the  $\ell_{ij}$  role in more detail. In particular, they explained that "*It has not as yet been fully evaluated what is the influence of these alternative combining rules in the context of cubic EoS, e.g., for activity coefficients, but there is little doubt that small changes in the covolume combining rule may result to big changes in the results*", as in the activity coefficient expression, the combining rule of the covolume appears in several parts of the cubic EoS" [38]. The use of the  $\ell_{ij}$  parameter tends to improve the free-volume combinatorial term of the CEoS and thus positively influences the modelling of size-asymmetric systems. In addition, this parameter brings flexibility to the modelling of both liquid-liquid equilibrium (LLE) and VLE data when the use of a single  $k_{ij}$  coefficient is not enough [37]. In the literature, the  $\ell_{ij}$  parameter is used with systems that are difficult to model, e.g., CO<sub>2</sub> + fish oil components [39,40], CO<sub>2</sub> + alcohols [41,42], and size-asymmetric alkane mixtures [43].

The use of the  $\ell_{ij}$  binary parameter in systematic combination with a  $k_{ij}$  coefficient (or any binary interaction coefficients of an activity-coefficient model embedded in the MRs) poses the risk of data overfitting (when the number of model parameters is higher than the number of parameters justified by the data) and thus the loss of generality of the model and difficult extrapolation.

To avoid this drawback, some CEoS developers have used a different combining rule for  $b_{ij}$  that is not as simple as Eq. (11) and, at the same time, does not involve a binary interaction parameter  $\ell_{ij}$  but a universal (i.e., component independent) constant  $s$  instead. This expression takes the following general form:

$$b_{ij} = \frac{1}{2}(b_i^{1/s} + b_j^{1/s})^s \quad (12)$$

There is no unanimity concerning the  $s$  value. In practice,  $s = 2$  was used in the UMR-PRU model [44], and  $s = \frac{4}{3}$  was chosen in the volume-translated Peng-Robinson (VTPR) model [45]. Recently, we selected  $s = \frac{3}{2}$  in a model referred to as *tc-PR- $a_{res}^{E-\gamma}$*  [46].

Notably, the simultaneous use of both the  $\ell_{ij}$  and  $s$  parameters in the MR for  $b_m$  (in this case, a factor  $(1 - \ell_{ij})$  is inserted into Eq. (12)) is unusual and causes an imbalance in the ratio between the number of added model parameters and the gain of accuracy. Chen et al. [47] who decided to use Eq. (12) in their new predictive Soave-Redlich-Kwong

(PSRK) model noted that “Although slightly better results can be obtained using  $\ell_{ij} \neq 0$ , it is understandable that phase equilibria are not very sensitive to the mixing rule for  $b_m$ , except when there is a significant difference in the molecular size” [47].

### 3.2. The volume-translation parameter for mixtures

In essence, this parameter is used to improve the prediction of liquid density from the CEoS while preserving phase-equilibrium conditions (see Section 1.2 above). Knowing this, the question of the selection of a MR for this parameter becomes rather simple to answer. According to Privat et al. [48], there is only one MR for the  $c$  parameter that allows the phase-equilibrium conditions applied to mixtures to remain unchanged:

$$c_m(\mathbf{z}) = \sum_{i=1}^N z_i \cdot c_i \quad (13)$$

### 3.3. The cohesive parameter for mixtures

Following Van der Waals' MRs, the cohesive parameter is expressed as a quadratic function of mole fractions:

$$a_m(T, \mathbf{z}) = \sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot a_{ij}(T) \quad (14)$$

In the family of models described in the present paper, the combining rule for  $a_{ij}$  is estimated as a geometric mean of pure-component cohesive parameters multiplied by a correction factor involving a so-called BIP, denoted  $k_{ij}$ , which is assumed to be temperature dependent:

$$a_{ij}(T) = \sqrt{a_i(T) \cdot a_j(T)} [1 - k_{ij}(T)] \quad \text{with} : k_{ij}(T) = k_{ji}(T) \quad (15)$$

CEoS predictions are very sensitive to  $k_{ij}$  values, as demonstrated by a representation of the deformation of an isothermal phase diagram of an arbitrarily selected binary system when passing from a negative  $k_{12}$  value to a positive value [49,50] (see Fig. 1).

It is observed that for very low  $k_{12}$  values, the phase diagram shows negative deviations from ideality (i.e., the molar excess Gibbs energy of the liquid phase  $g^E$  is negative), exhibiting or not exhibiting a negative azeotrope; as  $k_{12}$  increases, deviations from ideality decrease in magnitude and approach zero. For  $k_{12} = -0.019$ , the system exhibits ideal behaviour, thus demonstrating that a zero  $k_{12}$  does not correspond to an ideal solution. This result, however, was discussed 20 years ago by

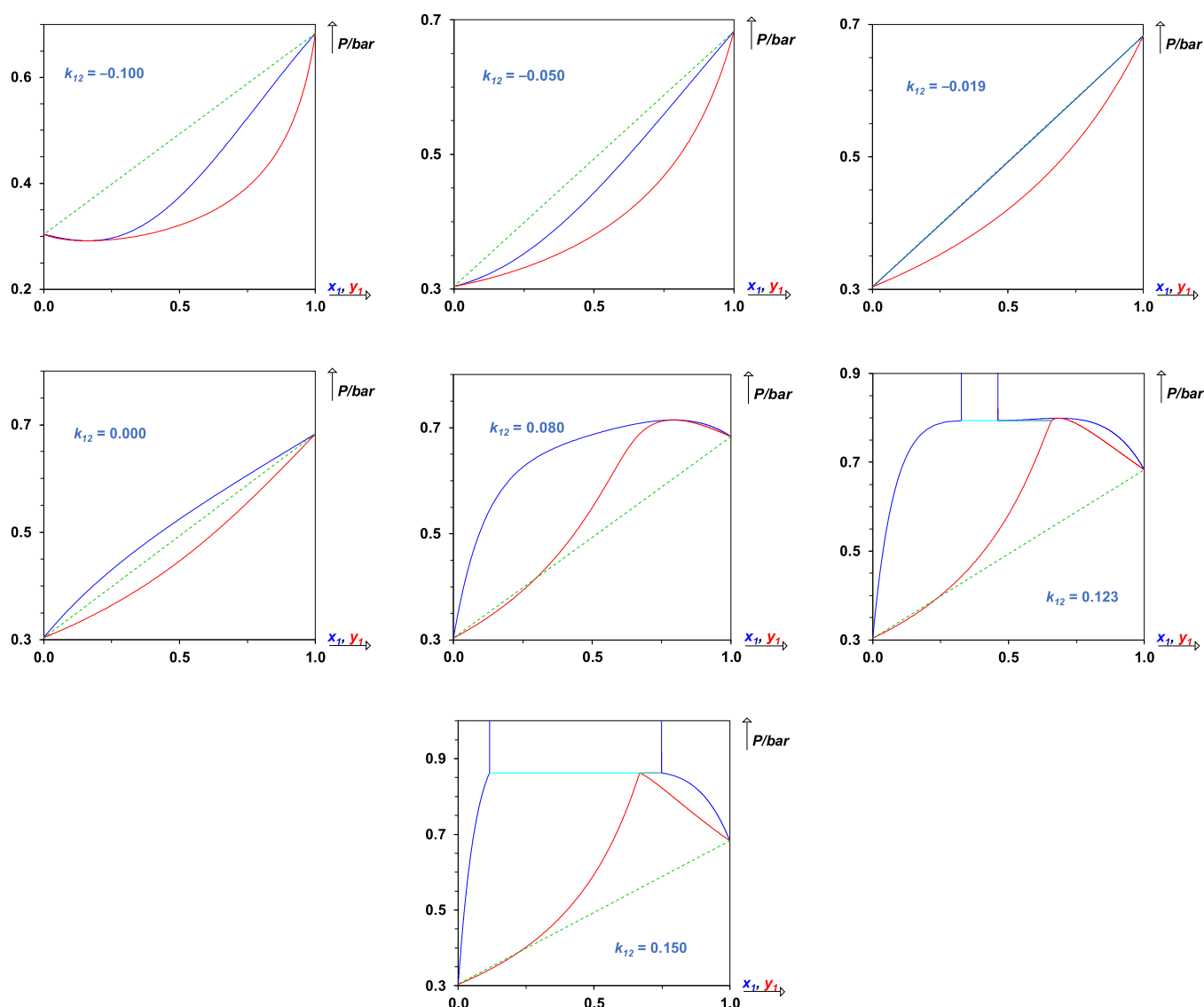


Fig. 1. Influence of the  $k_{12}$  value on the type of isothermal phase diagram, calculated with the Peng-Robinson EoS embedding Van der Waals mixing rules, for n-pentane(1) + acetone (2) at 298.15 K. Dashed line: Raoult's line [50].

Zabaloy et al. [51]. These authors developed a specific approach that recovers the ideal solution behaviour when the binary parameters are set to zero. For higher  $k_{12}$  values, deviations from ideality become positive ( $g^E > 0$ ) and increase to such an extent that a positive azeotrope appears and then, a liquid-liquid phase split arises for  $k_{12} > 0.1$ . It can be concluded that the phase behaviour of the mixture is very sensitive to the BIP value since nearly all possible types of phase diagrams can be met for  $k_{12} \in [-0.1, 0.15]$ .

Note that  $k_{ij}$  BIP values greater than one are considered nonphysical by some authors, as they induce  $a_m$  to change sign and thus cause attractive intermolecular forces to become repulsive. Although aware that  $k_{ij} > 1$  is unusual and can potentially lead to unphysical EoS predictions, we do not share the idea that  $k_{ij}$  is necessarily lower than 1 and that the attractive CEoS term becomes repulsive in such a case. For a simple binary system, the Van der Waals MR on  $a_m$  is  $a_m = z_1^2 a_1 + z_2^2 a_2 + 2z_1 z_2 \sqrt{a_1 a_2} (1 - k_{12})$ . Clearly, this quantity must be positive. This induces the following:

$$\text{for all } \mathbf{z} : k_{12} < 1 + \frac{z_1^2 a_1 + z_2^2 a_2}{2z_1 z_2 \sqrt{a_1 a_2}} \quad (16)$$

Therefore, considering  $k_{ij} > 1$  is not forbidden provided inequality (16) is satisfied.

Note that the systematic use of linear MRs for the  $b_m$  parameter and the lack of interest of CEoS developers over many decades with respect to cross-covolume interaction parameters (or equivalently, the universal covolume parameter  $s$ , introduced in Section 2.1) can be essentially explained by the high sensitivity of the phase-diagram topology to  $k_{ij}$  values that ousted the less visible effects of other EoS mixture parameters.

To better understand how  $k_{ij}$  coefficients are influenced by component properties, Coutinho et al. tried to establish a relation between molecular properties and the cross energy term  $a_{ij}$  of the CEoS through the London-Mie theory [52]. These authors reached the following conclusion: “The commonly employed  $k_{ij}$  interaction parameter is a strong function of both temperature and size difference between the components. The coupling of these effects makes generalizations difficult. In fact,  $k_{ij}$  sometimes increases with size difference, for example, low temperatures and lower asymmetries, while in most other cases, it decreases with increasing asymmetry”.

As mentioned in the previous discussion regarding Fig. 1, the  $k_{ij}$  parameter is linked narrowly to the nature of the deviations from ideality, but this link is not trivial. To establish the connection between the sign of  $g^E$  and  $k_{ij}$  in a simple way, it is proposed to consider the particular case where a linear MR is used for  $b_m$  (see Eq. (11)) and not to translate the EoS.

In this framework, it is possible to show [53,54] that the following equation (see Eq. (17)) relating  $a_m$  and  $b_m$  to the excess Gibbs energy of the mixture under infinite pressure ( $g_{P \rightarrow \infty}^{E, EoS}$ ) applies:

$$\begin{cases} \frac{g_{P \rightarrow \infty}^{E, EoS} / RT}{C_{EoS}} = \sum_{i=1}^N z_i \frac{a_i(T)}{RT b_i} - \frac{a_m(T, \mathbf{z})}{RT b_m(\mathbf{z})} \\ b_m(\mathbf{z}) = \sum_{i=1}^N z_i b_i \end{cases} \text{with } C_{EoS} = \frac{1}{\sqrt{u^2 - 4w}} \ln \left( \frac{\frac{u+2}{\sqrt{u^2 - 4w}} + 1}{\frac{u+2}{\sqrt{u^2 - 4w}} - 1} \right) \quad (17)$$

where  $C_{EoS}$  is a universal EoS-specific parameter. Its expression, valid for  $u^2 - 4w > 0$ , leads to  $C_{Soave} = \ln(2)$  for the Soave CEoS ( $u = 1, w = 0$ ) and  $C_{PR} = \frac{\sqrt{2}}{2} \ln(1 + \sqrt{2})$  for the Peng-Robinson EoS ( $u = 2, w = -1$ ).

$$\begin{aligned} \varepsilon_{ij}(T) &= C_{EoS} \left[ \frac{[\delta_i(T)]^2 + [\delta_j(T)]^2}{2} - \delta_i(T) \cdot \delta_j(T) [1 - k_{ij}(T)] \right] \text{ with } : \delta_i(T) = \frac{\sqrt{a_i(T)}}{b_i} \\ \Leftrightarrow k_{ij}(T) &= \frac{2 \varepsilon_{ij}(T) - [\delta_i(T) - \delta_j(T)]^2}{2 \delta_i(T) \cdot \delta_j(T)} \end{aligned} \quad (21)$$

For clarity, let us recall that Eq. (17) is the one used by Huron and Vidal [55] during the derivation of their MRs. These MRs are straightforwardly obtained by replacing in Eq. (17),  $g_{P \rightarrow \infty}^{E, EoS}$  by a well-established activity coefficient model such as, e.g., non-random two liquid (NRTL) or Van Laar.

Furthermore, assuming a quadratic MR for  $a_m$  (see Eqs. (14) and (15)), Eq. (17) makes it possible to determine the mathematical expression of  $g_{P \rightarrow \infty}^{E, EoS}$  and thus enables us to discuss the connections between the deviations from ideality and the BIP values. From Eq. (14), one has:

$$\begin{aligned} \sum_{i=1}^N z_i \frac{a_i(T)}{RT b_i} - \frac{a_m(T, \mathbf{z})}{RT b_m(\mathbf{z})} &= \sum_{i=1}^N z_i \frac{a_i(T)}{RT b_i} - \frac{\sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot a_{ij}(T)}{RT \sum_{j=1}^N z_j b_j} \\ &= \frac{\sum_{i=1}^N z_i \frac{a_i(T)}{b_i} \times \sum_{j=1}^N z_j \cdot b_j - \sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot a_{ij}(T)}{RT \sum_{j=1}^N z_j b_j} \\ &= \frac{\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N z_i z_j \frac{a_i \cdot b_j}{b_i} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N z_i z_j \frac{a_j \cdot b_i}{b_j} - \sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot a_{ij}(T)}{RT \sum_{j=1}^N z_j b_j} \\ &= \frac{\sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot b_i b_j \left[ \frac{1}{2} \frac{a_i}{b_i^2} + \frac{1}{2} \frac{a_j}{b_j^2} - \frac{a_{ij}(T)}{b_i b_j} \right]}{RT \sum_{j=1}^N z_j b_j} \end{aligned} \quad (18)$$

By comparing the final expression of Eq. (18) with Eq. (17) and replacing  $a_{ij}$  by its expression with respect to  $k_{ij}$  (see Eq. (15)), for the CEoS using Van der Waals MRs with no  $\ell_{ij}$ , the molar excess Gibbs energy under infinite pressure is:

$$\frac{g_{P \rightarrow \infty}^{E, EoS}}{RT} = \frac{\sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot b_i b_j \cdot C_{EoS} \left[ \frac{1}{2} \frac{a_i}{b_i^2} + \frac{1}{2} \frac{a_j}{b_j^2} - \frac{\sqrt{a_i(T) \cdot a_j(T)}}{b_i b_j} [1 - k_{ij}(T)] \right]}{RT \sum_{j=1}^N z_j b_j} \quad (19)$$

This expression is similar to a 1-parameter Van Laar activity-coefficient model extended to multicomponent systems [53,56–58] (note that the “1 parameter” denomination refers to the fact that the model involved only one symmetric binary interaction parameter per binary system):

$$\frac{g_{\text{VanLaar}}^E}{RT} = \frac{\sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot b_i b_j \cdot \varepsilon_{ij}(T)}{RT \sum_{j=1}^N z_j b_j} \text{ with } : \begin{cases} \varepsilon_{ij}(T) = \varepsilon_{ji}(T) \\ \varepsilon_{ii} = 0 \end{cases} \quad (20)$$

where  $\varepsilon_{ij}$  can be seen as a cross-interaction Van Laar parameter (in  $\text{J} \cdot \text{m}^{-3}$ ). By identifying Eqs. (19) and (20) and introducing the Scatchard-Hildebrand solubility parameters  $\delta$ , we arrive at:



This last relation is the searched connection between the BIP  $k_{12}$  of a binary system and the nature of the observed deviations from ideality on an isothermal phase diagram. This can be deduced from the sign of the Van Laar interaction parameter, i.e.,  $\varepsilon_{12} > 0 \Leftrightarrow g_{P \rightarrow \infty}^{E, EoS} > 0$  for positive deviations and the opposite for negative deviations. Note that this reasoning remains approximate since the relation is established under the infinite pressure assumption. In practice, the nature of deviations (positive or negative) persists generally from low to high pressure, and consequently, Eq. (21) can be used in most cases to deduce the nature of the deviations exhibited by a binary mixture (1) + (2) under a given pressure from its  $k_{12}$  value. A semiproof of this assertion can be found in [50] (see Table 2 and the corresponding comment).

Consequently, an ideal-solution behaviour that is, by definition, observed for a null excess Gibbs energy is associated with a null Van Laar parameter. Cancelling  $\varepsilon_{ij}$  in Eq. (21), the  $k_{ij}$  parameter of an ideal binary solution  $i + j$  is [50]:

$$k_{ij}^{ideal}(T) = -\frac{[\delta_i(T) - \delta_j(T)]^2}{2\delta_i(T) \cdot \delta_j(T)} \quad (22)$$

Remembering that solubility parameters are necessarily positive, it appears that an ideal-solution behaviour is always obtained for a negative  $k_{ij}$  value. In the same way, one can infer from Eq. (21) that systems exhibiting highly positive deviations from ideality are such that  $\varepsilon_{ij}(T) \gg 0 \Leftrightarrow k_{ij}(T) > 0$  and reciprocally for negative deviations. All these conclusions are perfectly supported by the isothermal phase diagrams shown in Fig. 1.

To conclude the discussion regarding the link between  $k_{ij}$  and the nature of deviations from ideality, let us review some characteristic behaviours of low-pressure (i.e., subcritical) binary systems and associate them to specific ranges of  $k_{ij}$ :

- Negative azeotropy: this behaviour can only be observed for systems showing convex isothermal functions  $g^E$  versus mole fraction  $z_i$  at a given temperature [59]. In practice, this feature is nearly always associated with negative deviations from ideality, and thus, negative azeotropy may arise for  $k_{ij}(T) < k_{ij}^{ideal}(T)$ .
- Positive azeotropy: this behaviour can only be observed for systems showing concave isothermal functions  $g^E$  versus  $z_i$  at a given temperature. In practice, this feature is observed in systems showing positive deviations from ideality, and thus, positive azeotropy may arise for  $k_{ij}(T) > k_{ij}^{ideal}(T)$ .
- Liquid-liquid phase split: this behaviour is observed for systems showing highly positive deviations from ideality [59]; thus, for  $k_{ij}(T) > 0 > k_{ij}^{ideal}(T)$ .

To conclude this section, note that if quadratic MRs are considered for both  $a_m$  and  $b_m$ , the expression of the excess Gibbs energy under infinite pressure is no longer a Van Laar expression but changes as follows:

$$\begin{aligned} \frac{g_{P \rightarrow \infty}^{E, EoS}}{C_{EoS}} &= \sum_{k=1}^N z_k \frac{a_k(T)}{b_k} - \frac{a_m(T, \mathbf{z})}{b_m(\mathbf{z})} + P \left( b_m(\mathbf{z}) - \sum_{k=1}^N z_k b_k \right) \\ &= \sum_{k=1}^N z_k \frac{a_k(T)}{b_k} - \frac{\sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot a_{ij}(T)}{\sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot b_{ij}} + P \sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot \left[ b_{ij} - \frac{1}{2} (b_i + b_j) \right] \end{aligned} \quad (23)$$

$$\begin{aligned} 1 - k_{ij}(T, \mathbf{z}) &= \frac{1}{2} \left[ \frac{b_i b_j}{\sqrt{a_i(T) a_j(T)}} [\delta_i(T)]^2 + [\delta_j(T)]^2 \right] - \frac{RT}{C_{EoS}} \frac{b_j \ln \gamma_i(T, \mathbf{z}) + b_i \ln \gamma_j(T, \mathbf{z})}{\sqrt{a_i(T) a_j(T)}} \\ \Rightarrow k_{ij}(T, \mathbf{z}) &= -\frac{[\delta_i(T) - \delta_j(T)]^2}{2\delta_i(T) \cdot \delta_j(T)} + \frac{RT}{2C_{EoS}} \frac{b_j \ln \gamma_i(T, \mathbf{z}) + b_i \ln \gamma_j(T, \mathbf{z})}{\sqrt{a_i(T) a_j(T)}} \end{aligned} \quad (27)$$

In Eq. (23), the pressure variable does not vanish in the expression of  $\frac{g_{P \rightarrow \infty}^{E, EoS}}{C_{EoS}}$ , which thus takes infinite values.

### 3.4. Use of composition-dependent $k_{ij}$ parameters

Aware that  $k_{ij}(T)$  coefficients cannot accurately model the most complex mixtures involving polar and associating compounds, some authors have decided to incorporate a composition dependency in the BIP expression:  $k_{ij}(T, \mathbf{z})$ . Although expressions stemming from this empirical modification go beyond the scope of the present article, which focuses on temperature-dependent BIPs, the reader is referred to the review by Lopez-Echeverry et al. that mentions some of these expressions (see Table 7 of [10]). In particular, expressions involving  $k_{ij}(T, \mathbf{z})$  can be especially useful in accounting for water traces that cannot be estimated accurately using a  $k_{ij}(T)$  coefficient.

Special caution must be taken with this type of model that may suffer from *Michelsen-Kistenmacher syndrome* [60]. The MR on  $a_m$  suffers from this undesirable syndrome when the  $a_m$  of a binary system (1) + (2) and the  $a_m$  of a ternary system (1) + (2) + (3), where (2) and (3) are strictly identical molecules, are different.

As a historical example of this syndrome, one can cite the  $k_{ij}(T, \mathbf{z})$  correlation proposed by Schwartzentruber and Renon (see Eq. (24)).

$$k_{ij}(T, \mathbf{z}) = k_{ij}^0 + k_{ij}^x (z_i - z_j) \quad \text{with} \quad \begin{cases} k_{ji}^0 = k_{ij}^0 \\ k_{ji}^x = -k_{ij}^x \end{cases} \quad (24)$$

Beyond correlations  $k_{ij}(T, \mathbf{z})$  that can be found in the literature, notably, most EoS/ $g^E$  MRs can be written in the form of Van der Waals MRs involving a  $k_{ij}(T, \mathbf{z})$  parameter. To prove this assertion, let us consider Huron-Vidal MRs (the use of, e.g., MHV1 MRs do not change anything with regard to the spirit of the demonstration).

According to Eq. (17), the  $a_m$  parameter is obtained from:

$$\begin{cases} a_m(T, \mathbf{z}) = b_m(\mathbf{z}) \sum_j z_j \frac{a_j(T)}{b_j} - b_m(\mathbf{z}) \frac{g^{E, \gamma}}{C_{EoS}} \\ b_m(\mathbf{z}) = \sum_j z_j b_j \end{cases} \quad (25)$$

By combining both lines of Eq. (25), introducing Scatchard-Hildebrand parameters (see Eq. (21)) and expressing the activity-coefficient model from the literature  $g^{E, \gamma}$  from Euler's theorem (i.e.,  $g^{E, \gamma} = RT \sum_i z_i \ln \gamma_i$ ), one arrives at:

$$\begin{aligned} a_m(T, \mathbf{z}) &= \sum_i z_i b_i \cdot \sum_j z_j \frac{a_j(T)}{b_j} - \sum_j z_j b_j \cdot \frac{RT \sum_i z_i b_i}{C_{EoS}} \\ &= \frac{1}{2} \sum_i \sum_j z_i z_j \cdot b_i b_j (\delta_i^2 + \delta_j^2) - \frac{1}{2} \frac{RT}{C_{EoS}} \sum_j z_i z_j (b_j \ln \gamma_i + b_i \ln \gamma_j) \\ &= \frac{1}{2} \sum_i \sum_j z_i z_j \cdot \left[ b_i b_j (\delta_i^2 + \delta_j^2) - \frac{RT}{C_{EoS}} (b_j \ln \gamma_i + b_i \ln \gamma_j) \right] \end{aligned} \quad (26)$$

By identifying Eqs. (26), (14) and (15), one obtains:

In Section 2.3, a connection is established between Van der Waals MRs involving a  $k_{ij}(T)$  on one hand and EoS/ $g^E$  MRs involving a Van Laar-type activity coefficient model on the other hand.

In the present section, this connection was extended in the sense that EoS/ $g^E$  MRs combined with any activity-coefficient model (UNIQUAC, Wilson, NRTL, etc.) can be recast in Van der Waals MRs involving a  $k_{ij}(T, z)$  coefficient, the expression of which is given in Eq. (27).

#### 4. Correlative methods for the estimation of BIPs involved in the cohesive parameter of the CEoS

Generally, the  $k_{ij}$  BIPs of CEoSs are fitted to VLE data, which is sometimes augmented by caloric data (heat capacity, enthalpy change on mixing, etc.). When the objective is to describe specific mixtures over limited temperature ranges,  $k_{ij}$  parameters can be chosen as constants.

Some decades ago, constant BIPs in CEoSs were used for a large variety of mixtures and temperature conditions. Although quite approximate, this practice can be explained by two essential reasons:

- (i) No generic temperature-dependent expression was known for  $k_{ij}$  values.
- (ii) Computing capacities were very limited with respect to current ones. Therefore, the fitting of  $k_{ij}$  parameters over large sets of binary-system and ternary-system data was not a widespread practice.

Note that for reducing the computational effort, the calculation of complex phase-behaviours of multicomponent systems involving dozens of compounds (e.g., petroleum fluids) was made essentially using matrix of constant  $k_{ij}$ .

Constant values for BIPs can be easily found in the literature from the 1970s and 1980s, the period in which the consideration of constant BIPs in extended conditions was a widespread assumption.

As an illustration, Fig. 2 is a scan copy of the renowned handbook by Reid et al. [61] edited in 1987. It provides typical values for BIPs related

to particular petroleum systems containing hydrocarbons, carbon dioxide, carbon monoxide and hydrogen sulfide. Even for complex systems such as those containing water, hydrocarbons and permanent gases, constant BIPs can be found in the open literature (e.g., [62,63]).

With increasing computing capacities, many correlations were developed in the 1980s and 1990s making it possible to estimate constant BIPs or temperature-dependent BIPs. These correlations were mainly empirical (i.e., not derived from theory), often expressed as functions of pure-component properties (such as critical temperature, pressure, molar volume, acentric factor, etc.) and applicable under limited conditions (specific mixture, specific temperature and composition conditions). Far from being exhaustive, we present here some of the most popular ones.

In the late 1960s, Chueh and Prausnitz derived a semitheoretical expression for the constant  $k_{ij}$  from London's theory [64] usable with mixtures of nonpolar compounds (e.g., alkanes) involving the critical molar volume  $v_c$  of species:

$$k_{ij} = 1 - \left( \frac{2\sqrt{v_{c,i}^{1/3} v_{c,j}^{1/3}}}{v_{c,i}^{1/3} + v_{c,j}^{1/3}} \right)^3 \quad (28)$$

Focusing on mixtures of light hydrocarbons and observing that critical molar volume data are not easily available in the literature for many species, Gao et al. reworked the expression by Chueh and Prausnitz and proposed Eq. (29) for constant BIPs, requiring the knowledge of the critical temperature  $T_c$  and critical compressibility factor  $z_c$  of species [65]:

$$1 - k_{ij} = \left( \frac{2\sqrt{T_{c,i} T_{c,j}}}{T_{c,i} + T_{c,j}} \right)^{\frac{1}{2}(z_{c,i} + z_{c,j})} \quad (29)$$

For mixtures of methane ( $i$ ) + heavier alkanes ( $j$ ), Kordas et al. proposed the following correlation for estimating the constant  $k_{ij}$  from the knowledge of the acentric factor of  $j$ . Light alkanes  $j$  are those lighter than n-eicosane, while heavy alkanes  $j$  are those heavier than the n-eicosane.

	Carbon dioxide		Hydrogen sulfide		Nitrogen		Carbon monoxide	
	SRK	PR	SRK	PR	SRK	PR	SRK	PR
Methane	0.093	0.092			0.028	0.031	0.032	0.030
Ethylene	0.053	0.055	0.085	0.083	0.080	0.086		
Ethane	0.136	0.132			0.041	0.052	-0.028	-0.023
Propylene	0.094	0.093			0.090	0.090		
Propane	0.129	0.124	0.088	0.088	0.076	0.085	0.016	0.026
Isobutane	0.128	0.120	0.051	0.047	0.094	0.103		
n-Butane	0.143	0.133			0.070	0.080		
Isopentane	0.131	0.122			0.087	0.092		
n-Pentane	0.131	0.122	0.069	0.063	0.088	0.100		
n-Hexane	0.118	0.110			0.150	0.150		
n-Heptane	0.110	0.100			0.142	0.144		
n-Decane	0.130	0.114						
Carbon dioxide			0.099	0.097	-0.032	-0.017		
Cyclohexane	0.129	0.105						
Benzene	0.077	0.077			0.153	0.164		
Toluene	0.113	0.106						

Fig. 2. Typical BIP values related to the Soave and Peng-Robinson CEoS for binary systems present in petroleum mixtures; scan copy extracted from [61].

$$\begin{cases} \text{Light alkanes : } k_{ij} = -0.13409\omega_j + 2.28543\omega_j^2 - 7.61455\omega_j^3 + 10.46565\omega_j^4 - 5.2351\omega_j^5 \\ \text{Heavy alkanes : } k_{ij} = -0.04633 - 0.04367\ln\omega_j \end{cases} \quad (30)$$

Correlations were also developed for systems containing CO<sub>2</sub> and various hydrocarbons. For such systems, BIPs values are much higher than zero, and  $k_{ij}$  is required for an acceptable description of their phase behaviour. The correlation proposed by Graboski and Daubert [66], applicable to mixtures of CO<sub>2</sub> ( $j$ ) and paraffin ( $i$ ), is associated with a modified version of the SRK EoS and requires the solubility parameters  $\delta$  as the input parameter.

$$k_{ij} = A + B|\delta_i - \delta_j| + C|\delta_i - \delta_j|^2 \quad (31)$$

To close this series of correlations generating constant BIPs, we cite the one by Nishiumi et al. that predicts  $k_{ij}$  coefficients for the Peng-Robinson EoS for a mixture containing PNA (paraffins, naphthenes, aromatics), alkynes, carbon dioxide, nitrogen and hydrogen sulfide (see Eq. (32)). This equation is remarkable for its generality (it is applicable to many types of mixtures). Similar to the one by Chueh and Prausnitz (see Eq. (28)),  $k_{ij}$  is expressed as a function of the critical molar volume; the acentric factor is also an input property.

$$1 - k_{ij} = C + D \frac{V_{c,i}}{V_{c,j}} + E \left( \frac{V_{c,i}}{V_{c,j}} \right)^2 \quad \text{with} \quad \begin{cases} C = c_1 + c_2|\omega_i - \omega_j| \\ D = d_1 + d_2|\omega_i - \omega_j| \end{cases} \quad (32)$$

We now arrive at temperature-dependent correlations for the  $k_{ij}$  BIP estimation.

Stryjek proposed a temperature-dependent correlation (see Eq. (33)) for the BIPs of the modified version of the Soave CEoS, applicable to mixtures of n-alkanes. Although the resulting  $k_{ij}$  values were of weak magnitude, the author claimed that correlation (33) was likely to significantly improve the modelling of such systems.

$$k_{ij} = k_{ij}^0 + k_{ij}^T [(T/K) - 273.15] \quad (33)$$

For systems containing CO<sub>2</sub> and n-alkanes modelled with the Peng-Robinson CEoS, Kato et al. proposed Eq. (34), in which the three coefficients ( $a$ ,  $b$  and  $c$ ) depend on the acentric factor of the n-alkane only.

$$k_{ij} = a(T - b)^2 + c \quad (34)$$

A similar approach was proposed by Moysan et al. [67]. For systems containing CO<sub>2</sub> ( $i$ ) and n-alkanes ( $j$ ), Kordas et al. [68] introduced the reduced temperature of carbon dioxide  $i$  and the acentric factors of alkanes  $j$  in the  $k_{ij}(T)$  expression given by Eq. (35).

$$k_{ij} = a(\omega_j) + b(\omega_j) \times T_{r,i} + c(\omega_j) \times T_{r,i}^3 \quad (35)$$

For systems containing {nitrogen or carbon dioxide or hydrogen sulfide}  $i$  and light alkanes  $j$ , Valderrama et al. [69] proposed a correlation (36) inspired by the study by Kordas et al.

$$k_{ij} = A(\omega_j) + B(\omega_j) / T_{r,j} \quad (36)$$

A correlation using the same input variables and applicable to the same systems was also proposed by Avlonitis et al. [70] for the Peng-Robinson EoS (see Eq. (37)).

$$k_{ij} = Q(\omega_j) - \frac{T_{r,i}^2 + A(\omega_j)}{T_{r,i}^3 + C(\omega_j)} \quad (37)$$

To conclude this section, the question of the relevance of the use of constant BIPs  $k_{ij}$  over large conditions can be debated. When constant  $k_{ij}$  values were introduced extensively in the CEoS formulation, mainly for petroleum applications, an increase in the accuracy of the calculation of phase equilibria of complex petroleum fluids was demonstrated (complex by the number and nature of compounds involved in such mixtures,

ranging from basic hydrocarbons to sulfur compounds, water and permanent gases).

This approach is probably outdated for the following reasons:

- Computing capacities have grown dramatically, thus allowing us to derive more complex and more generic expressions of  $k_{ij}$  coefficients. In particular, the temperature dependency of  $k_{ij}$  is a common option, enabling very accurate results for a large variety of mixtures.
- The constant  $k_{ij}$  value is specific to a given binary mixture, the temperature range used to fit it and the CEoS considered. Regarding the latter point, this means that if the EoS is modified (e.g., if the Soave EoS is replaced by Peng-Robinson or if the alpha function is changed or if mixing rules are different), then the  $k_{ij}$  value can no longer be used and must be updated.

The use of temperature-dependent correlations is undoubtedly a better option for the modelling of specific mixtures; as previously mentioned, the  $k_{ij}$  values obtained from correlations remain suitable for a given CEoS and not for the other ones.

In the next sections, general and powerful approaches are introduced to bypass the previous limitations, i.e., (i) to convert a  $k_{ij}$  value associated with a given CEoS to a  $k_{ij}$  value working with another CEoS and (ii) to predict  $k_{ij}$  from the group-contribution concept making it possible to generate BIPs for an infinite set of mixtures.

## 5. A theory for converting $k_{ij}$ BIP values from one CEoS to another

Let us suppose that we dispose of  $k_{ij}$  values for a given 2-parameter (i.e., attractive parameter and covolume) CEoS, e.g., the Soave CEoS, and that we wish to switch to another CEoS, e.g., the Peng-Robinson EoS, and to replace the Soave alpha function with the Twu function. A key question is as follows: it is possible to retain the values of the  $k_{ij}$  coefficients?

Based on the above, the answer to this question is clearly no. Indeed, we previously mentioned that EoS BIPs are EoS-specific parameters. To better understand why  $k_{ij}$  values change from one CEoS formulation to another one, we cite Coutinho et al. “the interaction parameters arise from the different simplifications and assumptions used in the derivation of the EoS mixing and combining rules, and they also take into account the various deficiencies and limitations of the EoS approach” [71].

When classical mixing rules are used (see Eqs. (11), (14) and (15)), the conversion of the  $k_{ij}$  BIPs suitable for a given model, i.e., a given CEoS using a given alpha function denoted {EoS<sub>1</sub>,  $\alpha_1$ }, to another model {EoS<sub>2</sub>,  $\alpha_2$ } is possible because of a simple theory inspired by the derivation of EoS/ $g^E$  MRs [72]. The starting point is therefore the equality of the excess Gibbs energies under infinite pressure coming from the 2 models:

$$\begin{aligned} g_{P \rightarrow \infty}^{E, EoS} &= \frac{C_{EoS_1}}{2} \frac{\sum_{i=1}^N \sum_{j=1}^N z_i z_j b_i^{EoS_1} b_j^{EoS_1} \epsilon_{ij}^{EoS_1}(T)}{\sum_{j=1}^N b_j^{EoS_1} z_j} \\ &= \frac{C_{EoS_2}}{2} \frac{\sum_{i=1}^N \sum_{j=1}^N z_i z_j b_i^{EoS_2} b_j^{EoS_2} \epsilon_{ij}^{EoS_2}(T)}{\sum_{j=1}^N b_j^{EoS_2} z_j} \end{aligned} \quad (38)$$

Covolumes of both EoSs being linked by the relation  $b_i^{EoS_1} = b_i^{EoS_2} \Omega_b^{EoS_1} / \Omega_b^{EoS_2}$ , Eq. (38), leads to the following equality:

$$C_{EoS_1} \cdot \Omega_b^{EoS_1} \cdot \xi_{ij}^{EoS_1}(T) = C_{EoS_2} \cdot \Omega_b^{EoS_2} \cdot \xi_{ij}^{EoS_2}(T) \tag{39}$$

Injecting Eq. (21) and relating  $\varepsilon_{ij}$  and  $k_{ij}$ , we arrive at:

$$\left\{ \begin{aligned} k_{ij}^{EoS_2} &= \frac{2\xi_{1 \rightarrow 2} k_{ij}^{EoS_1} \delta_i^{EoS_1} \delta_j^{EoS_1} + \xi_{1 \rightarrow 2} (\delta_i^{EoS_1} - \delta_j^{EoS_1})^2 - (\delta_i^{EoS_2} - \delta_j^{EoS_2})^2}{2\delta_i^{EoS_2} \delta_j^{EoS_2}} \\ \text{with } \xi_{1 \rightarrow 2} &= \frac{C_{EoS_1} \cdot \Omega_b^{EoS_1}}{C_{EoS_2} \cdot \Omega_b^{EoS_2}} \end{aligned} \right. \tag{40}$$

Eq. (40) thus offers a direct connection between the BIPs from 2 different two-parameter CEoSs. These 2 EoSs can be different in terms of mathematical formulation (i.e., values of  $u$  and  $w$ ) and/or in terms of alpha functions.

To validate this theory, two applications were envisaged and led to successful results:

- 1 A predictive Soave CEoS version was deduced from the Peng-Robinson-based PPR78 model using Eq. (40). It was shown that the model parameters obtained from those of PPR78 combined with Eq. (40) led to the same results as model parameters obtained from direct fitting to VLE data [72].
- 2 From the modelling of the phase behaviour of the H<sub>2</sub> + n-butane system at different temperatures, it is shown that the optimal  $k_{ij}$  coefficient associated with a given {EoS<sub>0</sub>,  $\alpha_0$ } reference model is not suitable for other {EoS,  $\alpha$ } models; however, Eq. (40) makes it possible to deduce an optimal  $k_{ij}(T)$  function for each of the considered {EoS,  $\alpha$ } models [73].

In addition, this theory was used successfully by Nasrifar et al. to develop a predictive version of the NB CEoS from the method used in the PPR78 model to predict  $k_{ij}(T)$  values (see e.g., [74]).

To conclude this section, the specific cases of a three-parameter CEoS, such as those proposed by Patel and Teja, Schmidt and Wenzel or Cismondi and Mollerup [21,22,75], are briefly addressed. In the pure-component versions of this class of CEoS, the universal parameters  $u$  and  $w$  become component specific through the introduction of a new component-specific parameter  $d$  that imposes the values of  $u(d)$  and  $w(d)$ .

In mixture versions of the three-parameter CEoS,  $d$  is made composition dependent using a mixing rule. Consequently,  $u$  and  $w$  are composition dependent (and can be written  $u(\mathbf{z})$  and  $w(\mathbf{z})$ ), and thus, the  $C_{EoS}$  coefficient, defined in Eq. (17), which is present in the expression of  $g_{p \rightarrow \infty}^{E, EoS}$ , is also composition dependent, i.e.,  $C_{EoS}(\mathbf{z})$ . In Eq. (40), if EoS 1 and/or EoS 2 are three-parameter CEoS, then the  $\xi_{1 \rightarrow 2}$  coefficient that depends on  $C_{EoS_1}$  and  $C_{EoS_2}$  is necessarily a function of the composition, and thus,  $k_{ij}^{EoS_2}$  is found to be composition dependent, even if  $k_{ij}^{EoS_1}$  is not. To the best of our knowledge, the validity of the theory enabling the connection of BIPs of different CEoSs has never been tested on three-parameter CEoSs.

## 6. Predictive methods for estimating BIPs involved in the cohesive parameter of CEoS

### 6.1. Bibliography

In the early 1990s, Abdoul, Rauzy and P neloux proposed for the first time a predictive method for the estimation of the  $k_{ij}$  BIPs of CEoSs [57]. This predictive approach was based on the group contribution (GC) concept. Their idea was to take advantage of (i) the connection between Van der Waals and EoS/ $g^E$  MRs through a Van Laar-type expression (as discussed above) and (ii) the existence of a GC method to estimate the binary parameters of the Van Laar model proposed by Redlich et al. and used in the 1970s to correlate the enthalpy of mixing data [76,77]. In their model formulation, these authors introduced an excess function  $E$  (derived from the Guggenheim quasi-lattice excess function EoS [53]). It can be observed that this theory leads to MRs that are strictly equivalent to Huron-Vidal MRs in which the quantity  $g_{p \rightarrow \infty}^E / C_{EoS}$  plays the same role as the  $E$  function. The  $E$  function consists of 2 contributions, the main one being a Van Laar-type expression ( $E_{Van\ Laar}$ ) involving a binary parameter  $E_{ij}$  estimated from the GC concept. However, to improve the correlation of size-asymmetric systems, Abdoul et al. decided to add a second term denoted  $E_{Size\ effects}$  accounting “for the differences of conformation of the molecules” and used to “correlate the heat effects arising from mixing of globular molecules with long-chain molecules” [57]. The general expression for the ARP MRs is given in Eq. (41).

$$\left\{ \begin{aligned} \frac{a_m(T, \mathbf{z})}{RTb_m(\mathbf{z})} &= \sum_{i=1}^N z_i \frac{a_i(T)}{RTb_i} - E(T, \mathbf{z}) \\ b_m(\mathbf{z}) &= \sum_{i=1}^N z_i b_i \\ E(T, \mathbf{z}) &= E_{Van\ Laar}(T, \mathbf{z}) + E_{Size\ effects}(T, \mathbf{z}) \\ E_{Van\ Laar}(T, \mathbf{z}) &= \frac{1}{2} \frac{\sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot b_i b_j \cdot E_{ij}(T)}{\sum_{j=1}^N z_j b_j} \quad \text{with } E_{ij}(T) = E_{ji}(T) \\ E_{Size\ effects}(T, \mathbf{z}) &= \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N z_i z_j \cdot Ech_{ij}(T) \\ \text{Group contribution method : } E_{ij}(T) &= -\frac{1}{2} \left[ \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk}) (\alpha_{il} - \alpha_{jl}) A_{kl} \left( \frac{T_0}{T} \right)^{\left( \frac{B_{kl}}{A_{kl}} - 1 \right)} \right] \\ Ech_{ij}(T) &= 2.95 (l_i - l_j)^2 \left[ \left( \frac{T_0}{T} \right)^4 - 2 \frac{T}{T_0} \right] \\ T_0 &= 298.15\ K \end{aligned} \right. \tag{41}$$

In Eq. (41),  $N_g$  is the number of different groups defined by the method, and  $\alpha_{ik}$  is the fraction of molecules ( $i$ ) occupied by group  $k$  (the occurrence of group  $k$  in molecule  $i$  divided by the total number of groups present in molecule  $i$ ).  $A_{kl}$  and  $B_{kl}$  are the group-binary-interaction parameters (G-BIPs) between groups  $k$  and  $l$  that are constant real numbers, symmetric ( $A_{kl} = A_{lk}$  and  $B_{kl} = B_{lk}$ ), and satisfy  $A_{kk} = B_{kk} = 0$ . These parameters were fitted to the fluid-phase equilibria and excess enthalpy experimental data. Regarding the  $B$  parameter, Abdoul et al. mentioned that they are “essential in excess enthalpy calculations”. The  $l_i$  parameters were introduced as “parameters of conformation for substituted alkanes and non-alkane hydrocarbons or as chain-length parameters for straight-chain alkanes (in fact they are the number of carbon atoms in these)” [57]. Note that Abdoul et al. proposed a simple correlation for the estimation of  $l_i$  parameters (see Eq. B1 in [57]). The introduction of a size-effect contribution in the  $E$  function introduced a slightly different relationship between the  $E_{ij}$  and the  $k_{ij}$  parameters (see Eq. (42)), making the  $k_{ij}$  parameter composition-dependent for size-asymmetric systems (i.e., systems for which  $Ech_{ij}(T) \neq 0$ ):

$$k_{ij}(T, \mathbf{z}) = \frac{\left[ E_{ij}(T) + \frac{b_m(z)}{b_i b_j} Ech_{ij}(T) \right] - [\delta_i(T) - \delta_j(T)]^2}{2\delta_i(T) \cdot \delta_j(T)} \quad (42)$$

The ARP model was developed for predicting the  $k_{ij}(T)$  parameters of weakly polar and nonassociating mixtures (PNA compounds and olefins). The authors of the model reported weak deviations for mixtures

containing these species, with a deviation of  $\approx 1\%$  for the bubble pressure data and  $< 1\%$  for dew-point composition data.

The main limitation of their approach lies in the small number of groups defined and thus the small number of chemical families likely to be described with this model. In addition, there is a serious risk of the nonsafe extrapolation of  $k_{ij}(T)$  when this model is utilized under temperature conditions that are very different from those used for the estimation of G-BIPs. This issue is discussed later.

For the continuity of the ARP model, Jaubert and Mutelet introduced the predictive Peng-Robinson model (PPR78) [35] in 2004, which was renamed E-PPR78 in the 2010s ( $E$  stands for *enhanced*). Developed continuously since then, the main strength of this model – beyond an appreciable accuracy – is the high number of groups defined, enabling the description of any mixture containing PNA, olefins, sulfur compounds ( $H_2S$  and mercaptans), permanent gases (He, nitrogen, oxygen, hydrogen, NO,  $NO_2$ ,  $CO_2$  and so on), polar compounds (water, ammonia), refrigerants, etc. The exhaustive list of groups defined currently in the PPR78 model is given in Table 1. In terms of model formulation, the main difference between the ARP and PPR78 models lies in (i) the presence (ARP) or absence (PPR78) of the  $E_{Size}$  effects contribution in the MRs, (ii) the alpha function present in the model and (iii) the GC scheme. Indeed, in ARP, a specific function (requiring the knowledge of the normal boiling point) was used for heavy compounds, while for other compounds, a Soave-type  $\alpha$ -function, especially that developed by Rauzy [78], was used instead. To ensure compatibility

**Table 1**

List of molecular groups defined in the PPR78/E-PPR78 models.

Group number	Group name	Example molecules involving the group	Paper introducing the group
1	-CH <sub>3</sub>	propane: CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	[35]
2	-CH <sub>2</sub> -	propane: CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	[35]
3	>CH-	Methylpropane: CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>3</sub>	[35]
4	>C<	Dimethylpropane: CH <sub>3</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -CH <sub>3</sub>	[35]
5	CH <sub>4</sub> (methane)	-	[35]
6	C <sub>2</sub> H <sub>6</sub> (ethane)	-	[35]
7	=CH <sub>ARO</sub> -	6 aromatic “CH” groups in benzene	[49]
8	=C <sub>ARO</sub> <	1 aromatic “C” group in toluene	[49]
9	C <sub>fused ARO</sub>	C atoms present in 2 different aromatic cycles. There are 2 C <sub>fused ARO</sub> in naphthalene	[49]
10	-CH <sub>2,cycl</sub> -	6 cyclic “CH <sub>2</sub> ” groups in cyclohexane	[81]
11	>CH <sub>cycl</sub> - and >C <sub>cycl</sub> <	1 cyclic “CH” group in methylcyclohexane	[81]
12	CO <sub>2</sub> (carbon dioxide)	-	[82]
13	N <sub>2</sub> (nitrogen)	-	[83,84]
14	H <sub>2</sub> S (hydrogen sulfide)	-	[85]
15	-SH	1 sulfhydryl group in methanethiol ( <i>aka</i> methyl mercaptan)	[86,87]
16	H <sub>2</sub> O (water)	-	[88]
17	C <sub>2</sub> H <sub>4</sub> (ethylene)	-	[89]
18	=CH <sub>2,alkene</sub> and =CH <sub>alkene</sub> -	Propylene: CH <sub>2</sub> =CH-CH <sub>3</sub>	[89]
19	=C <sub>alkene</sub> <	Isobutene: CH <sub>2</sub> =C(CH <sub>3</sub> )-CH <sub>3</sub>	[89]
20	=CH <sub>cycl, alkene</sub> - and =C <sub>cycl, alkene</sub> <	2 “=CH <sub>cycl, alkene</sub> ” in cyclopentene	[89]
21	H <sub>2</sub> (hydrogen)	-	[90]
22	C <sub>2</sub> F <sub>6</sub> (perfluoroethane)	-	[91]
23	-CF <sub>3</sub>	Perfluorobutane: CF <sub>3</sub> -CF <sub>2</sub> -CF <sub>2</sub> -CF <sub>3</sub>	[91]
24	-CF <sub>2</sub> - and >CF-	Perfluorobutane: CF <sub>3</sub> -CF <sub>2</sub> -CF <sub>2</sub> -CF <sub>3</sub>	[91]
25	=CF <sub>2</sub> and =CF-	Hexafluoropropylene: CF <sub>3</sub> -CF=CF <sub>2</sub>	[91]
26	R152a (CHF <sub>2</sub> -CH <sub>3</sub> )	-	[91]
27	R1234a (CF <sub>3</sub> -CH <sub>2</sub> F)	-	[91]
28	CO (carbon monoxide)	-	[92]
29	He (helium)	-	[92]
30	Ar (argon)	-	[92]
31	SO <sub>2</sub> (sulfur dioxide)	-	[93]
32	O <sub>2</sub> (oxygen)	-	[93]
33	NO (nitric oxide)	-	[93]
34	COS (carbonyl sulfide)	-	[94]
35	NH <sub>3</sub> (ammonia)	-	[94]
36	NO <sub>2</sub> (nitrogen dioxide)/N <sub>2</sub> O <sub>4</sub> (dinitrogen tetroxide)	-	[94]
37	N <sub>2</sub> O (nitrous oxide)	-	[94]
38	C <sub>2</sub> H <sub>2</sub> (acetylene : CH≡CH)	-	[95]
39	-C≡CH	Propyne: CH <sub>3</sub> -C≡CH	[95]
40	-C≡C-	2-butyne: CH <sub>3</sub> -C≡C-CH <sub>3</sub>	[95]

with commercial process simulators, Jaubert and Mutelet used the original alpha function proposed by Peng and Robinson for all components. In addition, observing that in the ARP model, “*decomposition into groups of the molecules is not straightforward and is sometimes difficult to understand*” [35], Jaubert and Mutelet utilized a classical approach to decompose molecules, inspired by UNIQUAC functional-group activity coefficients (UNIFAC).

Another predictive CEoS using a  $k_{ij}(T)$  parameter was proposed by Nasrifar and Bolland [79,80], who combined their CEoS version with the GC method used in the PPR78 model for estimating  $k_{ij}(T)$ .

In the next section, the performance of the PPR78/E-PPR78 model, which is, in our opinion, the most achieved version of a CEoS combined with a predictive method for  $k_{ij}(T)$ , is discussed in light of its successes and failures. General conclusions regarding its capacity and limitation are then drawn.

### 6.2. A short historical account of the first 10 years of development of the PPR78 model

The development of groups 1 to 21 of the PPR78 model has been described in a series of articles presenting both the methodology for estimating the G-BIPs (i.e., the  $A_{k\setminus}$  and  $B_{k\setminus}$  values involved in the  $E_{ij}$  expression given in Eq. (41)) and the predicted binary phase diagrams, arranged by chemical family (see Table 1). To achieve this goal, a comprehensive two-phase fluid equilibrium database was constituted; approximately 90,000 data were collected. Note that only the data deemed to be unquestionably doubtful were left aside to fit model parameters.

The work conducted from 2004 to 2009 was aimed essentially to develop groups present in anhydrous petroleum fluids (i.e., groups 1 to 15). The ability of the PPR78 model to represent the phase envelopes of synthetic petroleum fluids such as natural gases, gas condensates and heavy oils was shown in Jaubert et al. [96]. Some of the predictions presented in this article are illustrated in Fig. 3. A method aimed at predicting the  $k_{ij}$  between each pair of components in petroleum fluids containing pseudocomponents was proposed later [97].

One of the major challenges that followed this period was the addition of the water group. To do so, it was necessary to determine the interactions between water, a molecule considered to be a group, and the groups previously defined. This task was certainly the most ambitious one undertaken since 2004 because of the unanimously recognized difficulty in predicting both the solubility of hydrocarbon mixtures in water and the solubility of water in hydrocarbons. Because of the extreme difficulty for a CEoS to predict these two solubilities at the same time for a given binary system, model parameters were fitted to obtain approximate, although reasonable, predictions of the two types of solubilities [88]. While phase-equilibrium data used in previous studies devoted to adding a new group to PPR78 were essentially VLE data, many water-containing systems exhibit liquid-liquid phase split, and consequently, a consequent number of LLE data were included in the fitting database. Quantitatively, contrasting results were obtained, and it can be considered that the PPR78 model cannot predict the phase equilibria of aqueous systems in both the subcritical and supercritical domains for both low and high water contents with high precision. From a qualitative point of view, the conclusions are different. Global phase equilibrium diagrams (GPEDs) [98] and critical loci in particular were used to evaluate the capacity of the model to reproduce the global phase behaviour of a given system. The GPEDs of aqueous systems modelled by PPR78 show a good qualitative prediction of critical loci and, more generally, of the types of phase behaviours (according to the classification of Van Konynenburg and Scott [99,100]). Fig. 4 is an illustration of some of the – qualitatively acceptable – results obtained when applying the PPR78 model to water-containing systems.

To evaluate the global predictive capacities of the PPR78 EoS, we define several chemical families within which the deviations between model and experimental data are supposed to be uniform:

- hydrocarbons (HC) include alkanes, cycloalkanes, aromatic compounds and alkenes (with the exception of methane, ethane and ethylene),
- heavy permanent gases (HPG): CO<sub>2</sub>, ethane, and ethylene,
- light permanent gases (LPG): N<sub>2</sub>, H<sub>2</sub>, and methane,
- sulfur compounds (SC): H<sub>2</sub>S and mercaptans.

The “*objective function*”  $F_{obj}$  used in the fitting procedure for G-BIPs is now used as a global criterion of model accuracy. This function aggregates percent deviations on bubble-point and dew-point compositions, as well as on critical compositions and pressures. An expression of this function is provided in each paper devoted to the development of PPR78 (see, e.g., Eq. (7) in [35]). To allow a visual representation of the model performance, the values of  $F_{obj}$  for binary systems involving compounds within the 4 chemical families defined above are reported in Fig. 5.

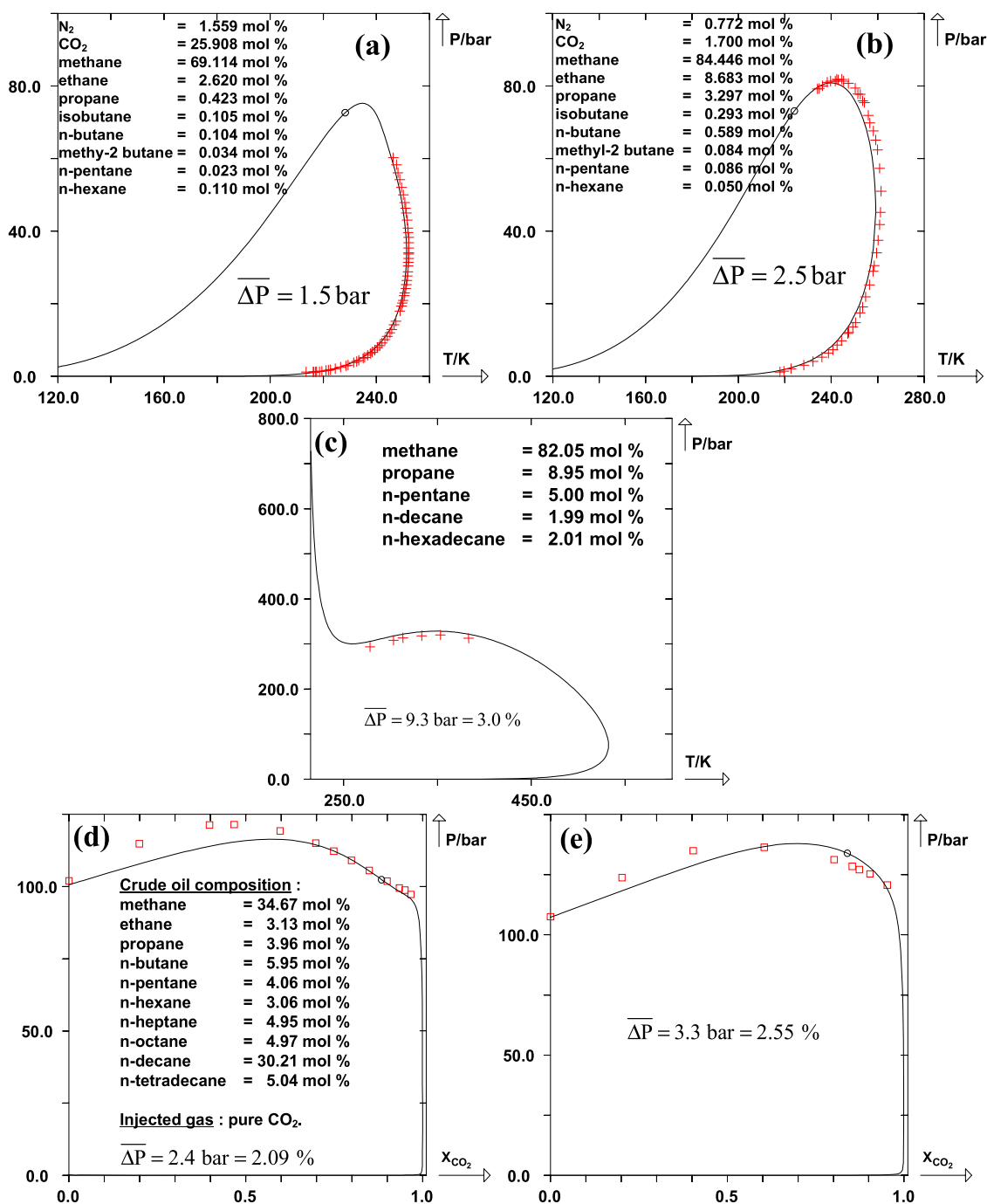
It can be observed first that the global prediction error of the PPR78 model (calculated over all chemical families and data types) is 7.3%. More specifically, binary systems in which the two components are both in the same chemical family show average errors of approximately 6% (see, e.g., the HC/HC, HPG/HPG and LPG/LPG systems). This relatively low deviation can be partially justified by the fact that systems made up of similar compounds exhibit weak deviations from ideality and consequently are characterized generally by Type-I or -II phase behaviour, according to Van Konynenburg and Scott. These systems are known to be those that the CEoSs represent with the most accuracy. Note, however, that Type-III phase behaviour may arise in binaries for which both compounds belong to the same chemical family but present highly different molecular sizes and shapes. The most important deviations observed for the binary systems containing sulfur compounds (and in particular, the SC/HC and SC/SC families) are not significant in our view for the two following reasons:

- The first reason is the low number of experimental points and the composition range they describe, which cannot be considered representative of SC/SC systems (only 51 data points, related to the same binary system: H<sub>2</sub>S + methanethiol, characterized by very high concentrations of H<sub>2</sub>S). Note that the deviation  $\delta$  on a given bubble or dew point at a given  $(T, P)$  is calculated here as the average between the absolute percent deviation on both component mole fractions:  $\delta = \frac{1}{2} \left[ \frac{|x_{1,exp} - x_{1,calc}|}{x_{1,exp}} + \frac{|x_{2,exp} - x_{2,calc}|}{x_{2,exp}} \right]$ . This procedure induces mechanically an important value of  $\delta$  when mole fractions are close to zero (i.e., when one component is nearly pure, while the other is present in trace amounts).
- On the other hand, most of the phase equilibrium data involving mercaptans, as well as some data related to hydrogen sulfide + hydrocarbon systems, show an important scatter of data (this is especially visible when comparing data originating from different sources but measured under similar conditions).

### 6.3. From PPR78 to E-PPR78

In a study published in the early 2010s, PPR78 authors realized that the PPR78 model could lead to nonnegligible and distributed deviations in the enthalpy ( $h^M$ ) and heat capacity ( $c_p^M$ ) changes on mixing data for various types of systems, including naphthenes and permanent gases [101]. Table 2 summarizes the deviations observed in the  $h^M$  data. For the  $c_p^M$  data, the average mean deviation between the experimental and predicted data reached the unacceptable value of 14.5 J·mol<sup>-1</sup>·K<sup>-1</sup>.

This observation encouraged PPR78 authors to develop a new version of their model in which the G-BIP values are fitted to both phase equilibrium data and calorific data. Indeed, PPR78 developers observed that the  $A_{k\setminus}$  parameters are much more sensitive to VLE data than the  $B_{k\setminus}$  parameters, thus suggesting a decoupling of the fitting procedure. Schematically speaking,  $A_{k\setminus}$  parameters are used to describe the VLE data, while  $B_{k\setminus}$  are used for the calorific data.



**Fig. 3.** Predictions of the phase behaviour of petroleum fluids by the PPR78 model ((+,  $\square$ ) experimental points, (O) calculated critical points, and lines: calculated saturation curves). (a) and (b): Phase envelopes of natural gases. (c) Phase envelope of a gas condensate. (d) and (e) Modelling of the swelling experiments of a petroleum fluid with pure CO<sub>2</sub> at 322 K and 338.7 K, respectively.  $\overline{\Delta P}$  denotes the mean deviation between the calculated and experimental pressures.

The redetermination of all G-BIPs over a database including the VLE/LLE and calorific data now confirmed this insight. It was observed that it is possible to maintain the model accuracy of the PPR78 model in terms of the VLE/LLE and critical data while dramatically improving the prediction of calorific ( $h^M$  and  $c_p^M$ ) data, as illustrated in Fig. 6. The PPR78 model with refitted parameters was named *E*-PPR78 (where *E* stands for *enhanced*) to emphasize the change in fitting procedure. More details regarding the mutation of PPR78 to *E*-PPR78 can be found in a recent article [102]. Since this transition, all G-BIP values of all subsequent groups were estimated systematically on both VLE/LLE and calorific data. Table 3 offers a global overview of the *E*-PPR78 model capacity to describe both types of data. An unprecedented number of

data were considered to fit the  $\frac{N_g(N_g-1)}{2} = 780$  G-BIPs, characterizing the interactions between the  $N_g = 40$  molecular groups defined in the model. Approximately 126 000 VLE/LLE data and 34 000 calorific data were used. On average, *E*-PPR78 shows a mean absolute percent error of approximately 9% on the VLE/LLE data and approximately 50% on the calorific data (Eqs. 1, 5, 10, 13, 16, 22, 30–31, 36, 39).

#### 6.4. Extrapolation of the $k_{ij}$ BIPs

The equation used for estimating the  $E_{ij}$  Van Laar parameter of the ARP and PPR78 models involves a  $\left(\frac{T_0}{T}\right)^{\frac{B_{k_{ij}}}{A_{k_{ij}}}-1}$  term (see Eq. (41)), which

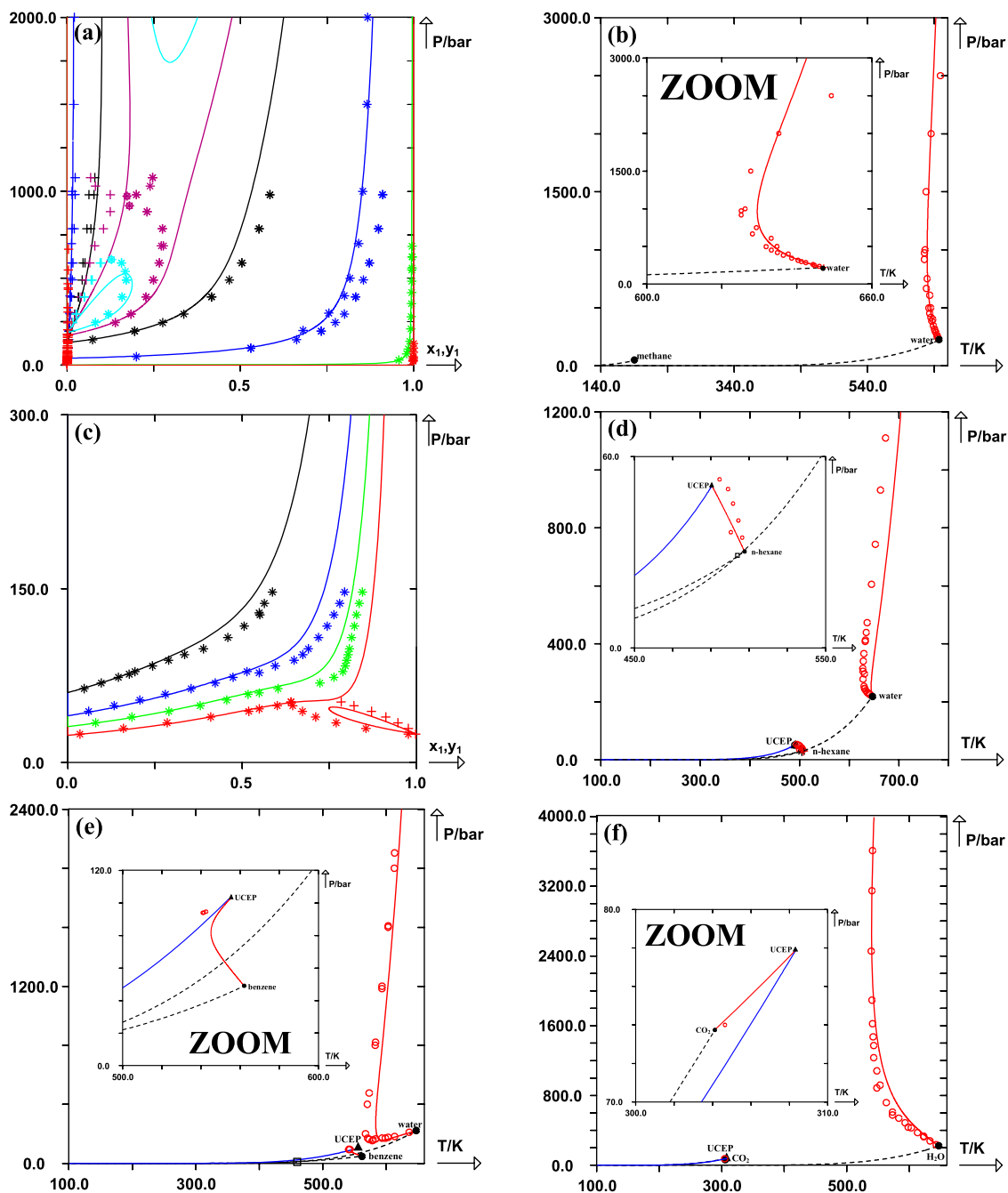


Fig. 4. Phase behaviour of aqueous systems predicted by the PPR78 model ((+) experimental bubble points, (\*) experimental dew points and (O) experimental critical points). (a) Phase diagrams of the methane(1) + water(2) system. (b) Critical locus of the methane + water system. (c) Isothermal phase diagrams of the n-hexane(1) + water(2) system. (d) Critical locus of the n-hexane + water system. (e) Critical locus of the benzene + water system. (f) Critical locus of the CO<sub>2</sub> + water system.



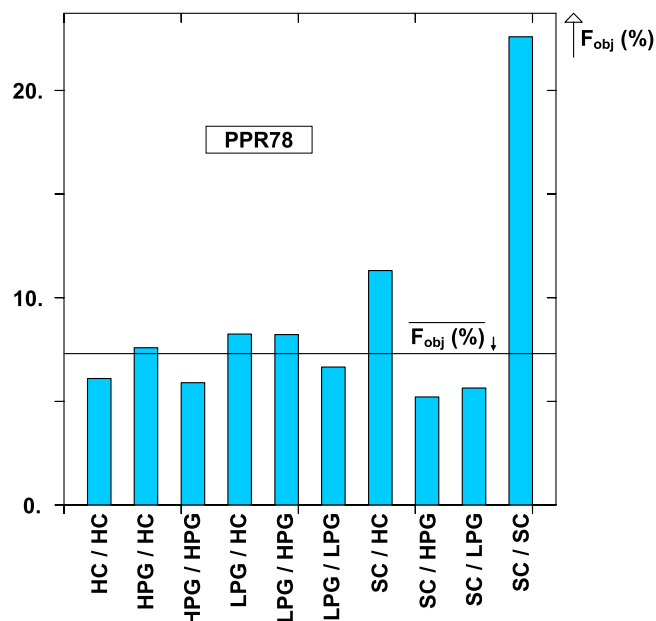


Fig. 5. Histogram representing the average errors  $F_{obj}$  between the predictions of the PPR78 model and experimental data. Compounds involved in these binary systems are divided into four chemical families: HC = hydrocarbons, HPG = heavy permanent gases, LPG = light permanent gases, and SC = sulfur compounds. The average value of  $F_{obj}$  calculated over the whole database (90 000 experimental data points) is highlighted with a horizontal straight line.

Table 2

Deviations between experimental  $h^M$  values and those predicted by the PPR78 model. The results are sorted by family. The  $i$ th row of the table shows deviations for binary systems such that the first compound belongs to the family  $i$  and whose second compound belongs to a family included between lines 1 and  $i$ .

Line	Chemical family	Data number	Relative mean deviation of the $h^M$ data	Absolute mean deviation of the $h^M$ data (J/mol)
1	alkanes	3405	628.70%	88.64
2	aromatic compounds	5544	88.20%	145.9
3	Naphthenes	8368	1490.00%	324.5
4	CO <sub>2</sub>	4940	64.96%	175.9
5	N <sub>2</sub>	883	16.34%	52.18
6	H <sub>2</sub> S	39	56.42%	48.73
7	Mercaptans	246	362.90%	395.5
8	Alkenes	3579	227.60%	173
9	H <sub>2</sub>	432	6.98%	25.69
	All	27436	595.60%	199.4

may induce divergence of the  $k_{ij}(T)$  values at low and/or high temperature depending on the exponent value; this divergence may entail nonphysical predictions. To avoid this situation, it is necessary to ensure that G-BIPs were fitted to the binary data, the temperature range of which includes the temperature  $T$  of the  $k_{ij}(T)$  coefficient to be estimated. Notably, G-BIP values are very sensitive to the quantity of data and the corresponding temperature range used for fitting them. Considering exhaustive (as far as possible) data collection enables the reduction in the influence of measurement uncertainties on their determination and a reduced risk of divergence under temperature conditions of practical applications. The quantity of data published each year has been increasing continuously during the past twenty years [103], and model constants of recent predictive models can be fitted to much more data and are thus likely to be more accurate than models parametrized well before. This is the reason why the ARP model presents a higher risk of predicting abnormally elevated  $k_{ij}$  values than PPR78. Indeed, to develop the ARP model, Abdoul et al. used approximately 39

000 experimental bubble and dew points and estimated 231 G-BIPs; therefore, 169 datapoints were used on average to estimate each ARP parameter. For the PPR78 model limited to the same systems as those considered by ARP developers, approximately 67 000 experimental bubble, dew and critical points were used (thus 1.7 times more than the number of data points considered for the ARP model) to estimate 204 model constants. On average, 328 datapoints were used to estimate each parameter of the PPR78 model. The determination of the G-BIPs of the ARP model on too little data and too limited temperature ranges can be observed for some binary and multicomponent systems. For instance, while the PPR78 and ARP models provide similar estimations of  $k_{ij}$  in most cases (see, e.g., Fig. 7(a)), large deviations between both models may appear in binary systems involving G-BIPs determined over an insufficient set of data, as illustrated in Fig. 7(b) and (c).

## 7. Comparison with other EoS approaches

In a recent paper, Piña-Martinez et al. [46] compared different CEoSs following a strict methodology relying on the use of a reference database for model evaluation, gathering 200 binary systems and various types of data (critical, VLE/LLE, VLE, calorific, etc.) [104]. Four different models were considered in their study:

- The PR-Van Laar model, which is similar to the  $E$ -PPR78 model except that the  $E_{12}(T)$  parameter of the excess function is not estimated from a GC method but from Eq. (43). This is derived from the GC-based expression and is obtained by assuming that each molecule of a binary system 1 + 2 consists of a single molecular group.

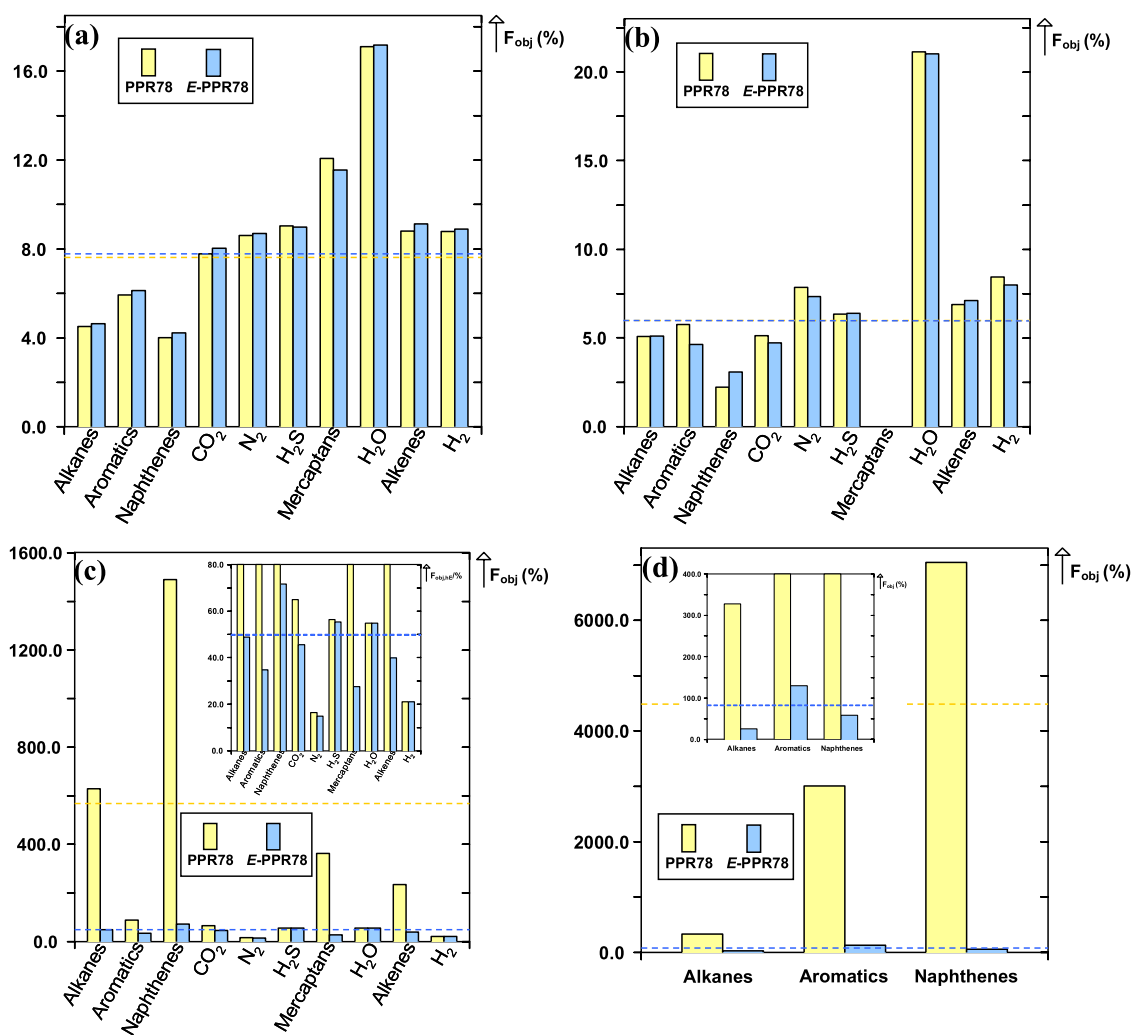
$$E_{12}(T) = A_{12} \left( \frac{T_0}{T} \right)^{\left( \frac{\beta_{12}}{\alpha_{12}} - 1 \right)} \quad (43)$$

In the PR-Van Laar model, BIPs  $A_{12}$  and  $B_{12}$  are fitted to the experimental data. Detailed results of the evaluation of this model can be found in [104].

- The  $tc$ -PR CEoS [27] combined with advanced EoS/ $g^E$  MRs (similar to Huron-Vidal MRs). Three different  $g^E$  models are considered: Wilson, UNIQUAC and NRTL.

Similarly, Nikolaidis et al. recently benchmarked the PC-SAFT EoS [105] using MRs with null BIPs [106]. All the EoSs considered in these studies were ascribed detailed and global marks (out of 20) which were calculated following the same methodology and criteria, making it possible to make a fair comparison between these models. Without providing details, a global mark is a good indication of how the EoS performs over a large set of properties of interest and for many types of binary systems, from the simplest ones (mixture of n-alkanes) to the most complex in terms of interaction (e.g., water or alcohols and hydrocarbons). The global marks obtained by these 5 EoSs are shown in Fig. 8. It can be observed that the PR-Van Laar approach is competitive with EoS using advanced EoS/ $g^E$  MRs involving a more sophisticated activity-coefficient model. More precisely, compared to more sophisticated approaches, the PR-Van Laar model can more efficiently model systems involving nonassociating species than the ones in which self- and cross-associations are taking place (this is well visible in Fig. 3 of [46]). Incidentally, the PC-SAFT EoS without BIPs underperforms. A fairer comparison of the CEoS with the PC-SAFT EoS involving BIPs is not yet available in the literature but should be published in the near future.

To conclude this section, it seems necessary to state that integrating  $g^E$  models into the mixing rules of cubic equations may result in the prediction of unrealistic critical loci at high pressures, especially when the BIPs imbedded in the  $g^E$  model are not fitted to critical data. Such models may also fail to simultaneously correlate VLE and LLE data and



**Fig. 6.** Graphical comparison of the values of objective function  $F_{obj}$  (expressing a measure of the average deviation between model and experimental data) calculated for the PPR78 (yellow) and E-PPR78 (blue) models. Calculations performed (a) on VLE (or LLE) data only (bubble and dew points), (b) on critical data, (c) on  $h^M$  data, (d) on  $c^M$  data.

can thus predict nonrealistic three-phase LLVE behaviour. All these possible weaknesses and the importance of properly parameterizing the EoS are extensively discussed by Polishuk et al. in many papers [107–110].

## 8. Conclusion

BIPs involved in the attractive term of the CEoS using Van der Waals MRs are more than the simple mathematical parameters used for improving the correlation of data. There is a close link between this approach and the Huron-Vidal EoS/ $g^E$  approach involving a Van Laar-type excess function. BIPs are directly connected to the Van Laar cross parameter and thus to the nature of the deviation from ideal behaviour.

Considering constant BIPs is senseless for describing a mixture over a significant temperature range. Many temperature-dependent correlations are available in the open literature for estimating BIPs that are generally limited to specific mixtures. For several decades, GC-based methods have become reference estimation methods for the estimation of  $k_{ij}$  BIPs of CEoSs. The PPR78/E-PPR78 model is probably the most successful model of this type. Proposing 40 molecular groups allows us to describe a large variety of mixtures containing real and/or pseudocomponents.

The main advantages of this approach are certainly the excellent balance between simplicity (e.g., the use of a model that can be easily

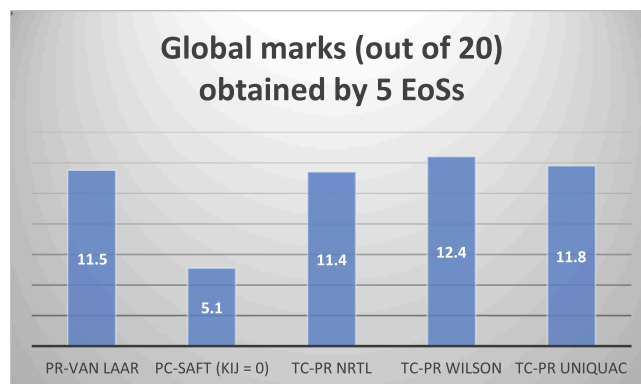
implemented in simulation software, the reasonable number of model parameters and their availability, etc.) and precision, as well as its large applicability to mixtures spanning from nonassociating and nonpolar compounds to moderately polar compounds.

We conclude this article with a remark presenting the main limitation of CEoSs using a  $k_{ij}$  approach and opening on the perspectives for CEoSs in general. When associating and nonpolar species are mixed, the results of the approach may be inaccurate from a quantitative viewpoint. However, this approach remains excellent for predicting global phenomena (critical behaviour, liquid-liquid and/or vapour-liquid-liquid phase splits, etc.) present in GPEDs. This observation applies more generally to all CEoSs using Van der Waals MRs and  $k_{ij}$  parameters (fitted or predicted). As an illustration, Fig. 9 shows the phase behaviour of such a system, n-hexane + 1-propanol, modelled with the PR-Van Laar model involving fitted parameters. The GPED highlights an excellent reproduction of the critical locus and azeotropic line. The isothermal phase diagram at 348.15 K seems unsatisfactory (prediction of the LLE region and heterogeneous azeotropy that do not exist), while the one at 493.15 K, which exhibits a homogeneous azeotrope, is much more accurate. This reveals that the model can qualitatively reproduce the phenomena experimentally observed but has difficulty predicting their beginning and end.

To improve the modelling of such systems, it is unnecessary to change the model family (the cubic EoS), which keeps advantages of

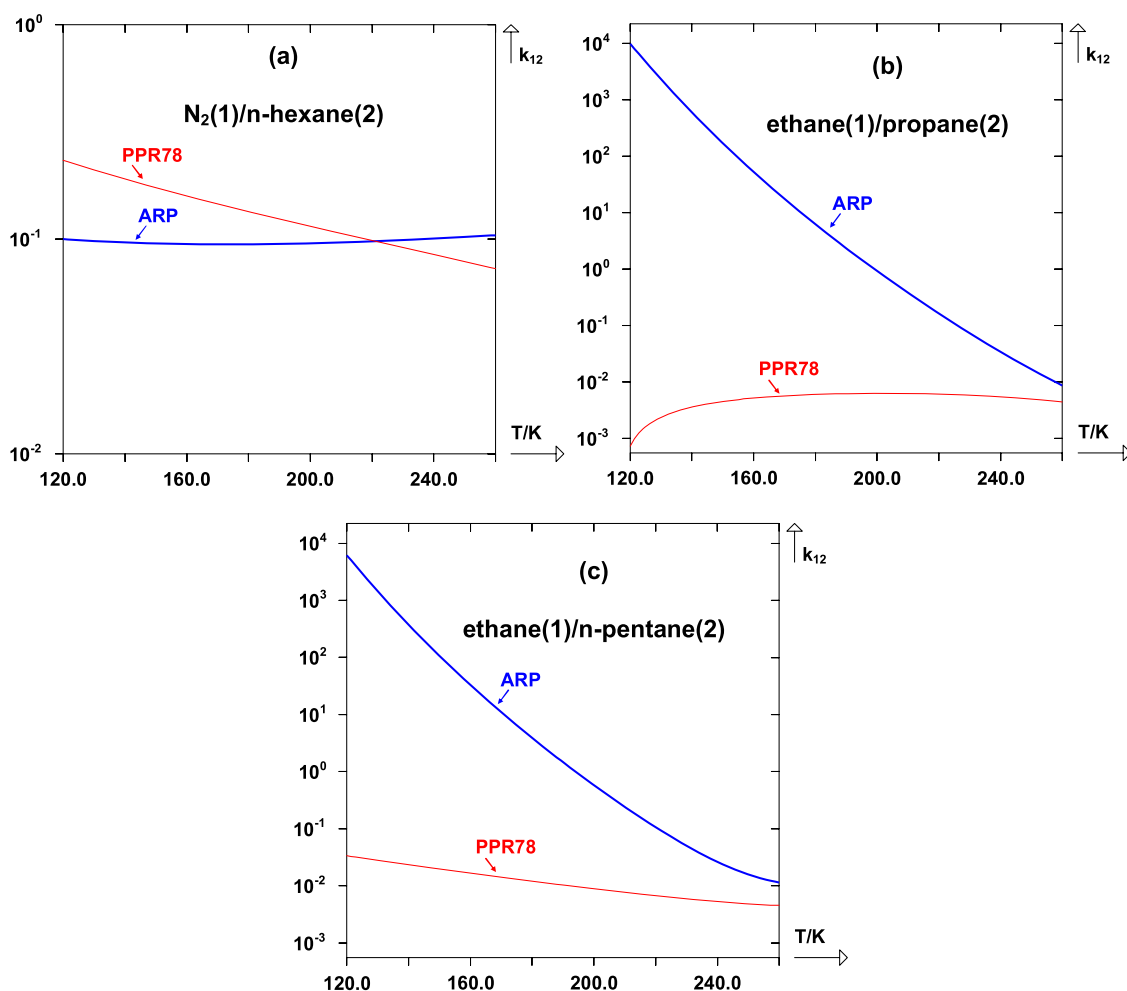
**Table 3**  
Overview of the global performances of the E-PPR78 model [102].

Group name, group number(s)	Mean absolute percent errors on VLE/LLE data	VLE/LLE data number	Mean absolute percent errors on calorific data ( $h^M$ and $c_p^M$ )	Calorific data number
Alkanes, 1 to 6	4.84	16308	46.84	3717
Aromatics, 7 to 9	6.3	11746	47.7	6413
Naphthenes, 10 to 11	4.21	8913	64.1	9438
CO <sub>2</sub> , 12	8.1	15917	45.78	4952
N <sub>2</sub> , 13	8.45	9118	11.6	900
H <sub>2</sub> S, 14	8.99	3917	54.28	39
Mercaptans, 15	10.1	1202	-	0
H <sub>2</sub> O, 16	23.26	8308	81.37	1631
Alkenes, 17 to 20	10.01	15228	40.03	3621
H <sub>2</sub> , 21	9.39	9553	21.4	567
Freons 22 to 27	9.32	3935	-	0
CO, 28	9.21	3225	9.21	44
He, 29	13.17	4742	7.97	1
Ar, 30	11.51	4095	45.67	878
SO <sub>2</sub> , 31	9.41	789	-	0
O <sub>2</sub> , 32	6.35	3072	11.74	56
NO, 33	10.25	298	-	0
COS, 34	10.8	226	-	0
NH <sub>3</sub> , 35	7.68	3347	27.21	252
NO <sub>2</sub> , 36	2.6	77	-	0
N <sub>2</sub> O, 37	7.86	708	104.95	104
Alkynes 38 to 40	8.49	1408	23.38	770
Total	8.97	126132	50.49	33629



**Fig. 8.** Comparison of the performances of the 5 EoSs following the methodology proposed in [104].

combining simplicity, reliability and a small number of parameters, but mixing rules should probably be modified. In particular, advanced MRs relying on a more sophisticated excess function than the Van Laar function can certainly perform better than the CEoS with Van der Waals MRs and  $k_{ij}$ , as highlighted by recent works combining the  $tc$ -PR EoS with EoS/ $g^E$  MRs along with the residual part of the Wilson excess function [46].



**Fig. 7.** Semilog plot of the temperature-dependent binary interaction parameters of three binary systems calculated with the PPR78 and ARP models.

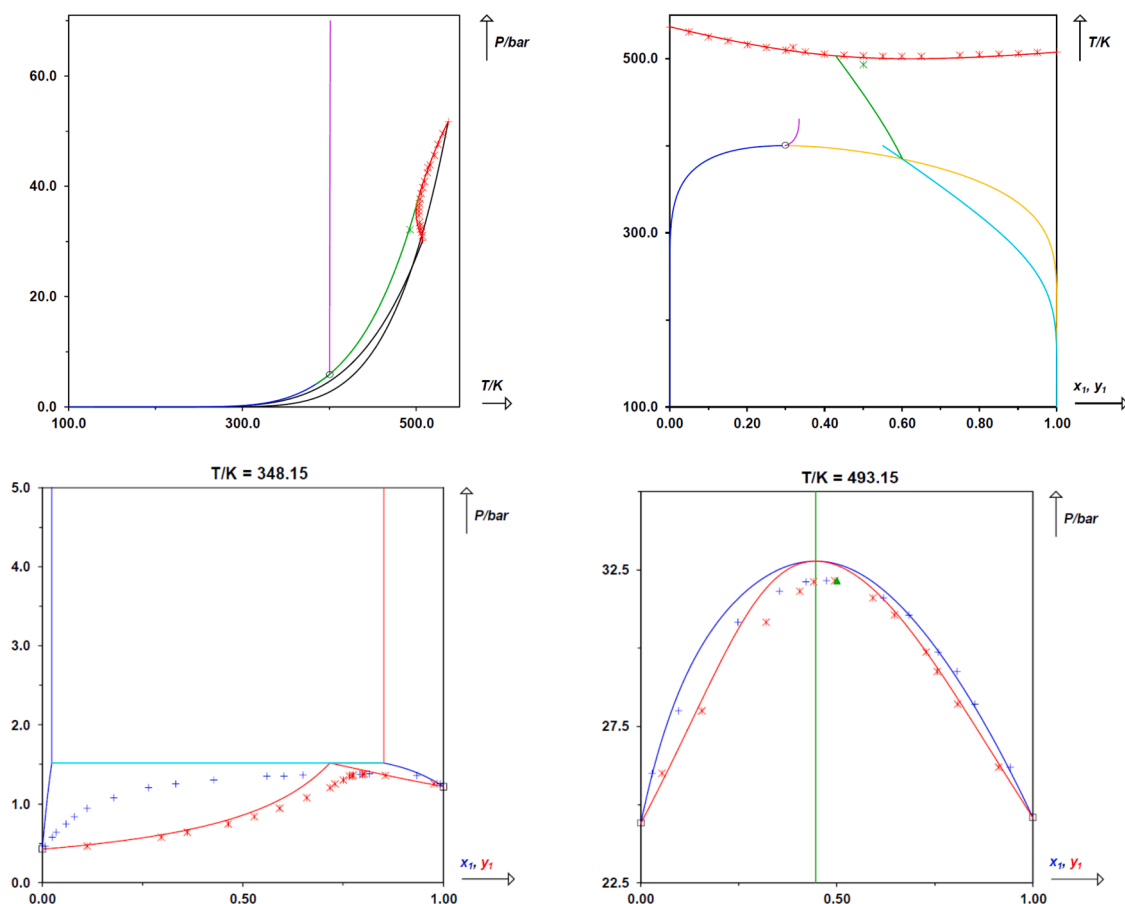


Fig. 9. Phase behaviour of the n-hexane(1) + 1-propanol(2) system modelled using the PR-Van Laar CEoS [104]. Upper panels: GPD represented in the (P,T) and (T, composition) planes. Lower panels: isothermal phase diagrams at two different temperatures. Lines: model predictions. Points: experimental data.

### CRedit authorship contribution statement

**Romain Privat:** Conceptualization, Methodology, Software, Writing – review & editing. **Jean-Noël Jaubert:** Conceptualization, Methodology, Software, Writing – review & editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data Availability

No data was used for the research described in the article.

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