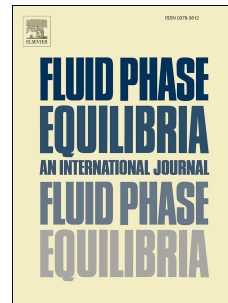


Journal Pre-proof

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Journal Pre-proof

Activity coefficients in nearly athermal mixtures predicted from equations of state: Don't blame the cubic when it is the lack of a third parameter!

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Abstract

The idea that cubic EoS's are very primitive and limited models, quite extended at present among researchers working on fluid properties and phase equilibria, has different roots, including some limitations observed specifically for classic and popular equations like Peng-Robinson (PR) or Soave-Redlich-Kwong (SRK). These are two-parameter models, i.e. they have only an attractive and a repulsive parameter to characterize each molecule, while other models like SAFT but also cubic –and still for non-associating molecules- introduce also a third parameter related somehow to the molecular structure or shape. One of the alluded limitations, actually a very clear one, is the complete failure in describing the non-ideality in nearly athermal mixtures, like those composed of n-alkanes with different chain lengths: SRK and PR predict positive deviations from ideality, which increase with the system asymmetry, while experimental measurements show exactly the opposite, i.e. increasing negative deviations from ideality.

This provides an excellent opportunity to try to clarify whether such failure is due to the cubic nature of these classic models or to their two-parameter character and/or to the classic van der Waals one-fluid (vdW1f) mixing rules typically used. With that motivation, in this work we used models representing three different categories, in a completely predictive way: a two-parameter cubic EoS (PR), a three-parameter cubic EoS (RKPR) and a three-parameter SAFT EoS (PC-SAFT). Their predictions of infinite dilution activity coefficients were analyzed and compared, in contrast to available data for different mixtures of n-butane to n-octane as the lighter compound and paraffins ranging from C16 to C36 as the heavier, in both extremes of dilution.

The obtained results, and their analysis, allowed us to extract very clear conclusions which were not present in the literature so far, regarding the importance of a third parameter in any type of EoS.

Introduction

The idea that cubic equations of state are rough and limited models for describing the properties and phase behaviors of mixtures is quite extended in part of our research community. When we try to ascertain what the rational grounds behind such idea are, we may find two possible situations.

Sometimes it is a specific comparison, having a classical cubic EoS like Soave-Redlich-Kwong (SRK)[1] or Peng-Robinson (PR) [2] on one hand, and a SAFT [3] or some other advanced equation on the other side. This type of comparison, even without association, is unfair, just as much as a race between a car and an airplane. This is so since two-parameter models like SRK or PR are just slightly distorted corresponding states models [4], while SAFT models have not only repulsive and attractive parameters, but also the third parameter which is associated to the molecular structure or shape, completely breaking the corresponding states limitations. This is a basic and objective difference, independently of the quality of attractive and repulsive terms in each case, which can of course explain limitations for describing certain properties, but in order to have a serious and fair comparison focused on the implications or limitations of those terms, any three-parameter equation of state should be compared with other three- and not two-parameter models.

In other cases, it is not a comparison, but a demonstration of a qualitatively incorrect trend or behavior predicted, again, by SRK or PR. This is the case with activity coefficients for n-alkane nearly athermal mixtures, which is clearly exposed for example in the book of Kontogeorgis and Folas [5]. In this work, mixtures are considered ‘athermal’ when they present a heat of mixing or excess enthalpy value equal to zero, according to the typical use in books, like for example those by Elliot & Lira [6] and Kontogeorgis & Folas [5]. For real mixtures with negligible heat of mixing, like those formed by n-alkanes and such as the considered in this work, the expression nearly athermal is usually employed. The reader should be aware, however, that in some works like that of Vahid et al. [7] the term athermal is applied to a more specific class of mixtures, namely those formed by hard-core molecules with no attractive energy, which are sometimes used in molecular simulation as a reference.

A useful way to assess the non-ideality of mixtures is through the “infinite dilution” activity coefficients (γ_i^∞), the limiting value of the activity coefficient when the concentration is close to zero ($\gamma_i^\infty = \lim_{x_i \rightarrow 0} \gamma_i$). Infinite dilution activity coefficients are important and widely used in chemical, biochemical and environmental engineering [8,9]. Typically, for

asymmetric ‘athermal systems’, such as solutions of alkanes, activity coefficients are below unity [10–13]. Solutions of n-alkanes do not present cross energy interaction effects between different molecules, then the nonideality of such mixtures is mainly attributed to size and shape differences of the components.

Sacomani and Brignole [14] analyzed the limitations of classical cubic EoS (particularly the SRK model) to properly predict the activity coefficients of binary n-alkane nearly athermal mixtures. They found that the “non-residual” contribution of the expression for the infinite-dilution activity coefficient, derived from the SRK equation for binary mixtures, provides very good predictions and allows for the reproduction of the observed trends for some linear and branched n-alkane asymmetric homologous series. Nevertheless, the residual or energetic contribution, which would be expected to be negligible but is not, worsens the quality of activity coefficient predictions in mixtures, leading to false positive deviations from ideality.

In Chapter 3 of the book by Kontogeorgis and Folas [5], in an interesting section on advantages and shortcomings of cubic EoS, they show for asymmetric mixtures between n-alkanes, that the Peng-Robinson EoS with classical mixing rules also predicts infinite dilution activity coefficient values above unity (positive deviations from ideality) while measured values indicate the opposite. It is also shown that an a/b mixing rule gives values below unity, in agreement with experimental observation. Kontogeorgis and Folas [5] attribute these EoS limitations to the parameter estimation for pure compounds and especially their extension to mixtures; and they suggest the use of advanced mixing rules (as the Wong and Sandler [8,15] or of Huron and Vidal [16,17]) to overcome this issue.

Vahid et al. [7], although from another perspective and following a different approach, also showed -as Sacomani and Brignole did for cubic EoS's- that the repulsive term from SAFT type models predicted the correct trends of negative deviations from ideal mixing for asymmetric homologous alkane mixtures.

In previous works, we have already shown that a three-parameter cubic EoS can achieve clear improvements over two-parameter models like SRK or PR (Appendix A). See for example the original development of the RKPR model by Cismondi and Mollerup [4], with focus on PVT behavior for pure substances, and the most recent and evolved work on predictive correlations for high-pressure phase behavior of asymmetric hydrocarbon mixtures by Tassin et al. [18], considering also densities and solid-liquid equilibria. Then, we may wonder... Is it really the cubic nature, i.e. the van der Waals repulsion term, the reason behind this

qualitatively incorrect trend for activity coefficients predicted by the SRK or the Peng–Robinson equations? Is it really necessary to turn to more complex mixing rules (i.e., Wong–Sandler or Huron–Vidal models), being impossible for the original van der Waals mixing rules to capture the right trend with a cubic EoS? Would three-parameter cubic equations of state suffer from the same limitations? How would their predictions compare to those from a three-parameter SAFT type equation?

To provide clear answers to these questions is the goal of this work.

It is not our intention to go deeper in the discussion of the theoretical correctness of each term in a model or to evaluate the behaviors at extreme conditions, e.g. infinite pressure limit, where simplified expressions can be used (for that, the reader is referred to some interesting books in the literature [5,9,19,20]). Instead, in order to answer the questions defined above, we simply need to evaluate the behaviors and trends predicted by different types of equations of state at near ambient conditions, where experimental measurements are available for asymmetric mixtures of alkanes. The specific choices we made, and some other details of the methodology are discussed in the next section.

Methodology

As a representative model of two-parameter cubic EoS's we chose the Peng–Robinson equation (PR) in its original version [2], probably the most used cubic EoS. To study whether its limitations can be overcome or not, and how, by a third parameter, we will use the RKPR EoS originally developed by Cismondi and Mollerup [4], and then successfully adopted by other groups for different systems and applications [21–27]. Finally, among the different SAFT versions, we choose the PC-SAFT EoS developed by Gross and Sadowski [28], which is likely to be the most used SAFT model at present.

When applied to specific compounds, a given equation of state can be parameterized according to different strategies, especially for three (or more) parameter models. Although it is beyond the scope of this work to review the different alternatives, it must be pointed out that various strategies and/or sets of parameters have been considered and published in the literature during the last two decades for both PC-SAFT and RKPR. For the first, in this work we will use the parameters by Tihic et al. [29]. Please note that pure compound parameter tables by Tihic et al. [29] can be used with either of both the original PC–SAFT [28] or the simplified PC-SAFT [30], since the latter only introduced changes in the mixing rules of the

original version. In this work, calculations were performed with the original PC-SAFT EoS of Gross and Sadowski [28]. In the case of PR and RKPR, as usual, parameters were obtained from critical constants and acentric factor, using values for critical temperature (T_c), critical pressure (P_c) and acentric factor (ω) from the DIPPR database [31]. Regarding the pure compound parameter δ_1 in the RKPR EoS, our recently proposed correlation for alkanes [18] is used:

$$\delta_1 = 2.70 + 0.4981(1 - e^{-CN/30.437}) \quad (1)$$

where CN is the Carbon Number of the n-alkane.

In relation to mixing rules for the cubic EoS's, note that, although we had previously achieved an excellent description of fluid phase behavior for these systems with the RKPR EoS and quadratic mixing rules for both the attractive and the repulsive parameters [32], some inconsistencies were detected later for the prediction of mixture volumes and solid-liquid equilibria, but corrected based on the use of a linear mixing rule for the co-volume [18]. Therefore, in this work we adopt a quadratic mixing rule only for the attractive parameter (a), (Eqs. 2 – 4) and a linear mixing rule for the co-volume (b) (as it has been the classic and most typically used approach with cubic EoS's), as well as for the third parameter (δ_1) (Eqs. 5 – 6). Moreover, for all alkane binaries studied in this work we adopt zero k_{ij} values for PR and RKPR EoS's.

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (2)$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_{ii} a_{jj}} \quad (3)$$

$$a_{ii} = a_{c,i} \left(\frac{3}{2+T_{r,i}} \right)^{k_i} \quad (4)$$

$$b = \sum_i x_i b_i \quad (5)$$

$$\delta_1 = \sum_i x_i \delta_{1,i} \quad (6)$$

Where x_i and x_j are molar fractions of component i and j respectively; k_{ij} is the attractive binary interaction parameter for the i and j binary system; $T_{r,i}$ is the reduced temperature for component i , k_i is the constant defining the temperature dependence of the attractive parameter for component i .

It is worth noting that the δ_1 parameter has not the same effect than introducing a volume shift parameter (typically called “c”) within a cubic EOS, as it was originally proposed by

Péneloux et al. [33] and then it was extended by other authors [34–36]. A volume shift parameter modifies EoS predicted volumes without affecting the predicted phase equilibria, whereas δ_1 acts as a true third parameter, which modifies both volume and equilibrium EOS predictions. When searching for systems to study, we encountered that important sets of measurements of infinite dilution activity coefficients were published a few decades ago for binary mixtures composed of n-butane, n-pentane, n-hexane, n-heptane and n-octane as the light component, and different heavier alkanes with carbon numbers ranging from 16 to 36 [10,12,13]. Most of those measurements are in the temperature range of interest covering from ambient conditions to 100°C. Therefore, our study will be focused on those five series of binary systems.

Finally, the activity coefficient logarithm value for the i species [$\ln(\gamma_i(T, P, x))$] will be calculated based on the corresponding logarithm of fugacity coefficient in solution [$\ln(\hat{\varphi}_i(T, P, x))$] and the pure compound fugacity logarithm [$\ln(\varphi_i(T, P))$] coefficient at the same system temperature and pressure (T, P):

$$\ln(\gamma_i(T, P, x)) = \ln(\hat{\varphi}_i(T, P, x) - \ln(\varphi_i(T, P))) \quad (7)$$

In most conditions considered, both compounds in pure states, as well as their mixtures, are in liquid state. In the few cases where the pure light compound is in gas state, e.g. n-hexane at 373.15 K, the metastable liquid at such temperature is considered in order to compute the fugacity coefficient in Eq. (7).

Results

In this section we compare experimental infinite dilution activity coefficients for n-alkane asymmetric mixtures with our predictions obtained with the following models: (a) original PC-SAFT with parameters by Tihic et al. [29], (b) PR-EoS and (c) RKPR-EoS, both with the pure compound properties from DIPPR [31]; and in the case of RKPR with the third parameter δ_1 correlated for alkanes by Tassin et al. [18]. PR and RKPR were both used with null interaction parameters ($k_{12}=0$ and $l_{12} = 0$) and classical mixing rules for a and b parameters.

Figures 1 and 3 show the predicted activity coefficients compared to the corresponding experimental data of Parcher et al. [12] and Kniaz [10] for binary mixtures of n-hexane and n-heptane infinitely diluted in heavier alkanes (with carbon numbers ranging from 16 to 36). Whereas, Figs. 2 and 4 illustrate the quality of predictions for heavy paraffins infinitely

diluted in n-hexane and n-heptane respectively, and the corresponding experimental data [10,12].

It is worth to mention that, while all measurements published by Parcher et al. [12] correspond to 373.15 K, for the binary systems containing n-pentane, n-hexane and n-heptane as the light compound, infinite dilution coefficients reported by Kniaz [10] have been measured at different temperatures from 250.8 K to 343.15 K (see Figs. 1 and 3).

Additional figures to those shown in this work, can be found in the Supplementary Material (Figs. S1 – S4). The reader will be able to find the activity coefficient predictions for binary mixtures of n-butane, n-pentane and n-octane infinitely diluted in heavier alkanes, as well as the quality of predictions for heavy paraffins infinitely diluted in n-pentane.

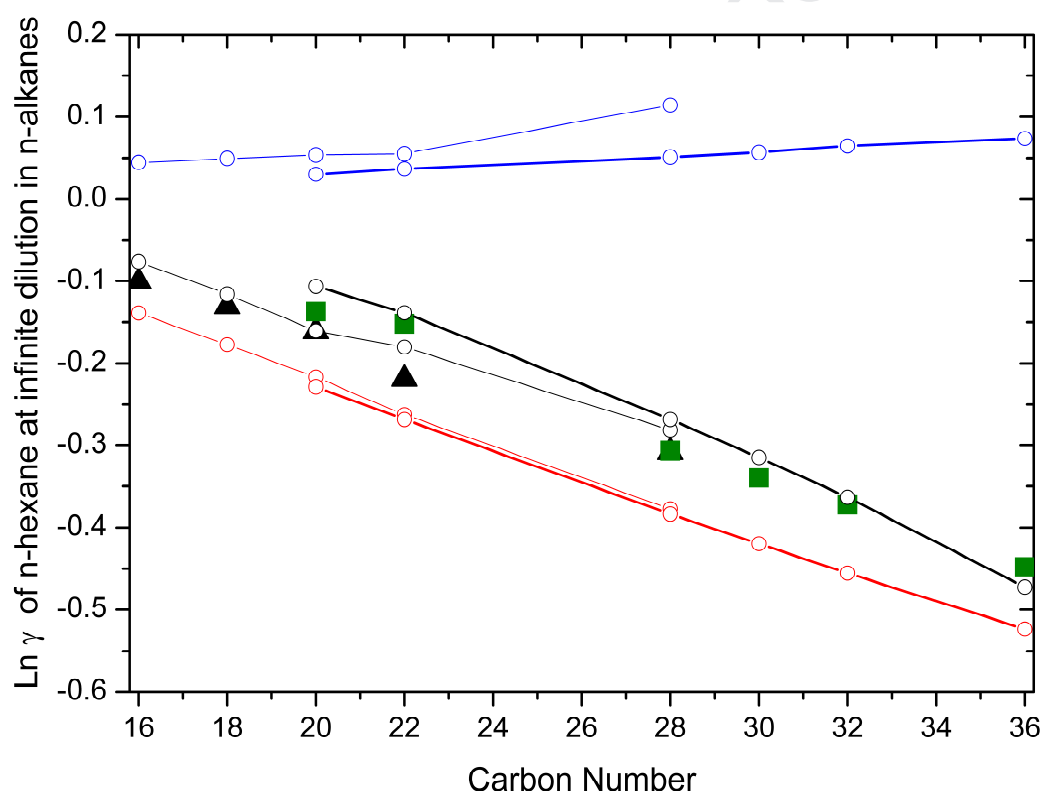


Figure 1. Experimental and predicted logarithms of activity coefficients at infinite dilution of n-hexane in n-alkane solvents as a function of the alkane carbon number. Full black triangles: experimental data at different temperatures from Kniaz [10]; full green squares: experimental data at 373.15 K from Parcher et al.[12]; empty black dots and black lines: predictions with RKPR EoS with δ_1 parameter correlated in [18]; empty red dots and red lines: predictions with PC-SAFT model with parameters according to ref. [29]; empty blue dots and blue lines: predictions with PR EoS. Thick and thin lines of the three models correspond to Parcher et al. [12] and Kniaz data [10] predictions, respectively. Notice that all predictions consider null interaction parameters.

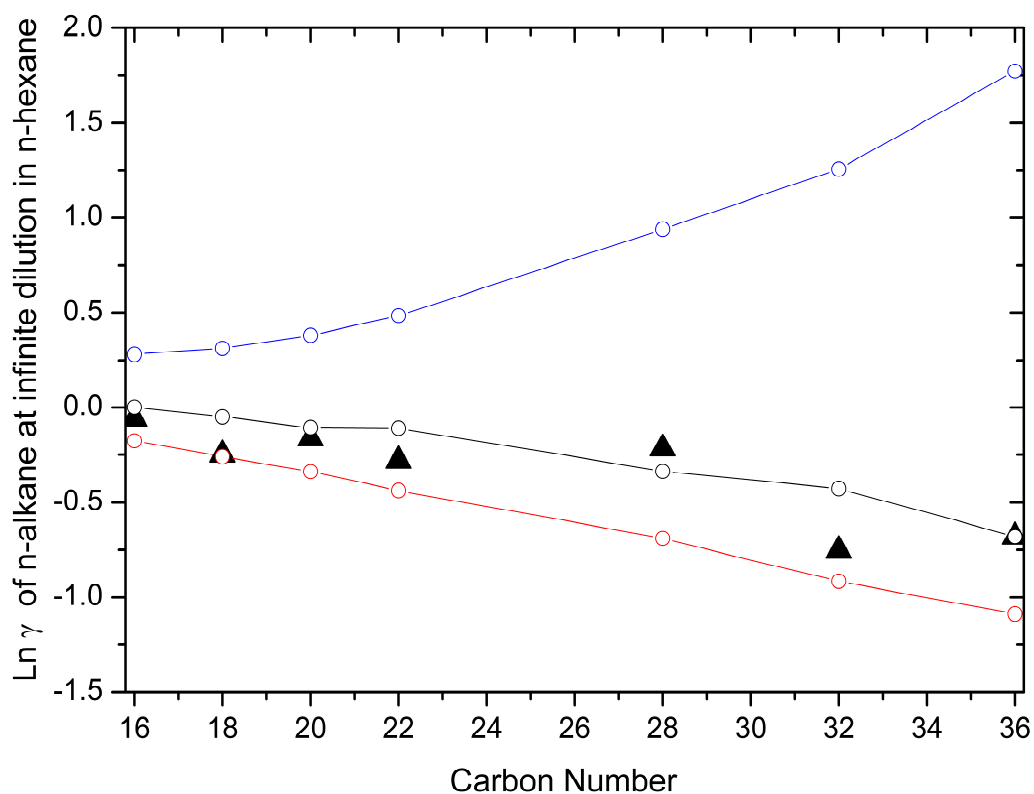


Figure 2. Experimental and predicted logarithms of activity coefficients at infinite dilution for n-alkane in n-hexane binary systems at different temperatures. Full black triangles: experimental data from Kniaz [10]; empty black dots and black lines: predictions with RKPR EoS with δ_1 parameter correlated in [18]; empty red dots and red lines: predictions with PC-SAFT model with parameters according to ref. [29]; empty blue dots and blue lines: predictions with PR EoS. Notice that all predictions consider null interaction parameters.

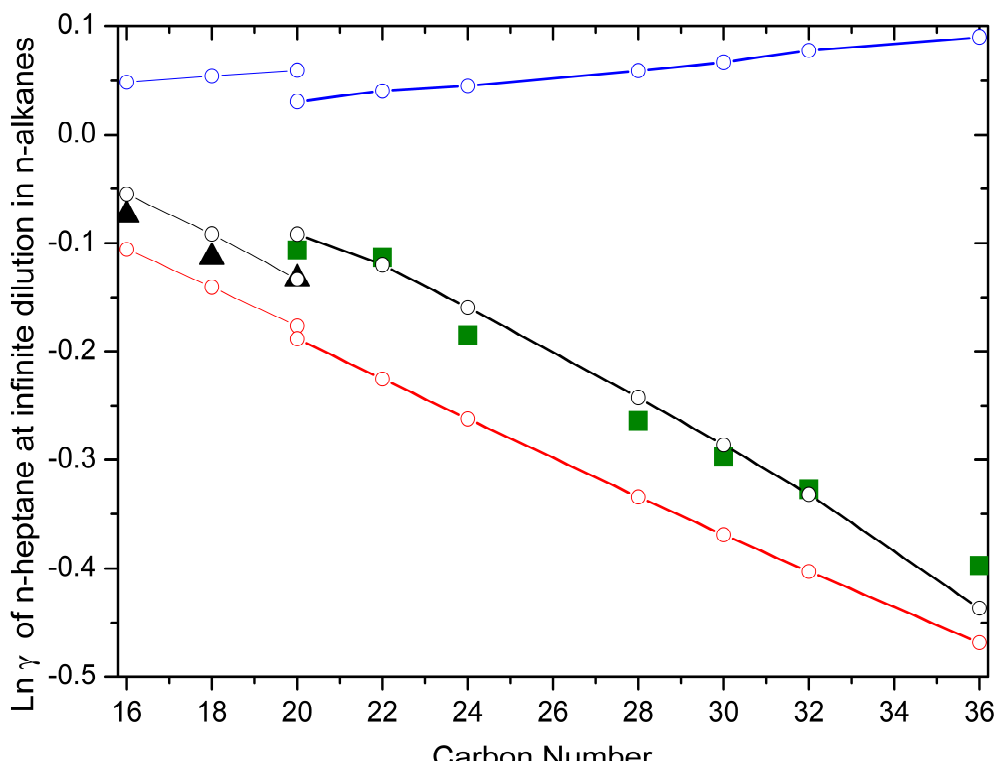


Figure 3. Experimental and predicted logarithms of activity coefficients at infinite dilution of n-heptane in n-alkane solvents as a function of the alkane carbon number. Full black triangles: experimental data at different temperatures from Kniaz [10]; full green squares: experimental data at 373.15 K from Parcher et al.[12]; empty black dots and black lines: predictions with RKPR EoS with δ_1 parameter correlated in [18]; empty red dots and red lines: predictions with PC-SAFT model with parameters according to ref. [29]; empty blue dots and blue lines: predictions with PR EoS. Thick and thin lines of the three models correspond to Parcher et al. [12] and Kniaz data [10] predictions, respectively. Notice that all predictions consider null interaction parameters.

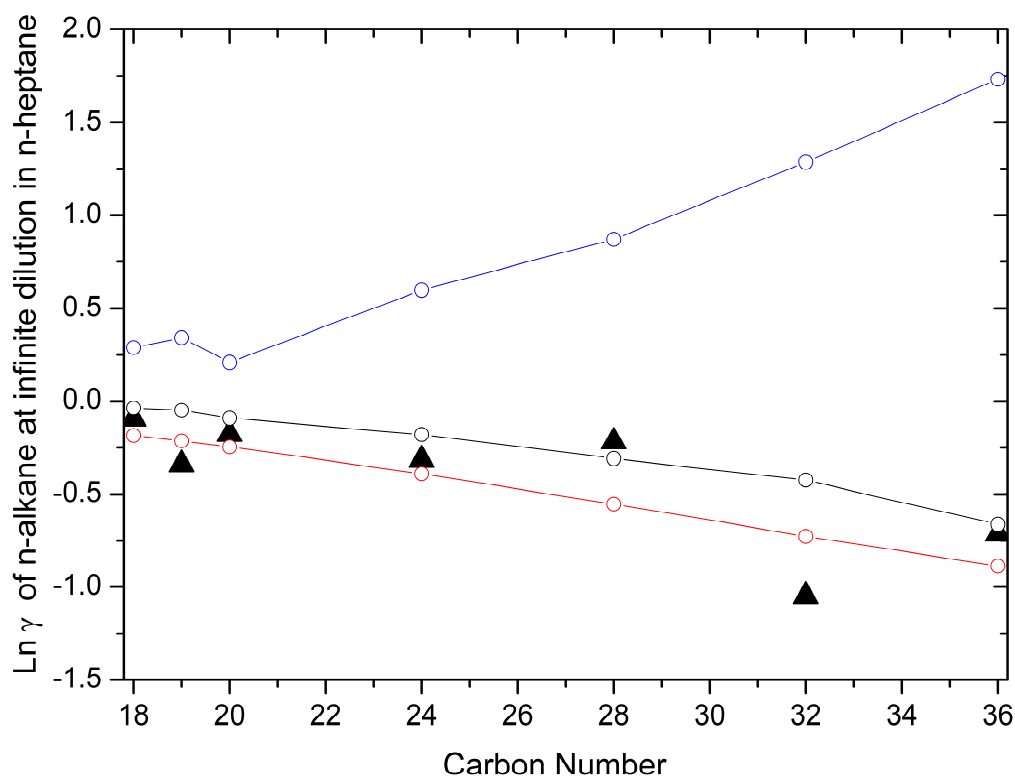


Figure 4. Experimental and predicted logarithms of activity coefficients at infinite dilution for n-alkane in n-heptane binary systems at different temperatures. Full black triangles: experimental data from Kniaz [10]; empty black dots and black lines: predictions with RKPR EoS with δ_1 parameter correlated in [18]; empty red dots and red lines: predictions with PC-SAFT model with parameters according to ref. [29]; empty blue dots and blue lines: predictions with PR EoS. Notice that all predictions consider null interaction parameters.

Table 1. Percentage average absolute deviations in γ^∞ for binary mixtures of light n-alkanes at infinite dilution in heavier n-alkanes (Cx indicates an n-alkane with x carbon atoms).

Binary system	% AAD in γ^∞	% AAD in γ^∞	% AAD in γ^∞	Experimental data from
	for PR-EoS	for PC-SAFT EoS	for RKPR-EoS	
C4 infinite diluted in n-alkanes	109.7	12.8	13.9	[12]
C5 infinite diluted in n-alkanes	40.9	8.6	4.1	[12]
C6 infinite diluted in n-alkanes	36.1	6.8	2.3	[12]
C7 infinite diluted in n-alkanes	30.4	6.4	1.6	[12]
C8 infinite diluted in n-alkanes	32.0	7.0	1.8	[12]

Table 2. Percentage average absolute deviations in γ^∞ for binary mixtures of heavy n-alkanes at infinite dilution in n-pentane-n-hexane and n-heptane (Cx indicates an n-alkane with x carbon atoms).

Binary system	% AAD in γ^∞ for PR-EoS	% AAD in γ^∞ for PC-SAFT- EoS	% AAD in γ^∞ for RKPR- EoS	Experimental data from
n-alkanes at infinite dilution in C5	746.5	33.8	34.1	[10]
n-alkanes at infinite dilution in C6	318.4	18.4	14.6	[10]
n-alkanes at infinite dilution in C7	360.6	16.9	23.4	[10]

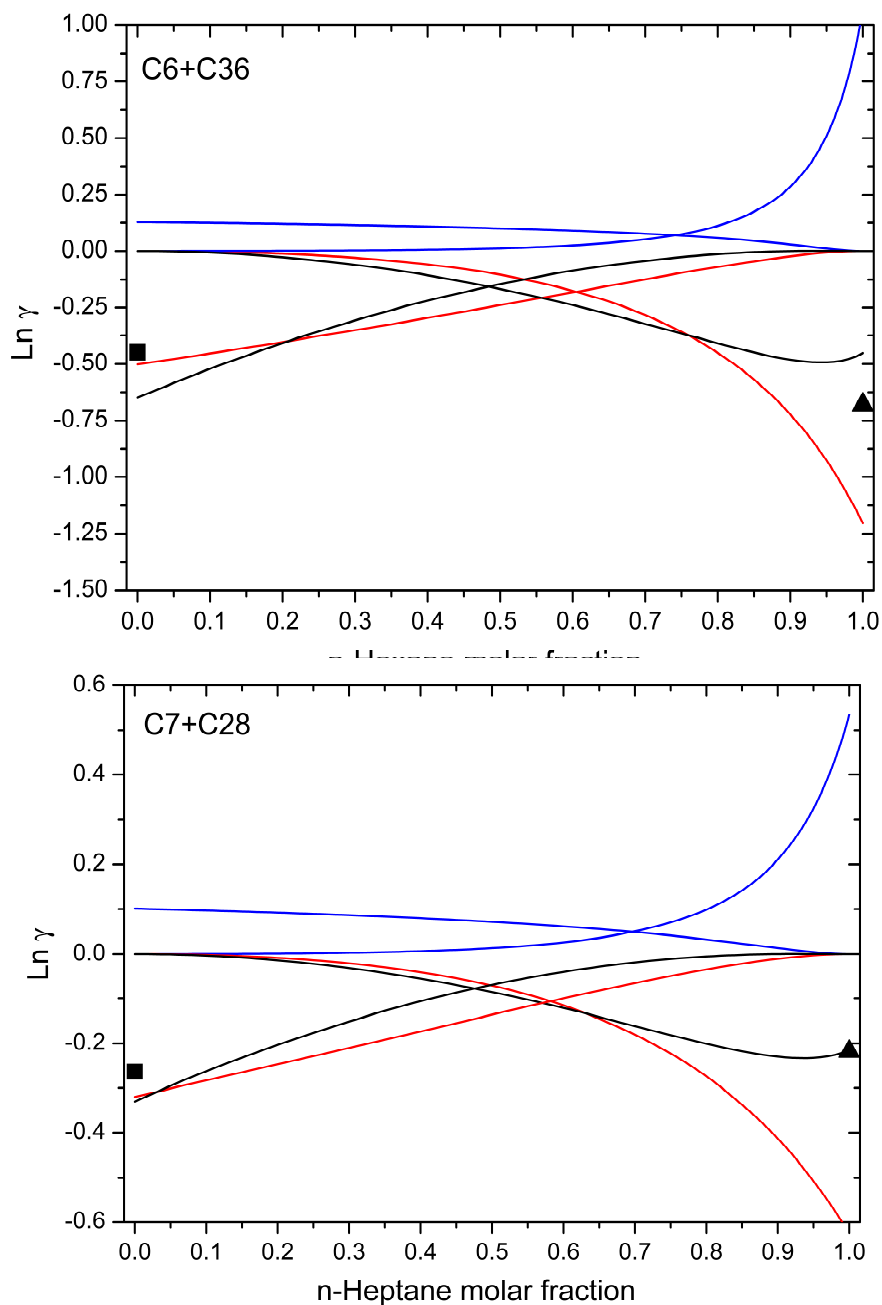
As Figs. 1 to 4 show, PR EoS yields positive deviations from Raoult's law for all the studied systems and conditions, whereas experimental data show negative deviations from Raoult's law (i.e. activity coefficient values below unity, or negative values for $\ln(\gamma^\infty)$), in a magnitude that increases with the system asymmetry (i.e., $\ln(\gamma^\infty)$ values become progressively more negative, see Figs. 1-4 and Figs. S1-S4 in Supplementary Material). Moreover, γ^∞ values predicted with PR-EoS have the highest deviations, as become evident from calculated percentage average deviations shown in Tables 1 and 2. This effect is more noticeable for the cases of heavy n-alkanes infinite diluted in C5, C6 or C7, where the % AAD are over 300% for all studied systems (see Table 2).

PC-SAFT and RKPR models yield negative deviations from Raoult's law for all cases, with the exception that RKPR predicts just a slightly positive deviation for C16 infinite diluted in C6 at 250.8 K, or ideal behavior in practical terms (see Fig. 2). In all cases (Figs. 1-4 and Figs. S1-S4 in Supplementary Material) PC-SAFT predictions go below those corresponding to RKPR and, based on the comparison with the experimental data, it seems that PC-SAFT tends to slightly exaggerate the negative deviations from ideality, while RKPR is in general closer to the observed behavior in these mixtures. This is confirmed by numbers in Tables 1 and 2, with two soft and one clear exception. The first soft exception corresponds to n-Butane infinitely diluted in paraffins (see Fig. S1 in Supplementary Material and Table 1). In this case deviations are similar but with opposite sign for PC-SAFT and RKPR, with data points falling always between both models. For reasons of scale affecting differently the points closer to one or the other model, average deviation in $\ln(\gamma^\infty)$ is slightly lower for RKPR while the AAD in γ^∞ -which is the one computed in Table 1- is slightly lower for PC-SAFT. Then, regarding the two other exceptions which involve systems with heavy n-alkanes

infinite diluted in C5 and C7 (see Table 2), we need to call the reader's attention about the following. When having a closer look at the data sets reported by Kniaz [10], one realizes that the activity coefficients measured for C32 are in all cases unexpectedly low (Figs. 2, 4 and S3 in Supplementary Material). This leads us to think that the n-Dotriacontane used in those experiments might have been contaminated with heavier compounds or there could have been another reason for these systematic deviations from the trend observed based on the other measurements reported by the same author. If we treat those points for C32 as outliers and recalculate the %AAD based on the other points, then the number is lower for RKPR in all cases.

From Table 1, and based on data from Pacher et al. [12], we see that for C5, C6, C7 or C8 infinite diluted in heavier n-alkanes, % AAD for RKPR is around 5 % lower than for PC-SAFT.

In order to illustrate the implications on the complete behavior of mixtures and given that most readers might be familiar with this type of plot as they appear in different books, Figs. 5a – 5b show complete predictions of activity coefficients for both compounds in a binary system. Two of the systems considered in this study and with available data points at both extremes are included, namely C6+C36 and C7+C28. Despite the fact that in the two systems the temperature corresponding to both experimental points differ in around 100 degrees (see Fig. 5 caption for experimental data details), we still included them given the soft effect of temperature on these activity coefficients, and for illustrative purposes, and we perform our calculations at an intermediate temperature of 325 K.



Figures 5a-5b. Complete curves of predicted activity coefficients at 325 K and 1 bar (in logarithmic scale) for the binary systems C6+C36 and C7+C28. Full black square: experimental data from Parcher et al.[12] (at 1 bar and 373.15 K); full black triangle: experimental data from Kniaz [10] (at 1 bar and 280.1 K for C6+C36; and 279.4 K for C7+C28); black lines: predictions with RKPR EoS with δ_1 parameter correlated in [18]; red lines: predictions with PC-SAFT model with parameters according to ref. [29]; blue lines: predictions with PR EoS.

Notice that all predictions consider null interaction parameters.

Summarizing, both PC-SAFT and RKPR are able to predict the proper behaviors for experimentally observed infinite dilution activity coefficients in the studied (nearly) athermal mixtures, and also their trends along asymmetric homologous series, whereas PR-EoS clearly fails. RKPR was used in this work with classic vdW1f mixing rules, and it performs comparably or better than PC-SAFT model to predict γ^∞ . In other words, it seems there was nothing wrong the classic vdW1f mixing rules, when a third parameter takes into account the evolution of shape in a family of compounds like n-alkanes, similarly to what the m parameter does in SAFT models, since RKPR and PC-SAFT models have demonstrated to be able to properly predict γ^∞ behavior in the studied systems. Note, although, that the third parameter is only present in the attractive term of the RKPR EoS, while for SAFT models it also appears in the repulsive term. Nevertheless, despite this specific difference, we know from the works of Sacomani and Brignole [14] and Vahid et al. [7] that both repulsive terms, either the van der Waals or the SAFT one based on hard chains of spheres, correctly predict the trends of negative deviations from ideal mixing for asymmetric mixtures of n-alkanes. Then, the picture changes when an equation of state is completed for real fluids: It was already known that the coupling with the attractive term in cubic EoS's like SRK or PR worsens the quality of activity coefficient predictions in mixtures, leading to false positive deviations from ideality [14]. Now, from the results presented in this work, we see that is not the case with PC-SAFT, which provides good predictions and a correct trend when the full equation is applied to real mixtures in near room conditions of temperature and pressure. Moreover, our results have also clearly shown the same with a cubic EoS, the RKPR, for which the essential difference with SRK or PR is having a third parameter that interpolates between their structures or density dependences and also go beyond. Therefore, we see that the same parameter that broke the limitation of a unique universal Z_c value for pure compounds (see **Appendix A**), corrects for the deviations from ideality when applied to mixtures.

Here, a question may naturally arise: How is it that this third parameter in a cubic EoS corrects these behaviors? In what follows, we provide some detailed insight and elements for an answer. For cubic EoS's, the logarithms of fugacity coefficients in Eq. (7) can be decomposed into different terms, as it is explained in detail in **Appendix B**, leading to the following decomposition for the logarithm of the activity coefficient:

$$\ln(\gamma_i) = F_i^{rep} + F_i^{att2P} + F_i^{att3P} + F_{Z_i} \quad (8)$$

The decomposition is done in such way that each term is functionally valid either for a 2P-EoS (SRK, PR) or a 3P-EoS (RKPR), the only formal difference being that a constant δ_1 parameter makes the F_i^{att3P} term vanish in a 2P-EoS.

Fig. 6 shows how the curves in Fig. 5a, for n-C6 + n-C36, are decomposed into these terms. The curves in Fig. 6, considering both components, reveal a higher complexity than one may expect in advance, but there are some important observations to make:

- In accordance with Sacomani and Brignole [14], we see that the non-residual contribution for the activity coefficient of the lighter compound would show the right behavior or type of deviation, but it is worsen and even inverted by the attractive term. Nevertheless, the picture is very different for the heavy compound.
- It is interesting to note that the attractive contributions of the RKPR EoS have low or moderate values, and may even neutralize each other, while the F_i^{att2P} term in the PR EoS diverges to important magnitudes, either positive or negative, for both components.
- Moreover, for n-C6 with the RKPR EoS, the 2-P attractive term is nearly zero in the whole range of composition, and it is very clear how the third-parameter term is the one that drives the logarithm of gamma to its position. The contributions are different for n-C36, but the result is also the right one.
- Overall, and considering the very different curves that both models show for the same term -in particular the repulsive one-, it becomes clear that what makes the difference is not only the presence of the extra term related to the third parameter compositional dependence, but also the different parameterization induced by different δ_1 values, in particular for the co-volume of the heavy compound (83.1 and 78.9 cc/mol in this case).

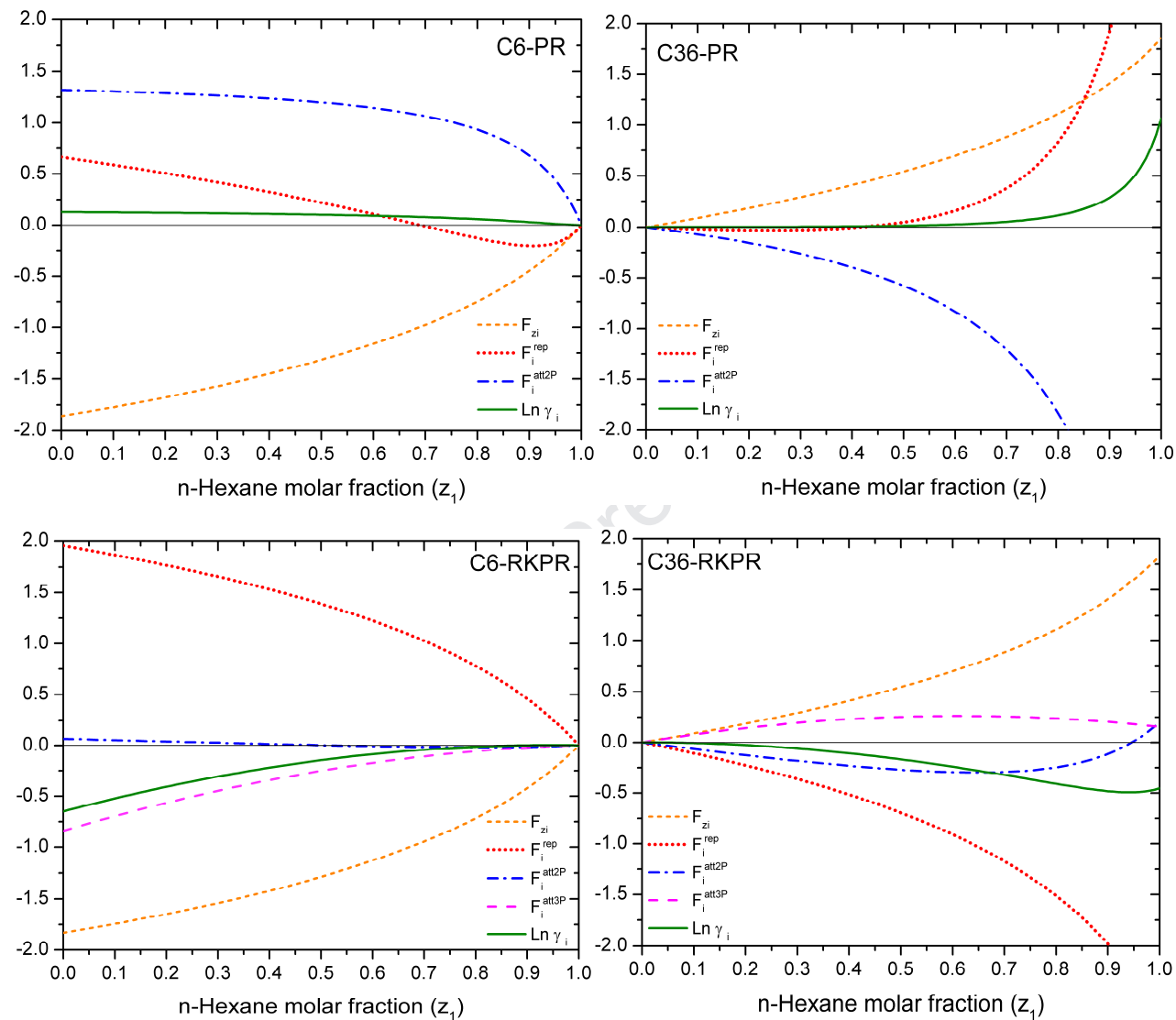


Figure 6. Complete curves of predicted logarithm of activity coefficient, and its terms (as defined in Eq. 8 and Appendix B) at 325 K and 1 bar for the binary system C6+C36. Predictions with PR EoS are found in the two images at the top, while the corresponding predictions with RKPR EoS are at the bottom. Notice that all predictions consider null interaction parameters.

Conclusions

In this work we have used three different EoS models in a completely predictive way, evaluating their performance to model asymmetric mixtures of n-alkanes based on activity coefficients, especially through infinite dilution values, for which an important collection of data is available in the literature. The three models included two cubic EoS, representative of the two-parameter (PR) and three-parameter (RKPR) categories, and the PC-SAFT EoS which, as every SAFT model in its non-associating version, has (at least) three parameters. Confirming trends already observed in the literature, and contrary to what experimental measurements show, PR predicted positive deviations from ideality in all cases. In turn, both PC-SAFT and RKPR predicted the right qualitative trends of negative deviations from ideality, with a magnitude that increases with molecular size asymmetry, and varying degrees of quantitative agreement with experimental data.

First of all, and coming back to our original questions inspired on observations by Kontogeorgis and Folas, we can now conclude that the simple and classic van der Waals mixing rules can perfectly capture the right trends of activity coefficients in asymmetric nearly athermal mixtures with a cubic EoS. Therefore, it is not necessary to turn to more complex mixing rules. The only requisite is that the model has the flexibility to consider different shapes of molecules, and their mixtures, and this is provided by a proper third parameter. Based on a detailed decomposition in different sub-terms for the system n-C6 + n-C36, and comparing these curves for the PR and RKPR EoS's, we could see how the fixing of the analyzed two-parameter pitfall is explained partially by the third-parameter composition dependence itself and partially by how the other pure-compound parameters are affected by a different δ_1 value in the RKPR.

Moreover, we have shown that when the comparison between a cubic and a SAFT model is a fair one, i.e. using a three-parameter EoS in both cases, performances are similarly good in describing the behavior of asymmetric mixtures, and it can be even better with the cubic EoS, as it has been observed in this work.

Third parameters have been present in SAFT EoS models since their origin, but this does not apply to the historical development of cubic EoS's. We hope that this contribution helps in convincing our colleagues in the research community that a third parameter is as necessary in cubic EoS's as it is in SAFT ones.

Journal Pre-proof

Appendix A. Equations of state with two and three parameters: PR, RKPR and PC-SAFT

Although the use of two and three-parameter cubic equations of state to describe the phase behavior of asymmetric mixtures has been previously discussed [32,37], the purpose of this appendix is to provide a summary of these types of equations and their main differences. In particular, we focus on those EoS used in this work: Peng-Robinson equation of state [2] (PR EoS) with two parameters, Generalized Redlich Kwong-Peng Robinson equation of state [4] (RKPR EoS) with three parameters and PC-SAFT, also of three-parameter type, but non-cubic. Mollerup & Michelsen [20] proposed the following general expression, shown in Eq. A1, in which all of the well-known cubic EoS are contained for particular pairs of values (δ_1 , δ_2):

$$P = \frac{RT}{v-b} - \frac{a(T)}{(v+\delta_1b)(v+\delta_2b)} \quad (\text{A1})$$

When δ_1 and δ_2 constants are $(1 + \sqrt{2}, 1 - \sqrt{2})$ respectively the PR equation is obtained [2], whereas $(0, 0)$ leads to the van der Waals EoS (vdW) [38] and $(1,0)$ to the Redlich Kwong EoS (RK) [39]. In Eq. A1, b and a are, respectively, the size (co-volume) and cohesive energy parameters; and the two parameters considered for PR, RK or vdW EoS, for example.

Furthermore, if we add the following restriction:

$$-\delta_1\delta_2 = \delta_1 + \delta_2 - 1 = c \quad (\text{A2})$$

and transform the constant δ_1 into a compound specific parameter, then we have a three-parameter equation of state which connects the RK ($c=0$) and PR ($c=1$) density dependences through the following expressions for the compressibility factor (Eqs. A3, A4 and A5):

$$Z_{RKPR} = \frac{1}{1-4\eta} - \frac{4\eta\tau}{(1+4\delta_1\eta)\left(1+4\frac{1-\delta_1}{1+\delta_1}\eta\right)} \quad (\text{A3})$$

$$\tau = \frac{a}{RTb} \quad (\text{A4})$$

$$\eta = \frac{b}{4v} \quad (\text{A5})$$

As it has been widely studied and discussed previously [4,22,32], the intrinsic limitations of two-parameter cubic equations of state to reproduce volumetric and derived properties in some cases, rather than from their empirical character, come from the fact that every two-

parameter equation of state for which the compressibility factor can be expressed in terms of two dimensionless variables that are direct or inversely proportional to the molar volume and/or the temperature, is a corresponding states model. This was demonstrated by Mollerup [20] and its details can be consulted in appendix A of the original work of the RKPR EoS [4]. Thus, Z_c results a characteristic constant for each particular two-parameter EoS, e.g. 3/8 for the vdW EoS [38], 0.307 for the PR EoS [2], or 1/3 for the RK EoS [39].

In order to overcome the limitations of a two-parameter cubic equation of state, a third compound-specific parameter in the density dependence of the equation of state is necessary to model different types of fluids and their asymmetric mixtures. In the case of RKPR EoS, this third parameter is δ_1 , a structural parameter, which increases with non-sphericity (and also with polarity, but polarity is not present in alkanes). This parameter comes from Eq. 11 in the “Pure compound parameters” section of our previous work [18], also reproduced as Eq. (1) in this work.

The expressions for the residual Helmholtz energy (A^{res}) and pressure in the RKPR EoS are the following (Eqs. A6, A7 and A8):

$$\frac{A^{res}}{RT} = -\ln\left(1 - \frac{b}{v}\right) - \frac{a}{RTb\left(\delta_1 - \frac{1-\delta_1}{1+\delta_1}\right)} \ln\left(\frac{v+\delta_1 b}{v + \frac{1-\delta_1}{1+\delta_1}b}\right) \quad (\text{A6})$$

$$a = a_c \left(\frac{3}{2+T_r}\right)^k \quad (\text{A7})$$

$$P = \frac{RT}{v-b} - \frac{a_c \left(\frac{3}{2+T_r}\right)^k}{(v+\delta_1 b)\left(v + \frac{1-\delta_1}{1+\delta_1}b\right)} \quad (\text{A8})$$

The covolume and the critical value of the attractive parameter for a pure substance are calculable from the following expressions:

$$b = \Omega_b \frac{RT_c}{P_c} \quad (\text{A9})$$

$$a_c = \Omega_a \frac{(RT_c)^2}{P_c} \quad (\text{A10})$$

Note that for simplicity, and in the context of pure compounds, only in this Appendix the “i” subscript is omitted for the different parameters and pure compound properties.

Ω_a and Ω_b are functions of the third parameter δ_1

$$\Omega_a = \frac{3y^2 + 3yd_1 + d_1^2 + d_1 - 1}{(3y + d_1 - 1)^2} \quad (\text{A11})$$

$$\Omega_b = \frac{1}{3y + d_1 - 1} \quad (\text{A12})$$

Where y and d_1 are intermediate variables defined as:

$$y = 1 + [2(1 + \delta_1)]^{1/3} + \left(\frac{4}{1 + \delta_1}\right)^{1/3} \quad (\text{A13})$$

$$d_1 = \frac{1 + \delta_1^2}{1 + \delta_1} \quad (\text{A14})$$

Further details of the deduction of these expressions can be found in the original reference of the RKPR EoS [4].

It is well-known that a temperature dependence for the attractive parameter a is required to achieve a reasonable quantitative agreement with experimental data, especially vapor pressures. Although with different coefficients, both the SRK [1] and PR [2] equations use:

$$\alpha = \frac{a(T)}{a_c} = \left(1 + m(1 - \sqrt{T_r})\right)^2 \quad (\text{A15})$$

known as Soave's classic α function, which works quite well for subcritical temperatures but is known to lead to inconsistencies in the supercritical region. Instead, the RKPR EoS employs another α function:

$$\alpha = \frac{a}{a_c} = \left(\frac{3}{2 + T_r}\right)^k \quad (\text{A16})$$

Adopting the two classical restrictions (T_c and P_c) for the determination of the three parameters at the critical point and having also adopted a standard procedure to determine the temperature dependence of a (adjusting k such that the vapor pressure implied by the acentric factor is reproduced), the RKPR EoS provides one extra degree of freedom (δ_1) in comparison to classic two-parameter cubic EOS (a and b) like SRK or PR. Different approaches were followed in previous articles: In the original RKPR development, Cismondi and Mollerup [4] proposed the relation $Z_c = 1.168 Z_c^{\text{exp}}$ as the default setting for non-associating fluids, which was later followed by other authors [22,23,27]. Remember that Z_c for RKPR-EoS is related to δ_1 through Eq. A3. In other works, Cismondi et al. decided to impose the reproduction of the liquid density at a specified temperature, either at the triple point [22] or at $\text{Tr} = 0.70$ [25].

In recent works [18,32,37] it was found that predictions of phase equilibria for asymmetric mixtures were quite sensitive to the values of δ_1 , and therefore it was proposed that this third parameter of the RKPR model could be defined based not only on properties of pure compounds, but also on the basis of properties of binary systems, particularly of the most difficult series to model among hydrocarbon mixtures: the asymmetric series of methane + n-alkanes. In summary, the approach adopted here was that the parameters of pure compounds come from reproducing Tc , Pc and ω , and imposing a value of δ_1 .

As PC-SAFT EoS [28] was also applied in the present work, it is also worth noting that, as in any three parameter EoS, its compressibility factor (Z_c) varies with its third parameter value. This has been detailed in [40], and we make here just a general and brief explanation. The compressibility factor of a three or a two parameter EoS can be expressed as follows:

$$Z = \frac{P(a,b,c,v,T)v}{RT} \quad (\text{A17})$$

In the general context of Eq. A17, b and a are, respectively, any pair of size and cohesive energy parameters in an EoS, particularly σ and ε/k in the PC-SAFT EoS. Accordingly, c denotes the dimensionless third parameter, which in PC-SAFT equals m . Moreover, the pure component critical conditions can be expressed as:

$$\left(\frac{v^2}{RT} \frac{\partial P(a,b,c,v,T)}{\partial v} \right)_c = 0 \quad (\text{A18})$$

$$\left(\frac{v^3}{RT} \frac{\partial^2 P(a,b,c,v,T)}{\partial^2 v} \right)_c = 0 \quad (\text{A19})$$

In the case of any two-parameter EoS, considering that c is a universal constant, there is a unique solution to Eqs A18 and A19, and Z_c is characteristic constant for such cases, as it was previously explained in this appendix. Otherwise, from Eq. A17, there is a different value of Z_c corresponding to each value of the third parameter of PC-SAFT (as well as for any three parameter EoS like RKPR EoS).

Appendix B. Decomposition of the $\ln(\gamma_i)$ expression in different contribution terms

In order to get a deeper understanding of the effect of the third parameter in a cubic EoS and how it corrects the behavior predicted for γ_i and γ_i^∞ , we propose here to decompose the logarithm of the fugacity coefficient in Eq. (7), and analyze its terms. For cubic EoS's, we first consider the general formulation for the $\ln(\hat{\varphi}_i)$, following the approach proposed by Michelsen and Mollerup [20] as shown in Eq. B1:

$$\ln(\hat{\varphi}_i) = -g + \frac{nb_i}{V-B} - \frac{D}{RT} \left(\frac{\partial f}{\partial B} \right)_{n,V,\delta_1} b_i - \frac{f}{RT} \left(\frac{\partial D}{\partial n_i} \right)_{T,n_j} - \frac{D}{RT} \left(\frac{\partial f}{\partial \delta_1} \right)_{n,V,B} \left(\frac{\partial \delta_1}{\partial n_i} \right)_{n_j} - \ln(Z) \quad (\text{B1})$$

It is worth noting that in Eq. B1, the term containing the δ_1 parameter derivative disappears in a 2P-EoS (SRK, PR). In Eq. B1 the variables n, g, D, f, B and δ_1 are defined as:

$$n = \sum_i n_i \quad (\text{B2})$$

$$g = \ln \left(1 - \frac{B}{V} \right) \quad (\text{B3})$$

$$D = \sum_i n_i \sum_j n_j a_{ij}(T) \quad (\text{B4})$$

$$f = \frac{1}{B \left(\delta_1 - \frac{1-\delta_1}{1+\delta_1} \right)} \ln \left(\frac{V+\delta_1 B}{V + \frac{1-\delta_1}{1+\delta_1} B} \right) \quad (\text{B5})$$

$$B = \sum_i n_i b_i \quad (\text{B6})$$

$$\delta_1 = \frac{\sum_i n_i \delta_{1i}}{n} \quad (\text{B7})$$

Equation B7 defines the mixture δ_1 parameter for RKPR EoS. Still, if applied to the PR EoS, one gets the same value as for every pure compound, i.e. $1 + \sqrt{2}$ (see appendix A).

In Eq. B1, the derivatives $\left(\frac{\partial D}{\partial n_i} \right)_{T,n_j}$, $\left(\frac{\partial f}{\partial B} \right)_{n,V,\delta_1}$, $\left(\frac{\partial f}{\partial \delta_1} \right)_{n,V,B}$ and $\left(\frac{\partial \delta_1}{\partial n_i} \right)_{n_j}$ are calculable as:

$$\left(\frac{\partial D}{\partial n_i}\right)_{T,n_j} = 2 \sum_j n_j a_{ij}(T) \quad (\text{B8})$$

$$\left(\frac{\partial f}{\partial B}\right)_{n,V,\delta_1} = - \frac{\left(f + V \left(\frac{-1}{(V+\delta_1 B)(V+\frac{1-\delta_1 B}{1+\delta_1})}\right)\right)}{B} \quad (\text{B9})$$

$$\left(\frac{\partial f}{\partial \delta_1}\right)_{n,V,B} = \frac{1}{\delta_1 - \frac{1-\delta_1}{1+\delta_1}} \left(\frac{1}{V+\delta_1 B} + \frac{2}{(V+\frac{1-\delta_1 B}{1+\delta_1})(1+\delta_1)^2} - f \left(1 + \frac{2}{(1+\delta_1)^2}\right) \right) \quad (\text{B10})$$

$$\left(\frac{\partial \delta_1}{\partial n_i}\right)_{n_j} = \frac{\delta_{1i} - \delta_1}{n} \quad (\text{B11})$$

Now, considering Eq. 7 of this paper, we can obtain $\ln(\gamma_i)$ by subtracting the logarithm of the pure compound “*i*” fugacity coefficient ($\ln(\varphi_i)$) to the logarithm of the fugacity coefficient of compound “*i*” in solution, given by Eq. B1. Furthermore, such equation can be decomposed into different terms that are functionally valid either for a 2P-EoS (SRK, PR) or a 3P-EoS (RKPR), as stated in Eq. (8), and which we have rewritten here:

$$\ln(\gamma_i) = F_i^{rep} + F_i^{att2P} + F_i^{att3P} + F_{Z_i} \quad (\text{B12})$$

Its detailed terms are:

$$F_i^{rep} = -g + \frac{nb_i}{V-B} - \left[-\ln\left(1 - \frac{n_i^0 b_i}{V_i^0}\right) + \frac{n_i^0 b_i}{V_i^0 - n_i^0 b_i} \right] \quad (\text{B13})$$

$$F_i^{att2P} = -\frac{D}{RT} \left(\frac{\partial f}{\partial B}\right)_{n,V,\delta_1} b_i - \frac{f}{RT} \left(\frac{\partial D}{\partial n_i}\right)_{T,n_j} - \left[-\frac{n_i^0 a_{ii}}{RT} \left(\frac{\partial f}{\partial B}\right)_{n,V,\delta_1}^0 b_i - \frac{f_i^0}{RT} 2n_i^0 a_{ii} \right] \quad (\text{B14})$$

$$F_i^{att3P} = -\frac{D}{RT} \left(\frac{\partial f}{\partial \delta_1}\right)_{n,V,B} \left(\frac{\partial \delta_1}{\partial n_i}\right)_{n_j} \quad (\text{B15})$$

$$F_{Z_i} = -\ln(Z) - [-\ln(Z_i^0)] \quad (\text{B16})$$

Considering that:

$$f_i^0 = \frac{1}{n_i^0 b_i \left(\delta_1 - \frac{1-\delta_1}{1+\delta_1}\right)} \ln\left(\frac{V_i^0 + \delta_1 n_i^0 b_i}{V_i^0 + \frac{1-\delta_1}{1+\delta_1} n_i^0 b_i}\right) \quad (\text{B17})$$

$$\left(\frac{\partial f}{\partial B}\right)_{n,V,\delta_1} = - \frac{\left(f_i^0 + V_i^0 \left(\frac{-1}{(V_i^0 + \delta_1 n_i^0 b_i) \left(V_i^0 + \frac{1-\delta_1}{1+\delta_1} n_i^0 b_i \right)} \right)\right)}{n_i^0 b_i} \quad (\text{B18})$$

Note that in Eq. B15 no pure-compound term appears being subtracted to the mixture term. The reason for that is that, due to its definition in Eq. B11, the composition derivative of the δ_1 parameter becomes zero when valued for the “ i ” compound in pure state.

In the results section of this paper, we numerically analyze the contribution of each term in Eq. B12 to the final value of $\ln(\gamma_i)$. It is worth mention that the proposed decomposition is valid for a 2P-EoS (SRK, PR) or a 3P-EoS (RKPR), being the only formal difference that a constant δ_1 parameter makes the F_i^{att3P} term vanish in a 2P-EoS.

List of symbols

- A Helmholtz energy
- a cohesive or energy parameter in an equation of state
- b general notation for the size-related parameter in an equation of state; co-volume in a cubic EoS
- c general notation for the dimensionless third parameter in an equation of state
- k constant defining the temperature dependence of the attractive parameter in the RKPR EoS
- m third parameter in SAFT-type equations of state: number of segments
(also, the characteristic constant in Soave's alpha function)
- n mole number
- P absolute pressure
- R universal gas constant ($R = 0.08314472 \text{ bar L mol}^{-1} \text{ K}^{-1}$)
- T temperature
- V total volume
- x molar fraction
- Z compressibility factor

Greek letters

- $\hat{\phi}$ fugacity coefficient in solution
- γ activity coefficient
- γ^∞ infinite dilution activity coefficient
- δ_1 third parameter in the RKPR EoS
- δ_2 non-adjustable parameter defined in terms of δ_1
- ε/k energetic parameter in PC-SAFT: square well potential depth
- η dimensionless variable relating the size parameter and the molar volume
- ρ molar density
- σ size parameter in PC-SAFT: segment diameter
- τ dimensionless variable relating the energetic parameter and the temperature

ω acentric factor

Subscripts

c critical property

i component

r reduced property

Superscripts

0 pure compound

res residual property

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Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: