



Updated versions of the generalized Soave α -function suitable for the Redlich-Kwong and Peng-Robinson equations of state

Andrés Pina-Martinez, Romain Privat, Jean-Noël Jaubert, Ding-Yu Peng

► To cite this version:

Andrés Pina-Martinez, Romain Privat, Jean-Noël Jaubert, Ding-Yu Peng. Updated versions of the generalized Soave α -function suitable for the Redlich-Kwong and Peng-Robinson equations of state. Fluid Phase Equilibria, 2019, 485, pp.264-269. 10.1016/j.fluid.2018.12.007 . hal-02136163

HAL Id: hal-02136163

<https://hal.univ-lorraine.fr/hal-02136163>

Submitted on 21 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Updated versions of the generalized Soave α -function suitable for the Redlich-Kwong and Peng-Robinson equations of state.

Andrés Pina-Martínez¹, Romain Privat^{1(*)}, Jean-Noël Jaubert^{1(*)}, Ding-Yu Peng²

⁽¹⁾ Université de Lorraine, École Nationale Supérieure des Industries Chimiques, Laboratoire Réactions et Génie des Procédés (UMR CNRS 7274), 1 rue Grandville, 54000, Nancy, France

⁽²⁾ University of Saskatchewan, Department of Chemical and Biological Engineering, Engineering Building, Saskatoon, Saskatchewan, S7N 5A9, Canada

(*) authors to whom the correspondence should be addressed

E-mails: jean-noel.jaubert@univ-lorraine.fr or romain.privat@univ-lorraine.fr

ABSTRACT

More than 40 years after their publication, updated versions of the generalized Soave α -function $\left(\alpha(T_r, \omega) = \left[1 + m(\omega) \left(1 - T_r^{0.5} \right) \right]^2 \right)$ suitable for the Redlich-Kwong (RK) and Peng-Robinson (PR) equations of state (EoS) are proposed in this work. The new mathematical expressions of $m_{RK}(\omega)$ and $m_{PR}(\omega)$ have been determined by correlating the optimal m values, fitted on vapor pressures (P^{sat}) and/or enthalpies of vaporization ($\Delta_{vap}H$) and/or saturated-liquid heat capacities ($c_{P,liq}^{sat}$) against the acentric factor ω . The correlations determined in this study can be considered as broad-based and sound since they were established for 1721 pure compounds belonging to many different chemical families (hydrocarbons, halogenated, oxygenated, sulfur, nitrogen compounds ...) for which experimental data were available. Significant improvements on the reproduction of vapor pressures were obtained for the PR EoS with respect to the original version. The updated SRK EoS achieved similar average deviations for the three properties of interest (P^{sat} , $\Delta_{vap}H$ and $c_{P,liq}^{sat}$), in comparison with the original SRK equation. A substantial improvement is also noticeable for heavy molecules with an acentric factor larger than 0.9.

Keywords: Alpha function; Cubic equation of state; Soave; Peng-Robinson; Redlich-Kwong

1. INTRODUCTION

As stated by Valderrama [1], the Soave-Redlich-Kwong (SRK) [2] and the Peng-Robinson [3] equations of state (EoS) are the most popular cubic equations currently used in research, simulations and optimizations that require thermodynamics and vapor-liquid equilibrium (VLE) properties. These two equations have been considered for all types of calculations, from simple estimations of pure-fluid volumetric properties and vapor pressures to descriptions of complex multicomponent systems. As a direct consequence, all commercially available process simulation packages (ProSim, Pro/II, Aspen, UniSim ...) include the SRK and PR EoS among their thermodynamic models. Such EoS are usually used in their *translated* form [4–6] in order to improve their abilities to predict liquid densities. They can be summarized as follows:

t-SRK:

$$P(T, v) = \frac{RT}{v-b} - \frac{a_c \cdot \alpha(T_r, \omega_{exp})}{(v+c)(v+b+2c)} \quad \text{with:} \quad \begin{cases} a_c = \frac{1}{9(\sqrt[3]{2}-1)} \frac{R^2 T_{c,exp}^2}{P_{c,exp}} \\ b = \frac{\sqrt[3]{2}-1}{3} \frac{RT_{c,exp}}{P_{c,exp}} - c \end{cases} \quad (1)$$

t-PR:

$$P(T, v) = \frac{RT}{v-b} - \frac{a_c \cdot \alpha(T_r, \omega_{\text{exp}})}{(v+c)(v+b+2c) + (b+c)(v-b)} \quad \text{with:} \quad \begin{cases} \eta_c = \left[1 + \sqrt[3]{4-2\sqrt{2}} + \sqrt[3]{4+2\sqrt{2}} \right]^{-1} \approx 0.25308 \\ a_c = \frac{40\eta_c + 8}{49 - 37\eta_c} \frac{R^2 T_{c,\text{exp}}^2}{P_{c,\text{exp}}} \approx 0.45724 \frac{R^2 T_{c,\text{exp}}^2}{P_{c,\text{exp}}} \\ b = \frac{\eta_c}{\eta_c + 3} \frac{RT_{c,\text{exp}}}{P_{c,\text{exp}}} - c \approx 0.07780 \frac{RT_{c,\text{exp}}}{P_{c,\text{exp}}} - c \end{cases} \quad (2)$$

c is the component-dependent volume-translation factor. It is usually [7] selected in order to exactly reproduce the experimental saturated liquid volume at a reduced temperature of 0.8. The temperature-dependent function $\alpha(T_r, \omega_{\text{exp}})$ in the attraction term of both the SRK and PR equations is the one developed by Soave. For a given pure compound (characterized by its acentric factor ω_{exp} and its critical temperature $T_{c,\text{exp}}$), the temperature-dependent function is expressed as:

$$\alpha_{\text{Soave}}(T_r, \omega_{\text{exp}}) = \left[1 + m(\omega_{\text{exp}}) \cdot (1 - \sqrt{T_r}) \right]^2 \quad (3)$$

with,

$$m = A + B\omega_{\text{exp}} + C\omega_{\text{exp}}^2 \quad (4)$$

or:

$$m = A + B\omega_{\text{exp}} + C\omega_{\text{exp}}^2 + D\omega_{\text{exp}}^3 \quad (5)$$

$T_r = T / T_{c,\text{exp}}$ is the reduced temperature; and A , B , C and D are universal constants that depend on the selected EoS.

In 1972, Soave [2] assumed ω values ranging from zero to 0.5 with a step of 0.05. For each of these eleven ω values, he determined the corresponding m values enabling to exactly reproduce reduced vapor pressures at $T_r = 0.7$ calculated as: $P_r^{\text{sat}}(T_r = 0.7) = 10^{-\omega-1}$. Such m values were correlated against ω with the following second order polynomial:

$$m_{RK} = 0.480 + 1.574\omega - 0.176\omega^2 \quad (6)$$

In 1976, Peng and Robinson [3] determined suitable m values for their EoS for 14 hydrocarbons (methane, ethane, propane, i-butane, n-butane, cyclohexane, benzene, i-pentane, n-pentane, n-hexane, n-heptane, n-octane, n-nonane and n-decane) and 3 permanent gases (N_2 , CO_2 , H_2S) by minimizing the deviations between the calculated and experimental vapor pressures. They used vapor pressure data from the normal boiling point to the critical point. These optimized m values were correlated against the acentric factor and the resulting equation was:

$$m_{PR} = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (7)$$

As recently noted by Lopez-Echeverry et al. [8], since 1976 many papers have been devoted to improving the Soave α -function. The most recent is likely the one published by Yang et al. [9] only a few weeks ago. We will only cite some of them, which were essentially written by Soave himself or by Peng and Robinson. As a first example, in 1978 Graboski and Daubert [10] refit the constants in Eq. (6). The regression was based on a detailed set of hydrocarbon vapor pressure data compiled by the American Petroleum Institute. The regression equation for m_{RK} based on such data was derived to be:

$$m_{RK} = 0.48508 + 1.55171\omega - 0.15613\omega^2 \quad (8)$$

As a second example, in 1993 Soave [11] correlated vapor pressures generated by the Lee-Kesler equation in order to derive – for the RK EoS – the following two-parameter α -function, which is particularly suitable for heavy hydrocarbons:

$$\alpha(T_r) = 1 + m(1 - T_r) + n(1 - \sqrt{T_r})^2 \quad \text{with:} \quad \begin{cases} m = 0.484 + 1.515\omega - 0.044\omega^2 \\ n = 2.756m - 0.700 \end{cases} \quad (9)$$

Soave [11] also explained that the 2 parameters m and n in Eq. (9) can be adjusted separately to accurately correlate the experimental vapor pressures of polar substances. A few months later, Soave [12] advised dividing the m values returned by Eq. (6) by a factor 1.18 so the translated SRK EoS would accurately predict the fugacity coefficients of pure gaseous fluids at high temperatures pressures.

As a third example, in 1978 Robinson and Peng [13] proposed a piecewise expression of m . They recommended generating m values for substances whose acentric factors are lower than or equal to that of n-decane by Eq. (7), which was published in 1976. For heavier molecules, they advised estimating m by a third order polynomial of the acentric factor:

$$\begin{cases} m_{PR} = 0.37464 + 1.54226\omega - 0.26992\omega^2 & \omega \leq \omega_{n\text{-decane}} \\ m_{PR} = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3 & \omega > \omega_{n\text{-decane}} \end{cases} \quad (10)$$

Eq. (10) received a considerable acclaim and is specifically used in the well-acknowledged PPR78 model [14–16].

This short bibliographic review makes it possible to conclude that the correlations of m parameters against ω have always been conducted on a small number of hydrocarbons in order to either exactly reproduce the vapor pressure at $T_r = 0.7$ or to minimize the deviations between the calculated and experimental vapor pressures. In this paper, we decided to follow the conclusions of one of our recent studies [17], in which we demonstrated that safe α -function parameters can only be obtained if the data regressions are performed considering at least the vapor pressure (P^{sat}) data. As was done in our previous paper [17], and thanks to the DIPPR database, we were able to find 1721 compounds with available and accurate vapor pressures. Moreover, for 1523 of these 1721 compounds, the DIPPR database also provided enthalpies of vaporization ($\Delta_{vap}H$) and/or saturated liquid heat capacity ($c_{P,liq}^{sat}$) data.

For each of these 1721 compounds, m_{RK} and m_{PR} were determined in order to minimize the deviations between the calculated and available experimental data, which included P^{sat} and/or $\Delta_{vap}H$ and/or $c_{P,liq}^{sat}$. To the best of our knowledge, $\Delta_{vap}H$ and $c_{P,liq}^{sat}$ data have never been used to calibrate the Soave α -function and no fittings have been conducted on such a large number of components. Eventually, these optimized m values were correlated against the acentric factor in order to update the generalized Soave α -function suitable for the RK and PR EoS.

At this step, it is worth noting that the Soave α -function does not pass the consistency test proposed by Le Guennec et al. [18,19], which stipulates that α -functions must obey the following list of constraints to guarantee safe property predictions in both the subcritical and supercritical domains:

$$\alpha(T_c) = 1 \text{ and for all } T: \begin{cases} \alpha \geq 0 & \text{and } \alpha(T_r) \text{ continuous} \\ \frac{d\alpha}{dT_r} \leq 0 & \text{and } \frac{d\alpha}{dT_r} \text{ continuous} \\ \frac{d^2\alpha}{dT_r^2} \geq 0 & \text{and } \frac{d^2\alpha}{dT_r^2} \text{ continuous} \\ \frac{d^3\alpha}{dT_r^3} \leq 0 \end{cases} \quad (11)$$

However, as explained by Le Guennec et al. [18], the 1972 Soave α -function is consistent, i.e., it satisfies the constraints given in Eq. (11), up to a temperature that is generally higher than 1500 K. This is the reason why this study was conducted and the reason why the Soave α -function is certainly the most used α -function in chemical industries.

2. UPDATED SOAVE m PARAMETER

As stated in the introduction, thanks to the DIPPR database we were able to find 1721 compounds belonging to many different chemical families (hydrocarbons, halogenated, oxygenated, sulfur, nitrogen compounds ...) for which at least the vapor pressure data could be accurately generated from a temperature-dependent correlation (see the **Supplementary Material** section for the entire listing of the 1721 compounds). In addition, for 1523 compounds among these 1721, other experimental data, such as the enthalpy of vaporization ($\Delta_{vap}H$) and/or saturated liquid heat capacity ($c_{P,liq}^{sat}$), were also available. **Table 1** summarizes the available property data for the 1721 compounds considered in this study.

Table 1. Distribution of the 1721 retained compounds according to the accurate property data available in the DIPPR database.

| Accurate property data available in the DIPPR database | Number of compounds |
|--|---------------------|
| $(P^{sat} + \Delta_{vap}H + c_{P,liq}^{sat})$ | 759 |
| $(P^{sat} + \Delta_{vap}H)$ | 694 |
| $(P^{sat} + c_{P,liq}^{sat})$ | 70 |
| (P^{sat}) | 198 |
| TOTAL: | 1721 |

First, the optimal m parameters for each of the 1721 considered compounds have been determined. Our first task was thus to generate pseudo-experimental data thanks to the correlations available in the DIPPR database. The rules used for the generation of the pseudo-experimental data along with a long discussion on the accuracy of the data can be found in one of our recently published papers [20], which used the same database.

3. RESULTS

The optimized m parameters for each of the 1721 compounds considered in this study are reported in the **Supplementary material** section for both the PR and the RK EoS. As illustrated in **Fig. 1**, they have been correlated against ω_{exp} for both cubic EoS. The resulting expressions are the following third order polynomials:

$$m_{PR} = 0.3919 + 1.4996\omega - 0.2721\omega^2 + 0.1063\omega^3 \quad (12)$$

$$m_{RK} = 0.4810 + 1.5963\omega - 0.2963\omega^2 + 0.1223\omega^3 \quad (13)$$

To have an overview of the capabilities of these two new expressions, they are compared with the original polynomials for both the PR and RK equations. The Mean Absolute Percentage Error (MAPE) on P^{sat} , $\Delta_{vap}H$ and $c_{P,liq}^{sat}$ calculated with the original and the updated Soave α -functions are reported in **Table 2** (the detailed results obtained with the updated α -functions for each of the 1721 compounds are available in the **Supplementary material** section).

Table 2. Comparison of the MAPEs calculated with the original and the updated Soave α -functions. Application to the PR and RK EoS.

| | Peng-Robinson | | Redlich-Kwong | |
|---|---|---|---|---|
| | Original Soave α -function [Eq. (7)] | Updated Soave α -function [this work – Eq. (12)] | Original Soave α -function [Eq. (6)] | Updated Soave α -function [this work – Eq. (13)] |
| MAPE on P^{sat} (1721 compounds) | 2.7% | 1.8% | 2.2% | 2.1% |
| MAPE on $\Delta_{vap}H$ (1453 compounds) | 3.1% | 2.8% | 2.9% | 2.9% |
| MAPE on $c_{P,liq}^{sat}$ (829 compounds) | 7.1% | 6.8% | 5.3% | 5.3% |

A graphical comparison of the original and updated polynomials can be found in **Fig. 1**.

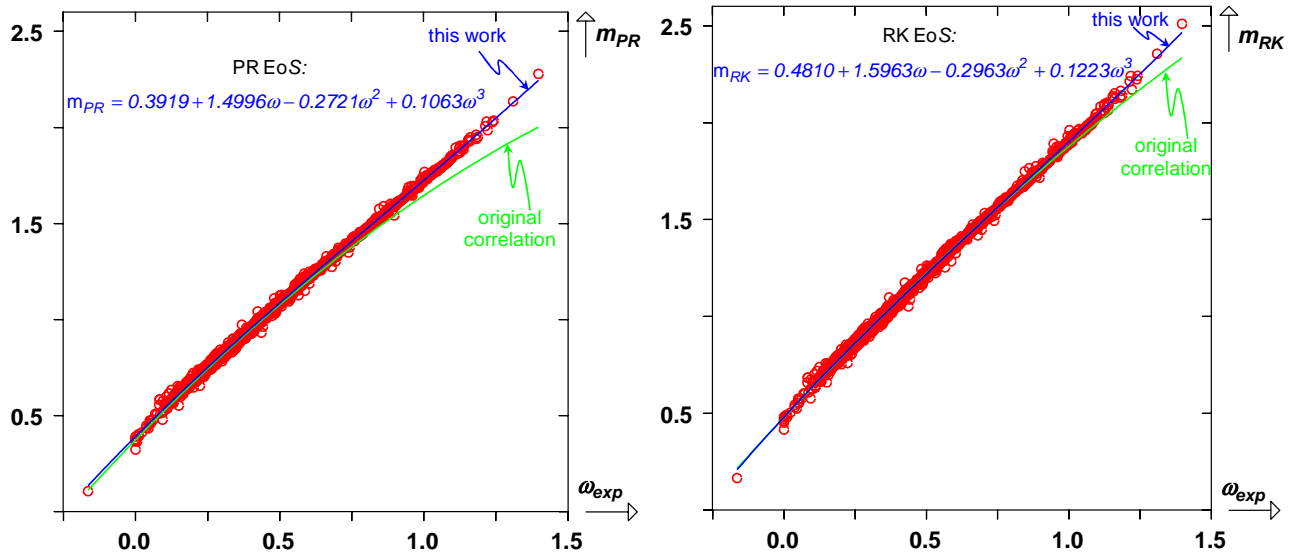


Figure 1. Correlation of optimized m parameter against ω_{exp} for both the PR and RK EoS. Comparison between the original correlation and the one determined in this work. Each of the 1721 open circles represent a pure compound.

First, **Table 2** highlights that the accuracies of both EoS are quite similar. This is especially true with the updated Soave α -functions (the use of the original Soave α -functions indeed gives an advantage to the SRK EoS). It is also possible to conclude that the use of a one-parameter α -function (like the one developed by Soave) makes it impossible to

simultaneously catch P^{sat} , $\Delta_{vap}H$ and $c_{P,liq}^{sat}$. Indeed, for both EoS, the MAPE on $c_{P,liq}^{sat}$ is greater than 5%.

Second, it is possible to highlight the decrease of 0.9% of the MAPE on P^{sat} when the updated Soave α -function, instead of the original version, is coupled with the PR EoS.

Third, by focusing only on the average overall deviations, it is observed that there is no difference between the original and updated Soave α -functions coupled with the RK EoS. All three properties of interest (P^{sat} , $\Delta_{vap}H$ and $c_{P,liq}^{sat}$) are reproduced with the same accuracy. This demonstrates the pertinence of the approach used by Soave in 1972, who determined the m values in order to exactly reproduce the experimental vapor pressures at $T_r = 0.7$. However, it is worth noting that the updated α -function is more accurate than the original α -function for very heavy molecules. Such an improvement is not reflected in the average deviations given in **Table 2** because the number of very heavy compounds (124) is small in comparison to the total number of compounds (1721). However, the significant divergence between the 2 polynomials when ω_{exp} is larger than 0.9 is prominent in **Fig. 1** (right panel) and this point certainly deserves further development. Indeed, a similar behavior is observed with the PR EoS and, as highlighted by **Fig. 1** (left panel), the significant divergence between the 2 polynomials begins as soon as ω_{exp} is larger than 0.7. As summarized in **Table 3**, in these regions where the original and updated polynomials do not coincide, the updated α -function makes it possible to significantly improve the MAPE on P^{sat} for both EoS. For the PR EoS, a roughly three-fold decrease on the MAPE on P^{sat} is obtained for the 276 compounds for which $\omega_{exp} \geq 0.7$, while for the SRK EoS, the MAPE on P^{sat} is reduced by a factor 1.5 for the 124 compounds for which $\omega_{exp} \geq 0.9$.

Table 3. Comparison of the MAPEs on P^{sat} calculated with the original and the updated Soave α -functions for molecules whose ω_{exp} is larger than 0.7 and 0.9 for PR and SRK EoS, respectively.

| Peng-Robinson EoS with: | | MAPE on P^{sat} (for the 276 compounds for which $\omega_{exp} \geq 0.7$) |
|---|--|--|
| Original Soave α -function [Eq. (7)] | | 6.5% |
| Updated Soave α -function [this work – Eq. (12)] | | 1.9% |
| Redlich-Kwong EoS with: | | MAPE on P^{sat} (for the 124 compounds for which $\omega_{exp} \geq 0.9$) |
| Original Soave α -function [Eq. (6)] | | 4.5% |
| Updated Soave α -function [this work – Eq. (13)] | | 3.1% |

As shown in **Fig. 2**, it is possible to assess the similarities and differences – across the 11 defined chemical families – of the deviations in the vapor pressures reported in **Table 3**.

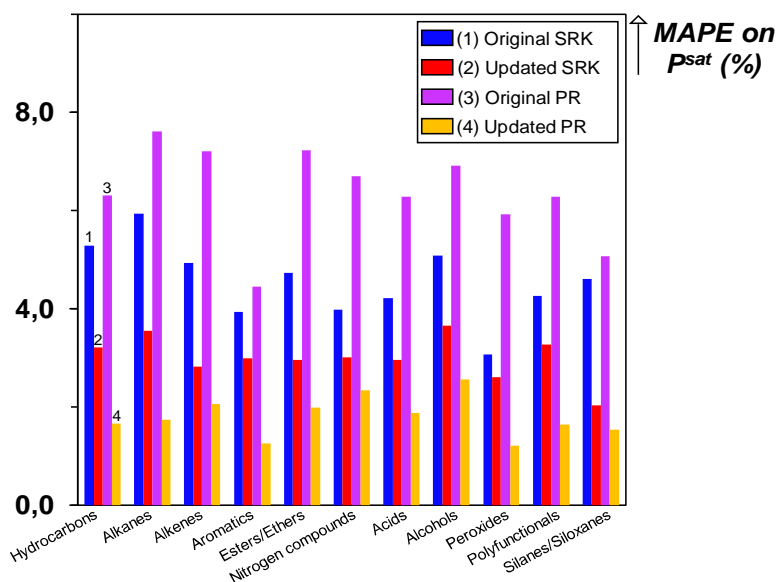


Figure 2. MAPE on P^{sat} for 11 chemical families. For each family, the order of series is bar #1: original SRK, bar #2: updated SRK, bar #3: original PR, and bar #4: updated PR.

For all the chemical families, the updated α -function is more accurate than the original α -function for both the PR and SRK EoS. With the aim of focusing on applications specific to the oil and gas industry where cubic EoS are widely used, the *hydrocarbons* family, which groups the Alkane + the Alkenes + the Aromatics families, was also defined. For such a family, the conclusions are identical: whatever the EoS, much lower deviations on the vapor pressure data are obtained with the updated versions of the α -functions. At this step, it would be interesting to analyze the temperature dependence of the deviations on P^{sat} reported in **Table 3** for heavy molecules. It was thus decided to plot the MAPE on P^{sat} as a function of the reduced temperature for both EoS. Such curves were plotted between $T_r = 0.73$ and $T_r = 1$ because it was the temperature interval in which pseudo-experimental data could be generated by the correlations available in the DIPPR database. In **Fig. 3** it is possible to observe that the updated versions of the α -functions perform much better, regardless of the temperature.

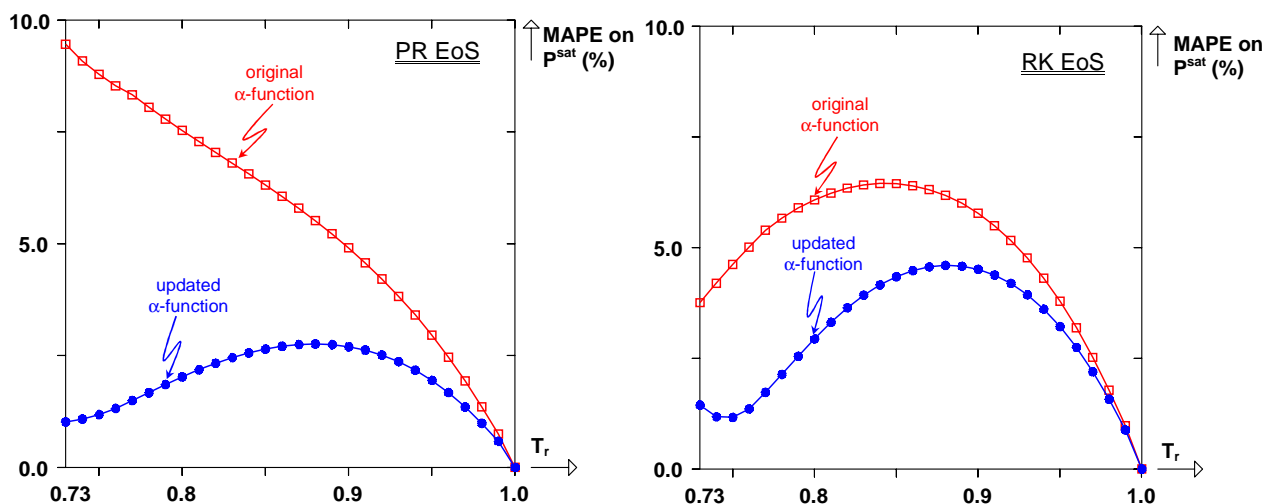


Figure 3. MAPE on P^{sat} for heavy molecules (see **Table 3**) plotted against the reduced temperature for PR (left) and RK (right) EoS. (□) Original α -function, (●) Updated α -function.

At this step, it was also decided to estimate the MAPE on the liquid molar volumes. Among the 1721 compounds considered in this paper, the DIPPR database has accurate correlations to estimate the liquid molar volumes at saturation (v_{liq}^{sat}) for 1489 of them. As was previously done for the P^{sat} , $\Delta_{vap}H$ and $c_{P,liq}^{sat}$ properties, for each of these 1489 compounds the DIPPR correlation was used to generate 50 equidistant liquid molar volume data points between T_{min} and $T_{max} = 0.9T_c$. In this case, T_{min} is the minimum temperature at which v_{liq}^{sat} can be estimated from the DIPPR correlation, whereas $T_{max} = 0.9T_c$ is the highest temperature at which the volume-translation concept has a beneficial effect. By denoting $v_{liq}^{sat,t-CEoS}$ as the molar volume calculated with the translated EoS [see Eqs. (1) and (2)], the MAPE on v_{liq}^{sat} is calculated as:

$$MAPE = \frac{100}{50} \sum_{i=1}^{50} \left| \frac{v_{liq}^{sat,DIPPR} \left(T_i^{v_{liq}^{sat}} \right) - v_{liq}^{sat,t-CEoS} \left(T_i^{v_{liq}^{sat}} \right)}{v_{liq}^{sat,DIPPR} \left(T_i^{v_{liq}^{sat}} \right)} \right| \quad (14)$$

These MAPEs are reported in **Table 4** for both the PR and RK EoS in their translated and untranslated versions (the detailed results obtained with the updated α -functions for each of the 1489 compounds are available in the **Supplementary material** section).

Table 4. Comparison of the MAPEs on v_{liq}^{sat} calculated with the original and the updated Soave α -functions. Application to the translated and untranslated PR and RK EoS.

| | Peng-Robinson | | Redlich-Kwong | |
|--|---|---|---|---|
| | Original Soave α -function [Eq. (7)] | Updated Soave α -function [this work – Eq. (12)] | Original Soave α -function [Eq. (6)] | Updated Soave α -function [this work – Eq. (13)] |
| MAPE on v_{liq}^{sat} (1489 compounds) ($T_r < 0.9$) | <i>Untranslated</i> | | <i>Untranslated</i> | |
| | 8.5% | 8.5% | 19% | 19% |
| | <i>Translated</i> | | <i>Translated</i> | |
| | 2.2% | 2.2% | 3.8% | 3.8% |

Such a table highlights that the reproduction of the experimental v_{liq}^{sat} data is dramatically improved for both EoS when a volume translation is applied. Another key conclusion is that the choice of the α -function (original or updated) has a negligible impact on the MAPE on v_{liq}^{sat} . In addition, for completing our analysis the average deviations on the molar critical volume are reported in **Table 5** (the detailed results obtained with the updated α -functions for each of the 1489 compounds are available in the **Supplementary material** section).

Table 5. Comparison of the MAPEs on the molar critical volume (v_c) calculated with the original and the updated Soave α -functions. Application to the translated and untranslated PR and RK EoS.

| | Peng-Robinson | | Redlich-Kwong | |
|---------------------------------|---|---|---|---|
| | Original Soave α -function [Eq. (7)] | Updated Soave α -function [this work – Eq. (12)] | Original Soave α -function [Eq. (6)] | Updated Soave α -function [this work – Eq. (13)] |
| MAPE on v_c | <i>Untranslated</i> | | <i>Untranslated</i> | |

| | | | | | |
|------------------|-------------------|-----|---|-------------------|-----|
| (1489 compounds) | 21% | 21% | ⋮ | 31% | 31% |
| | <i>Translated</i> | | | <i>Translated</i> | |
| | 20% | 20% | | 24% | 24% |

At the critical point, the volume-translation parameter c has too small an influence on the calculated critical volume (v_c) to obtain a good match with the experimental value. Although the influence of the volume translation concept is more visible on the RK EoS, the PR CEoS yields better predictions of v_c . **Table 4** and **Table 5** definitively demonstrate the superiority of the PR EoS to correlate the molar volumes in comparison with the SRK EoS.

To conclude this section, we must say a few words about VLE calculations for binary systems when classical vdW one-fluid mixing rules that involve a temperature-independent interaction parameter (k_{12}) are considered. A prerequisite for the successful correlation of binary systems is accurate knowledge of the vapor pressure of each pure component; this is certainly the dominant factor, whereas the second most important factor is k_{12} . Consequently, by improving the prediction of the vapor pressure data, the updated correlations developed in this study without a doubt contribute to a better correlation of binary systems. A key question we also need to address is how much change in the interaction parameter is needed when we switch from the original to the updated correlation? It is indeed acknowledged that numerical values of k_{12} are specific to the considered α -function. To answer this question, we decided to refer to the work by Jaubert and Privat [20], who developed an equation that makes it possible to calculate the k_{12} suitable for a desired α -function (e.g., the updated α -function developed in this work) knowing the corresponding k_{12} value for another α -function (e.g., the original Soave α -function). Such an equation is written as:

$$k_{12}^{updated} = \frac{2k_{12}^{original} \delta_1^{original} \delta_2^{original} + (\delta_1^{original} - \delta_2^{original})^2 - (\delta_1^{updated} - \delta_2^{updated})^2}{2\delta_1^{updated} \delta_2^{updated}} \quad (15)$$

with: $\delta_i^{original} = \frac{\sqrt{a_{c,i} \cdot \alpha_i^{original}}}{b_i}$ and $\delta_i^{updated} = \frac{\sqrt{a_{c,i} \cdot \alpha_i^{updated}}}{b_i}$

Eq. (15) was used for several binary systems and the change in k_{12} was found to be small after switching from the original to the updated correlation. Consequently, it is possible to continue use of the numerical values of k_{12} available in commercial process simulation software for hundreds of binary systems when the updated correlations developed in this paper are used. It is however obviously advised to update the k_{12} values, thanks to Eq. (15).

4. CONCLUSION

In this study, updated versions of the generalized Soave α -function suitable for the RK and PR EoS have been proposed. Significant improvements on the reproduction of vapor pressure data have been obtained for the PR EoS with respect to the original version. The updated SRK EoS achieved similar average overall deviations for the three properties of interest (P^{sat} , $\Delta_{vap}H$ and $c_{P,liq}^{sat}$) in comparison with the original SRK equation. However, the use of the updated α -function developed in this study significantly reduces the MAPE on P^{sat} for heavy molecules with an acentric factor larger than 0.9.

This paper also allows us to conclude that the accuracies of the PR and SRK EoS are very similar, except for the molar volumes, which are better predicted with the PR EoS.

To conclude, we do encourage developers of commercial process simulation software to update the parameters of the $m(\omega_{exp})$ function involved in Soave α -functions as reported in Eqs. (12) and (13) of the present study.

ACKNOWLEDGEMENTS

The French Petroleum Company TOTAL, and more particularly Dr. Laurent AVAULLÉE and Freddy GARCIA (experts in thermodynamics), are gratefully acknowledged for sponsoring this research.

SUPPLEMENTARY MATERIAL

Supplementary material related to this article, which includes optimized m_{PR} and m_{RK} parameters for each of the 1721 compounds considered in this study along with the MAPE on P^{sat} and/or $\Delta_{vap}H$ and/or $c_{P,liq}^{sat}$ and/or v_{liq}^{sat} and/or v_c calculated with the generalized updated α -functions and the reported volume-translation parameter c , can be found at <http://dx.doi.org/10.1016/j.fluid.2019.??>.

REFERENCES

- [1] J.O. Valderrama, The State of the Cubic Equations of State, *Ind. Eng. Chem. Res.* 42 (2003) 1603–1618. doi:10.1021/ie020447b.
- [2] G. Soave, Equilibrium constants from a modified Redlich-Kwong equation of state, *Chem. Eng. Sci.* 27 (1972) 1197–1203. doi:10.1016/0009-2509(72)80096-4.
- [3] D. Peng, D. Robinson, A New Two-Constant Equation of State, *Ind. Eng. Chem. Fundam.* 15 (1976) 59–64. doi:10.1021/i160057a011.
- [4] A. Péneloux, E. Rauzy, R. Freze, A consistent correction for Redlich-Kwong-Soave volumes, *Fluid Phase Equilibria*. 8 (1982) 7–23. doi:10.1016/0378-3812(82)80002-2.
- [5] J.-N. Jaubert, R. Privat, Y. Le Guennec, L. Coniglio, Note on the properties altered by application of a Péneloux-type volume translation to an equation of state, *Fluid Phase Equilibria*. 419 (2016) 88–95. doi:10.1016/j.fluid.2016.03.012.
- [6] R. Privat, J.-N. Jaubert, Y. Le Guennec, Incorporation of a volume translation in an equation of state for fluid mixtures: which combining rule? Which effect on properties of mixing?, *Fluid Phase Equilibria*. 427 (2016) 414–420. doi:10.1016/j.fluid.2016.07.035.
- [7] Y. Le Guennec, R. Privat, J.-N. Jaubert, Development of the translated-consistent tc -PR and tc -RK cubic equations of state for a safe and accurate prediction of volumetric, energetic and saturation properties of pure compounds in the sub- and super-critical domains, *Fluid Phase Equilibria*. 429 (2016) 301–312. doi:10.1016/j.fluid.2016.09.003.
- [8] J.S. Lopez-Echeverry, S. Reif-Acheran, E. Araujo-Lopez, Peng-Robinson equation of state: 40 years through cubics, *Fluid Phase Equilibria*. 447 (2017) 39–71. doi:10.1016/j.fluid.2017.05.007.
- [9] F. Yang, Q. Liu, Y. Duan, Z. Yang, On the temperature dependence of the α function in the cubic equation of state, *Chem. Eng. Sci.* 192 (2018) 565–575. doi:10.1016/j.ces.2018.08.014.
- [10] M.S. Graboski, T.E. Daubert, A Modified Soave Equation of State for Phase Equilibrium Calculations. 1. Hydrocarbon Systems, *Ind. Eng. Chem. Process Des. Dev.* 17 (1978) 443–448. doi:10.1021/i260068a009.
- [11] G. Soave, Improving the treatment of heavy hydrocarbons by the SRK EOS, *Fluid Phase Equilibria*. 84 (1993) 339–342. doi:10.1016/0378-3812(93)85131-5.
- [12] G. Soave, M. Barolo, A. Bertucco, Estimation of high-pressure fugacity coefficients of pure gaseous fluids by a modified SRK equation of state, *Fluid Phase Equilibria*. 91 (1993) 87–100. doi:10.1016/0378-3812(93)85081-V.
- [13] D.B. Robinson, D.-Y. Peng, The characterization of the heptanes and heavier fractions for the GPA Peng–Robinson programs (RR-28), *Res. Rep. GPA.* (1978) 1–36.
- [14] J.-N. Jaubert, F. Mutelet, VLE predictions with the Peng-Robinson equation of state and temperature-dependent k_j calculated through a group contribution method, *Fluid Phase Equilibria*. 224 (2004) 285–304. doi:10.1016/j.fluid.2004.06.059.

- [15] J.-N. Jaubert, R. Privat, F. Mutelet, Predicting the phase equilibria of synthetic petroleum fluids with the PPR78 approach, *AIChE J.* 56 (2010) 3225–3235. doi:10.1002/aic.12232.
- [16] J.-W. Qian, R. Privat, J.-N. Jaubert, Predicting the phase equilibria, critical phenomena, and mixing enthalpies of binary aqueous systems containing alkanes, cycloalkanes, aromatics, alkenes, and gases (N_2 , CO_2 , H_2S , H_2) with the PPR78 equation of state, *Ind. Eng. Chem. Res.* 52 (2013) 16457–16490. doi:10.1021/ie402541h.
- [17] A. Pina-Martinez, Y. Le Guennec, R. Privat, J.-N. Jaubert, P.M. Mathias, Analysis of the combinations of property data that are suitable for a safe estimation of consistent T_w α -function parameters: updated parameter values for the translated-consistent tc -PR and tc -RK cubic equations of state, *J. Chem. Eng. Data.* 63 (2018) 3980–3988. doi:10.1021/acs.jced.8b00640.
- [18] Y. Le Guennec, S. Lasala, R. Privat, J.-N. Jaubert, A consistency test for α -functions of cubic equations of state, *Fluid Phase Equilibria.* 427 (2016) 513–538. doi:10.1016/j.fluid.2016.07.026.
- [19] Y. Le Guennec, R. Privat, S. Lasala, J.-N. Jaubert, On the imperative need to use a consistent α -function for the prediction of pure-compound supercritical properties with a cubic equation of state, *Fluid Phase Equilibria.* 445 (2017) 45–53. doi:10.1016/j.fluid.2017.04.015.
- [20] J.-N. Jaubert, R. Privat, Relationship between the binary interaction parameters (k_{ij}) of the Peng-Robinson and those of the Soave-Redlich-Kwong equations of state: application to the definition of the PR2SRK model, *Fluid Phase Equilibria.* 295 (2010) 26–37. doi:10.1016/j.fluid.2010.03.037.