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Thermodynamics and Molecular-Scale Phenomena

Assessing the performance of non-associating SAFT-type equations of state to reproduce vapor pressure, liquid density, enthalpy of vaporization, and liquid heat capacity data of 1800 pure fluids

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Abstract

The performance of the PC-SAFT and *I*-PC-SAFT EoS in correlating P^{sat}, v_{liq}^{sat}, $\Delta_{vap}H$, $c_{P,liq}^{sat}$, and critical coordinates of 1800 pure compounds that consist of 1252 non-self-associating and 548 self-associating compounds is evaluated. The PC-SAFT equation is able to reproduce P^{sat} and v_{liq}^{sat} data with a deviation close to 1%, which meets highest standards. The counterpart is however a large deviation on the critical pressure. The *I*-PC-SAFT EoS exactly reproduces the critical pressure and temperature and accurately correlates P^{sat}. Its weak point is a larger liquid density deviation. The key conclusion of this article is however the absence of correlation between the strength of association and the accuracy with which the experimental data were correlated. Regardless of the EoS, poor results are obtained for more than 15% of the non-self-associating compounds but 60% of the self-associating compounds are accurately correlated although no association term was included in the considered EoS.

KEYWORDS

database, enthalpy of vaporization, *I*-PC-SAFT, liquid density, liquid heat capacity, PC-SAFT, pure component, role of association, SAFT-type equation of state, vapor pressure

1 | INTRODUCTION

Equations of state (EoS) are one of the most commonly used tools in chemical and process engineering due to their capacity of predicting thermodynamic properties of pure compounds and mixtures at any given state. It is therefore clear that their performance at predicting such properties must be studied carefully and systematically to quantify their strengths and weaknesses. Recently, Jaubert et al.[1] proposed a reference database to evaluate the accuracy of an EoS or to cross-compare two EoS when they are used to correlate the properties of binary mixtures. Their proposed database contains phase equilibrium data (VLE, LLE, VLLE), property change on mixing data (enthalpy or heat capacity),[2] azeotropic data and critical point data for 200 binary systems made up of different pair combinations of 107 non-associating and self-associating pure compounds. In addition, a complete methodology was proposed to assess the performance of EoS to correlate (or predict) binary system behaviors.[3,4] However, it is well-known that, in order to properly correlate binary systems, an EoS must be able to accurately represent the pure-compound properties first. Regardless of the level of sophistication of any thermodynamic model or the number of parameters and form of the

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mixing rules employed, if the vapor pressures of each pure compound are inaccurate, the predictions of the binary system are compromised. As a convincing illustration, the reader is referred to Figure 3 in Agarwal et al.[5]

In this context, Piña-Martinez et al.[6] recently defined a database containing over 300,000 pseudo-experimental data points for pure components. These data come from a carefully selected portion of the DIPPR database[7] for 1800 different pure components representing all chemical families, and including 1252 non-self-associating (NSA) and 548 self-associating (SA) compounds. For each of the 1800 pure components, 50 vapor pressure and 50 liquid density pseudo-experimental data points were generated from the correlations available in the DIPPR database. Among the 1800 fluids, 1536 also possess an accurate correlation for $\Delta_{vap}H$ and 890 for $c^{sat}_{P,liq}$ making possible to generate 50 data points for each of these properties. The critical properties (T_c, P_c, and v_c) are available for the 1800 components so that in the end, the resulting database contains 306,700 high-quality pseudo-experimental data points. Although only the most accurate correlations available in the DIPPR database were kept (i.e., correlations with the lowest errors reported by the DIPPR), we cannot exclude the case where data with high experimental uncertainty would have been used by the DIPPR to determine the parameters of a correlation (as the DIPPR error only quantifies the mean deviation between data points and correlated data). Although the real experimental uncertainty is unknown, it is believed that DIPPR correlations associated with low errors are statistically accurate and can be used for determining EoS parameters.

Note: It is worth noting that EoS only predict residual properties. Consequently, for estimating liquid heat capacity, it is necessary to add a perfect-gas heat capacity term ($c_{P,PG}$) to the residual heat capacity. Therefore, an accurate correlation for the $c_{P,PG}(T)$ function is also needed when accurate $c^{sat}_{P,liq}$ data are available.

Table 1 summarizes the data available in such a database. For more details, and in particular the temperature range on which the data were generated, the reader is referred to the paper by Piña-Martinez et al.[6] Table 2 presents a summary of the chemical families in which the 1800 compounds are distributed. In addition, Table 2 presents the distribution of NSA and SA compounds among the chemical families. As previously stated, the 1800 pure compounds are divided into 1252 NSA compounds and 548 SA compounds so that the molecule dataset contains 70% of NSA and 30% of SA compounds. The process used to determine the associating character (NSA or SA) of a given molecule can be found in Piña-Martinez et al.[6] In short, the screening charge density distribution, sigma-profile (σ-profile), was generated for each compound. If the σ-profile presents peaks below a hydrogen-donor sigma-cutoff value and above a hydrogen-acceptor sigma-cutoff value, it is concluded that the molecule can form hydrogen bond (HB) with another similar molecule and thus tends to self-associate.

The above-presented database was used by Piña-Martinez et al.[6] in order to assess the accuracy of four cubic equations of state (CEoS): original SRK, original Peng–Robinson (PR), *tc*-RK, and *tc*-PR where *tc* designates the *translated* and *consistent*[8–10] versions of such EoS. In this article, we seek to assess the performances of molecular-based EoS, in particular those belonging to the statistical associating fluid theory (SAFT)[11] family. This type of EoS is far more recent than CEoS, as they have only been around for the last 30 years, while the CEoS have a century and a half long tradition. Thus, it is key to evaluate the performance of SAFT-type EoS as their powerful molecular-based theoretical background has proven to be efficient at modeling a wide array of compounds and mixtures. Their true power has however not yet been clearly assessed on thousands of pure components. In this article, it was decided—somewhat arbitrary—to focus on the following two versions of the SAFT EoS:

TABLE 1 Overview of the data available in the database proposed by Piña-Martinez et al.[6]

Property	Number of pure components for which the property is available	Number of data points
P^{sat}	1800	90,000 (50 per component)
v^{sat}_{liq}	1800	90,000 (50 per component)
$\Delta_{vap}H$	1536	76,800 (50 per component)
$c^{sat}_{P,liq}$ [a]	890	44,500 (50 per component)
T_c	1800	1800
P_c	1800	1800
v_c	1800	1800
Total		306,700

[a]An equivalent number of $c_{P,PG}$ data is available in order to be able to calculate $c^{sat}_{P,liq}$ from an EoS.

a. The perturbed chain SAFT (PC-SAFT) proposed by Gross and Sadowski,[12] which modifies the original SAFT EoS by using a hard-chain fluid as reference and using a dispersion term based on the perturbation theory of Barker and Henderson[13] and
b. The *Industrialized*-PC-SAFT (*I*-PC-SAFT) proposed by Moine et al.[14] which is a volume-translated version of the PC-SAFT EoS in which the three molecular parameters (m, σ, ε/k) are constrained to exactly reproduce the experimental critical temperature and pressure and the experimental acentric factor. The volume translation[15,16] is determined in order to exactly reproduce the liquid density at $T_r = 0.8$.

In this study, it was decided to evaluate the capabilities, strengths, and weaknesses of these models in their most basic form, that is, *without* adding an associating term.

There are two main reasons for this choice: the first is that we wanted to characterize the influence of the associating term, that is, to understand how associating compounds would be correlated in the absence of a specific associating term. The second one is that in many cases, users of commercial process simulators can be led to represent self-associating compounds with a SAFT-type EoS without any association term due to a lack of a database containing the associating parameters (by default, they are set to zero).

In summary, the performance of the PC-SAFT and the *I*-PC-SAFT EoS without an association term will be evaluated over a large number of non-associating and self-associating molecules by determining their capacity at correlating the following properties: P^{sat}, v^{sat}_{liq}, $\Delta_{vap}H$, $c^{sat}_{P,liq}$, T_c, P_c, and v_c.

TABLE 2 List of the chemical families and corresponding distribution of the 1800 pure compounds available in the database proposed by Piña-Martinez et al.[6]

Chemical family	Number of compounds	Proportion of compounds (%)	Number of NSA compounds	Number of SA compounds
Alcohols	131	7.3%	4	127
Alkanes	163	9.1%	163	0
Alkenes	122	6.8%	122	0
Alkynes	18	1.0%	18	0
Amines/amides	102	5.7%	0	102
Aromatics	158	8.8%	158	0
Epoxides	18	1.0%	16	2
Esters/ethers	238	13.2%	203	35
Halogen compounds	232	12.9%	197	35
Inorganic compounds	70	3.9%	61	9
Ketones/aldehydes	80	4.4%	78	2
Nitriles	31	1.7%	9	22
Nitrogen compounds	99	5.5%	64	35
Organic acids	82	4.6%	0	82
Organic salts	13	0.7%	11	2
Other compounds	9	0.5%	3	6
Peroxides	11	0.6%	3	8
Polyfunctional compounds	68	3.8%	14	54
Silicon compounds	61	3.4%	56	5
Sulfur compounds	94	5.2%	72	22
Total	1800	100%	1252 (70%)	548 (30%)

2 | BRIEF OVERVIEW OF THE STUDIED MOLECULAR-BASED EoS

2.1 | PC-SAFT EoS

The PC-SAFT EoS is the first model to be evaluated in this work and all the details about its theoretical basis can be found in the original publication by Gross and Sadowski.[12] The non-associating version of PC-SAFT is used in this article, which means that all components are treated as non-associating compounds, regardless of their affiliation as SA or NSA. The PC-SAFT requires three molecular parameters, proper of each individual pure compound: m, σ, and ε/k. The parametrization procedure used here is the one proposed by Ramirez-Velez et al.[17] In brief, optimal (m, σ, ε/k) parameters are obtained by minimizing an objective function (see Equation 1) that takes into account the deviations between calculated and experimental P^{sat} and ρ_{liq}^{sat} only:

$$\begin{cases} OF_{\text{component } j} = \dfrac{1}{N_T}\left[3\sum_{i=1}^{N_T}\left[\dfrac{P_{j,calc}^{sat}(T_i)-P_{j,\exp}^{sat}(T_i)}{P_{j,\exp}^{sat}(T_i)}\right]^2 + 2\sum_{i=1}^{N_T}\left[\dfrac{\rho_{liq,j,calc}^{sat}(T_i)-\rho_{j,\exp}^{sat}(T_i)}{\rho_{liq,j,\exp}^{sat}(T_i)}\right]^2\right]. \\ N_T = 50 \text{ is the number of temperature points} \end{cases} \quad (1)$$

The key point in Equation (1) is to use weighting factors for P^{sat} and ρ_{liq}^{sat} fixed at 3 and 2, respectively. Ramirez-Velez et al.[17] also concluded that including $\Delta_{vap}H$ and/or $c_{P,liq}^{sat}$ data in the regression procedure was not a necessity since it only marginally improved the reproduction of these properties and that not including either P^{sat} or ρ_{liq}^{sat} was highly unadvised. Resulting (m, σ, ε/k) parameters are reported in Appendix A1 for the 1800 pure components. It is believed

TABLE 3 MAPE on P^{sat}, v_{liq}^{sat}, $\Delta_{vap}H$, $c_{P,liq}^{sat}$, T_c, P_c, and v_c as predicted by the PC-SAFT, *I*-PC-SFAT, and *tc*-PR EoS

EoS	MAPE on P^{sat} (1800 fluids)	MAPE on v_{liq}^{sat} (1800 fluids) ($T_r < 0.9$)	MAPE on $\Delta_{vap}H$ (1536 fluids)	MAPE on $c_{P,liq}^{sat}$ (890 fluids)	MAPE on T_c (1800 fluids)	MAPE on P_c (1800 fluids)	MAPE on v_c (1800 fluids)	Global average deviation over the 306,700 available data points
PC-SAFT	1.18%	0.95%	3.25%	4.17%	2.28%	20.8%	4.38%	*2.2%*
I-PC-SAFT	2.08%	4.60%	4.00%	4.10%	0%[a]	0%[a]	12.4%	*3.6%*
tc-PR	0.98%	2.08%	1.92%	2.53%	0%[a]	0%[a]	19.6%	*1.9%*

[a]Such MAPEs are exactly zero since the *I*-PC-SAFT and *tc*-PR EoS are parameterized in order to exactly reproduce $T_{c,\exp}$ and $P_{c,\exp}$.

that this article is the first one in which molecular parameters suitable for the PC-SAFT EoS are published for 1800 pure compounds. Such parameters can be used immediately in any commercial process simulator and complete the set of parameters previously published by Ramirez-Velez et al.[17] for 1252 NSA components.

2.2 | *I*-PC-SAFT EoS

The *Industrialized*-PC-SAFT (*I*-PC-SAFT) EoS proposed by Moine et al.[14] is a volume-translated version of the original PC-SAFT, in which, molecular parameters of pure species are determined to exactly reproduce the experimental critical temperature, pressure, and acentric factor while the volume translation is calculated in order to exactly reproduce the experimental liquid density at $T_r = 0.8$. As an advantage of the parametrization method inherent to the *I*-PC-SAFT EoS, fastidious fitting procedures to experimental data are avoided; the three molecular parameters for a pure compound, are straightforwardly obtained from the following correlations:

$$\begin{cases} m_i \approx 0.5959\omega_{i,\exp}^2 + 7.5437\omega_{i,\exp} + 0.9729 \\ \varepsilon_i/k \approx T_{c,i,\exp}/\left(4.7968\cdot 10^{-6}m_i^5 - 3.0895\cdot 10^{-4}m_i^4 + 7.8649\cdot 10^{-3}m_i^3 - 0.10215m_i^2 + 0.75358m_i + 0.63659\right) \\ \sigma_i \approx \left[\varepsilon_i/k \cdot \frac{k}{P_{c,i,\exp}} 10^{\left(1.6345\cdot 10^{-7}m_i^6 - 1.1346\cdot 10^{-5}m_i^5 + 3.1389\cdot 10^{-4}m_i^4 - 4.4618\cdot 10^{-3}m_i^3 + 3.6282\cdot 10^{-2}m_i^2 - 0.22498m_i - 0.77655\right)}\right]^{1/3} \end{cases} \quad (2)$$

Resulting (m, σ, ε/k) parameters and the corresponding volume shift (c) are reported in Appendix A1 for the 1800 pure components.

expressed in terms of mean absolute percentage errors (MAPEs) defined by Equation (3) as the average of the absolute percentage deviations between experimental and calculated properties over N_T temperature points.

$$MAPE_X = \frac{100}{N_T}\sum_{i=1}^{N_T}\left|\frac{X_{j,\exp}(T_i) - X_{j,calc}(T_i)}{X_{j,\exp}(T_i)}\right|. \quad (3)$$

$X_{j,\exp}(T_i)$ and $X_{j,calc}(T_i)$ correspond to the calculated and experimental values of the component j's property X, at temperature T_i. In the present study, $N_T = 50$.

The MAPEs on $\left\{P^{sat}, v_{liq}^{sat}, \Delta_{vap}H, c_{P,liq}^{sat}, T_c, P_c, v_c\right\}$ are reported in Table 3 for the PC-SAFT and *I*-PC-SAFT EoS. The detail of deviations for each molecule are reported in Appendix A2. For possible comparison, the MAPEs obtained with the *tc*-PR EoS, which was found to be the most accurate of the four cubic equations of state evaluated against the same database in our previous article[6] are recalled.

As stated above, the parameters of the PC-SAFT EoS are fitted over experimental P^{sat} and v_{liq}^{sat} data. Table 3 shows that this equation is able to reproduce such data with a deviation close to 1% which is really excellent. The deviations on $\Delta_{vap}H$ and $c_{P,liq}^{sat}$ are higher but remain very good. The counterpart however is a huge deviation on the critical pressure.

The *I*-PC-SAFT EoS is parameterized in order to exactly reproduce the critical pressure and temperature but at the expense of a larger liquid density deviation, with an average value around 5%. Such an EoS should be particularly suitable to estimate non-volumetric properties of close-to-criticality fluids.

3 | ASSESSING THE ACCURACY OF THE PC-SAFT AND *I*-PC-SAFT EoS: RESULTS AND DISCUSSION

In this section, the performances of PC-SAFT and *I*-PC-SAFT are evaluated by assessing their accuracy over the 306,700 data points relative to the 1800 pure compounds contained in the reference database proposed by Piña-Martinez et al.[6] Deviations are

TABLE 4 MAPE on P^{sat}, v_{liq}^{sat}, $\Delta_{vap}H$, $c_{P,liq}^{sat}$, T_c, P_c, and v_c depending on the associating character (NSA or SA) of the fluids as predicted by the PC-SAFT, *I*-PC-SFAT, and *tc*-PR EoS

EoS		MAPE on P^{sat} (1800 fluids)	MAPE on v_{liq}^{sat} (1800 fluids) ($T_r < 0.9$)	MAPE on $\Delta_{vap}H$ (1536 fluids)	MAPE on $c_{P,liq}^{sat}$ (890 fluids)	MAPE on T_c (1800 fluids)	MAPE on P_c (1800 fluids)	MAPE on v_c (1800 fluids)	Global average deviation
PC-SAFT	NSA	0.97% (1252 fluids)	0.85% (1252 fluids)	3.04% (1114 fluids)	3.35% (695 fluids)	2.34% (1252 fluids)	20.5% (1252 fluids)	3.95% (1252 fluids)	2.0% (*219,406 data points*)
	SA	1.66% (548 fluids)	1.19% (548 fluids)	3.78% (422 fluids)	7.07% (195 fluids)	2.15% (548 fluids)	21.5% (548 fluids)	5.34% (548 fluids)	2.8% (*87,294 data points*)
I-PC-SAFT	NSA	1.83%	4.35%	3.68%	3.27%	0%[a]	0%[a]	12.1%	3.3%
	SA	2.65%	5.18%	4.84%	7.05%	0%[a]	0%[a]	13.0%	4.5%
tc-PR	NSA	0.91%	2.00%	1.96%	2.07%	0%[a]	0%[a]	19.1%	1.8%
	SA	1.15%	2.28%	1.83%	4.17%	0%[a]	0%[a]	20.7%	2.1%

[a]Such MAPEs are exactly zero since the *I*-PC-SAFT and *tc*-PR EoS are parameterized in order to exactly reproduce $T_{c,\exp}$ and $P_{c,\exp}$.

As discussed in one of our previous papers,[14] the main difference between PC-SAFT and *I*-PC-SAFT is the parameterization that modifies dramatically the model performances especially, the capability to predict v_{liq}^{sat} and P_c. From Table 3, it can be concluded that a choice has to be made between an accurate correlation of v_{liq}^{sat} or P_c: it is indeed impossible to obtain simultaneously accurate predictions for both properties. In accordance with Moine et al.,[14] it is believed that the embedding of three component-dependent parameters in an EoS is not enough to describe accurately all the properties of a pure component.

The PC-SAFT and *tc*-PR EoS have similar accuracy. The PC-SAFT EoS, however predicts better liquid molar volumes, whereas the *tc*-PR EoS takes the lead for the correlation of the critical coordinates (T_c and P_c) and the energetic properties ($\Delta_{vap}H$ and $c_{P,liq}^{sat}$). To answer a question raised by one of the reviewers of this article, speed of sound (w) and Joule–Thomson coefficients (μ_{JT}) data were not included in the proposed database simply because such data are only available for a restraint number of pure components. What can be said about their correlation? It is believed that SAFT-type EoS should correlate such data more accurately than CEoS because the parametrization of CEoS, that gives priority to the reproduction of critical coordinates and vapor pressure data, entails a non-satisfactorily reproduction of the isothermal compressibility (κ_T) and the isobaric volume expansivity (α_P) that are needed to calculate w and μ_{JT} through the following equation:

$$\begin{cases} w = v\sqrt{\dfrac{c_P/c_v}{M(\kappa_T v)}} & \text{with: } \kappa_T v = -\left(\frac{\partial v}{\partial P}\right)_T \\ \mu_{JT} = \dfrac{v(\alpha_P T - 1)}{c_P} & \text{with: } \alpha_P = \dfrac{1}{v}\left(\dfrac{\partial v}{\partial T}\right)_P \end{cases}. \tag{4}$$

Due to their parametrization that traditionally involves liquid-density data, SAFT EoS are less concerned with this shortcoming.

3.1 | Influence of the associating character of components

As made in our previous paper devoted to CEoS, we believe interesting to investigate if the MAPEs reported in Table 3 are significantly different between the NSA and SA components. Indeed, as previously stated, the evaluated SAFT-type EoS do not include an association term. MAPE on P^{sat}, v_{liq}^{sat}, $\Delta_{vap}H$, $c_{P,liq}^{sat}$, T_c, P_c, and v_c for the 1252 NSA and 548 SA compounds are shown in Table 4. It can be observed that for both SAFT-type EoS (PC-SAFT and *I*-PC-SAFT), the difference in performance between NSA and SA compounds is more pronounced than with the *tc*-PR EoS. When SAFT-type EoS are used, the global average deviation increases of about 1% when we move from the NSA to the SA compounds. Although significant, this increase is not very large and the deviations observed for SA compounds remain quite acceptable for most of practical applications. As it was previously observed with CEoS,[6] the most impacted property is $c_{P,liq}^{sat}$ for which the deviation more than doubles when switching from NSA to SA compounds. It is however believed that the large MAPEs on $c_{P,liq}^{sat}$

TABLE 5 MAPE on P^{sat}, v_{liq}^{sat}, $\Delta_{vap}H$, $c_{P,liq}^{sat}$, T_c, P_c, and v_c as predicted by the PC-SAFT EoS for the 20 chemical families defined in Table 2

	MAPE on:							
Chemical family	P^{sat}	v_{liq}^{sat}	$\Delta_{vap}H$	$c_{P,liq}^{sat}$	T_c	P_c	v_c	**Global average deviation**
Alcohols	2.23%	1.33%	4.47%	10.6%	1.23%	14.8%	5.21%	**3.6%**
Alkanes	0.55%	0.62%	2.30%	1.85%	2.15%	18.4%	3.49%	**1.4%**
Alkenes	0.78%	0.71%	3.13%	3.03%	2.18%	18.5%	2.79%	**2.0%**
Alkynes	1.05%	0.84%	3.08%	3.08%	1.84%	14.2%	2.81%	**2.0%**
Amines/amides	1.28%	0.85%	3.27%	5.08%	2.01%	18.6%	5.68%	**2.2%**
Aromatics	0.84%	0.95%	3.05%	2.53%	2.80%	25.6%	3.03%	**1.9%**
Epoxides	0.60%	0.73%	2.85%	3.88%	2.61%	19.9%	4.73%	**2.0%**
Esters/ethers	1.10%	0.71%	2.94%	3.65%	2.15%	21.5%	4.45%	**1.9%**
Halogen compounds	1.04%	0.91%	3.32%	4.41%	2.51%	20.1%	3.18%	**2.2%**
Inorganic compounds	2.04%	1.52%	4.42%	7.32%	2.34%	19.1%	9.89%	**3.5%**
Ketones/aldehydes	0.99%	0.84%	3.34%	3.59%	2.70%	23.5%	2.10%	**2.0%**
Nitriles	2.42%	2.81%	5.80%	7.50%	5.67%	56.2%	5.25%	**4.4%**
Nitrogen compounds	1.38%	1.32%	3.60%	3.41%	2.82%	25.3%	5.61%	**2.3%**
Organic acids	1.53%	0.97%	3.83%	9.01%	1.96%	23.6%	5.15%	**2.7%**
Organic salts	1.72%	1.49%	3.61%	3.48%	3.01%	27.0%	8.01%	**2.4%**
Other compounds	2.27%	1.32%	4.57%	3.25%	2.55%	21.8%	6.17%	**2.8%**
Peroxides	1.30%	1.18%	3.16%	3.57%	0.82%	8.38%	6.79%	**2.0%**
Polyfunctional compounds	1.32%	1.02%	3.08%	8.44%	1.86%	17.4%	5.08%	**2.3%**
Silicon compounds	1.26%	0.88%	3.12%	5.91%	1.62%	15.4%	4.28%	**2.2%**
Sulfur compounds	0.80%	0.77%	2.54%	2.78%	2.34%	18.9%	4.78%	**1.7%**

observed for SA compounds are not very significant for two reasons: (i) less than 200 SA compounds have experimental $c_{P,liq}^{sat}$ data and (ii) the calculated standard deviation on heat capacities is high (>5%) as a consequence of huge deviations observed for a small number of components. In other words, a small number of huge deviations tend to increase a lot the value of the average MAPE, making it biased.

From Tables 5 and 6, which give the MAPE on P^{sat}, v_{liq}^{sat}, $\Delta_{vap}H$, $c_{P,liq}^{sat}$, T_c, P_c, and v_c for each chemical family of compounds as defined in Table 2, the same conclusion is reached: alcohols, amines/amides, nitriles, nitrogen compounds, organic acids, and peroxides that tend to self-associate show higher deviations than hydrocarbons (alkanes, alkenes, alkynes) but the difference in accuracy due to association is not always obvious. As an example, regardless of the SAFT-type EoS, the global average deviation on amines/amides, nitrogen compounds, and epoxides is similar to the average deviation observed on alkenes.

Tables 5 and 6 also highlight that the highest deviations are obtained with nitriles. Such an unexpected result can be explained by noticing that most of the 31 nitriles available in the DIPPR are polyfunctional (in additional to the nitrile group, some contain double bonds, others contain a hydroxyl group, a NH_2 group, a methoxy group, ...). It is believed that such a complexity explains better the observed loss of accuracy than the associating character of such components.

To have a deeper insight into the role played by association and to better understand the relationship between the ability of an EoS to accurately reproduce the properties of pure species and the strength of association, it is now decided to use the criterion for quality modeling defined in our previous paper.[6] Using this latter, molecules will be labeled as well or badly represented and it will be possible to analyze how the SA and NSA fluids distribute between the two categories. The proposed criterion of modeling quality compares the deviations obtained on P^{sat} and v_{liq}^{sat} for a given fluid to the mean deviations obtained for all the NSA fluids. For a given molecule, if deviations on P^{sat} and v_{liq}^{sat} are slightly lower than the corresponding mean values for NSA fluids, the molecule is considered as well-modeled. Otherwise, it falls in the badly-modeled category.

Quantitatively speaking, a pure component j will be considered as well-modeled by a given EoS provided:

$$\begin{cases} \left(MAPE_{P^{sat}}^{EoS}\right)_j \leq \overline{MAPE}_{P^{sat}}^{EoS,NSA} + SD_{P^{sat}}^{EoS,NSA} \\ \text{and} \\ \left(MAPE_{v_{liq}^{sat}}^{EoS}\right)_j \leq \overline{MAPE}_{v_{liq}^{sat}}^{EoS,NSA} + SD_{v_{liq}^{sat}}^{EoS,NSA} \end{cases} . \quad (5)$$

where $SD_X^{EoS,NSA}$ and $\overline{MAPE}_X^{EoS,NSA}$ denote the mean standard deviation (SD) and MAPE for property X calculated with a given EoS over the 1252 NSA components of the database (see Table 7 for the numerical values). If one or both conditions of Equation (5) are not satisfied, the pure component is considered as badly-modeled. Results are

TABLE 6 MAPE on P^{sat}, v_{liq}^{sat}, $\Delta_{vap}H$, $c_{P,liq}^{sat}$, T_c, P_c, and v_c as predicted by the *I*-PC-SAFT EoS for the 20 chemical families defined in Table 2

	MAPE on:							
Chemical family	P^{sat}	v_{liq}^{sat}	$\Delta_{vap}H$	$c_{P,liq}^{sat}$	T_c	P_c	v_c	**Global average deviation**
Alcohols	3.50%	4.12%	5.77%	10.8%	0.0%	0.0%	9.89%	***5.1%***
Alkanes	1.25%	4.46%	3.02%	1.83%	0.0%	0.0%	11.1%	**2.7%**
Alkenes	1.66%	4.14%	3.42%	3.00%	0.0%	0.0%	10.7%	**3.1%**
Alkynes	2.19%	2.70%	3.59%	2.39%	0.0%	0.0%	9.25%	**2.7%**
Amines/amides	2.31%	4.21%	4.16%	4.40%	0.0%	0.0%	9.51%	***3.6%***
Aromatics	1.68%	4.90%	3.73%	2.87%	0.0%	0.0%	13.7%	**3.3%**
Epoxides	1.22%	4.00%	3.07%	3.26%	0.0%	0.0%	12.8%	**2.9%**
Esters/ethers	2.18%	4.87%	4.12%	3.18%	0.0%	0.0%	14.2%	**3.7%**
Halogen compounds	1.83%	3.95%	3.54%	4.24%	0.0%	0.0%	10.8%	**3.3%**
Inorganic compounds	2.69%	4.49%	3.58%	8.12%	0.0%	0.0%	16.2%	**4.4%**
Ketones/aldehydes	1.61%	4.29%	4.23%	3.88%	0.0%	0.0%	12.0%	**3.4%**
Nitriles	2.30%	16.0%	5.68%	8.67%	0.0%	0.0%	26.9%	***8.2%***
Nitrogen compounds	2.23%	4.86%	4.55%	3.83%	0.0%	0.0%	11.7%	***3.8%***
Organic acids	2.90%	5.17%	5.68%	9.13%	0.0%	0.0%	16.1%	***4.9%***
Organic salts	2.81%	6.22%	5.39%	3.83%	0.0%	0.0%	17.8%	**4.8%**
Other compounds	2.93%	4.37%	7.37%	2.72%	0.0%	0.0%	16.2%	**4.6%**
Peroxides	2.15%	2.60%	3.89%	3.53%	0.0%	0.0%	8.57%	***2.9%***
Polyfunctional compounds	2.27%	4.19%	4.52%	7.98%	0.0%	0.0%	10.8%	**3.9%**
Silicon compounds	2.44%	4.04%	4.25%	5.32%	0.0%	0.0%	9.56%	**3.7%**
Sulfur compounds	1.48%	3.96%	3.22%	1.84%	0.0%	0.0%	12.9%	**2.7%**

TABLE 7 Average MAPE on P^{sat} and v_{liq}^{sat} as predicted by the PC-SAFT and *I*-PC-SAFT for the 1252 NSA compounds and corresponding standard deviations (SD)

PC-SAFT			
MAPE on P^{sat} (%)	0.97%	MAPE on v_{liq}^{sat}	0.85%
SD on P^{sat} (%)	0.95%	SD on v_{liq}^{sat}	0.74%
MAPE + SD (%)	**1.92%**	MAPE + SD	**1.59%**
I-PC-SAFT			
MAPE on P^{sat}	1.83%	MAPE on v_{liq}^{sat}	4.35%
SD on P^{sat}	1.54%	SD on v_{liq}^{sat}	2.95%
MAPE + SD	**3.38%**	MAPE + SD	**7.30%**

presented in Figures 1 and 2 for the PC-SAFT and *I*-PC-SAFT EoS and deserve discussion. For possible comparison, results obtained with the *tc*-PR EoS, as published in our previous paper,[6] are recalled in Figure 3. A major feature is the huge similitude between SAFT-type EoS and the *tc*-PR EoS. Indeed, regardless of the considered EoS (PC-SAFT, *I*-PC-SAFT, or *tc*-PR), about 75% of the pure components are well-represented, according to the criterion defined in Equation (5) (see the left panel in each figure). As reported in Table 2, the database contains 70% of NSA fluids and 30% of SA components. In the absence of an association term, it could be believed that the well-modeled molecules are essentially NSA fluids. This is however not the case at all. Indeed, as previously reported in our article devoted to CEoS, almost 65% of the SA molecules are well-modeled (see the right panel in Figures 1–3), while almost 17% of the NSA compounds are badly-modeled (refer to the middle panel in Figures 1–3). Once again, we might have been tempted to believe that all the NSA fluids would be well-modeled by SAFT-type EoS that do not embed an association term, but this is not the case. Similarly, one would not have predicted that more than half of the SA molecules would be accurately modeled in the absence of an association term.

In order to go further, it was decided to investigate a potential correlation between the strength of the hydrogen bond and the accuracy with which the experimental data were correlated. In other words, working with SA compounds, we wanted to investigate if it was possible to claim that properties of weakly-associating molecules are better correlated by non-associating versions of EoS than those of strongly-associating molecules.

To answer this question, the COSMOtherm tool for predictive property calculation of liquids that combines quantum chemistry and the COSMO-RS thermodynamic model[18,19] was used to calculate the hydrogen-bond enthalpy ($-\Delta_{HB}H$) of the 548 SA fluids. The reason for such a choice is twofold. First, we are not aware of the existence of another predictive model and second its high accuracy has been demonstrated by Klamt et al.[20,21] These latter conclude one of their

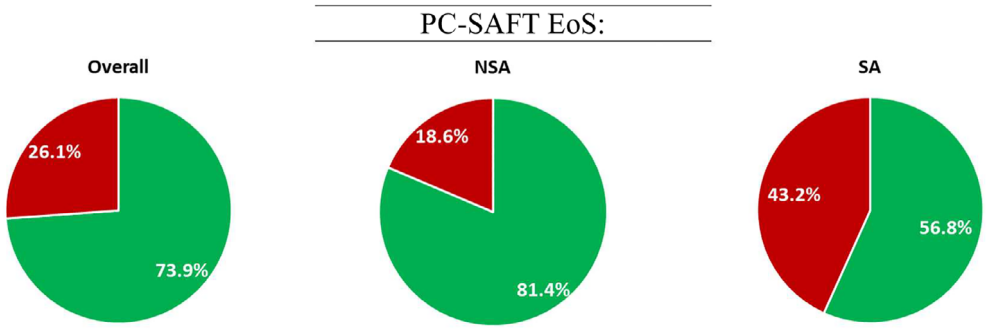

FIGURE 1 Ratio of well and badly modeled molecules by the PC-SAFT EoS classified into non-self-associating (NSA) and self-associating (SA) fluids. Green: Well-modeled molecules. Red: Badly-modeled molecules

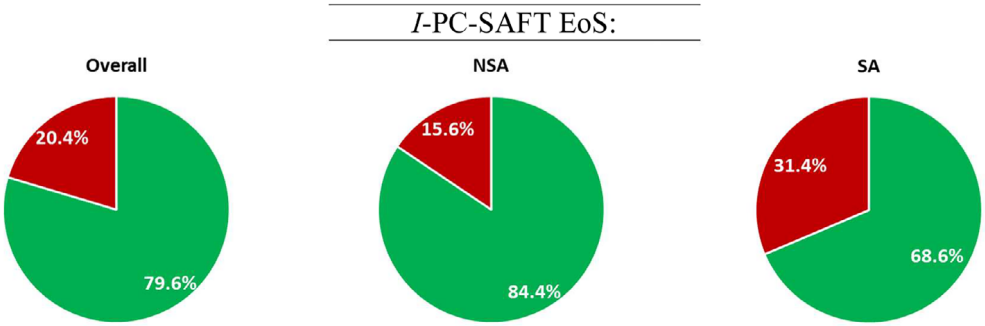

FIGURE 2 Ratio of well and badly modeled molecules by the *I*-PC-SAFT EoS classified into non-self-associating (NSA) and self-associating (SA) fluids. Green: Well-modeled molecules. Red: Badly-modeled molecules

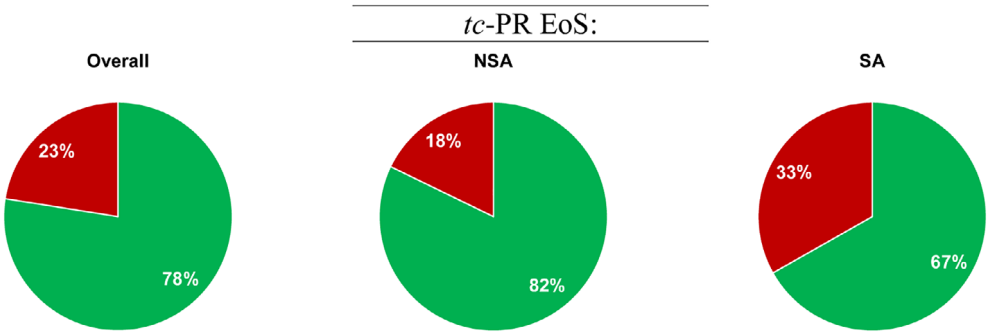

FIGURE 3 Ratio of well and badly modeled molecules by the *tc*-PR EoS classified into non-self-associating (NSA) and self-associating (SA) fluids. Green: Well-modeled molecules. Red: Badly-modeled molecules

papers[21] by: "the relations presented herein between experimental hydrogen-bond enthalpies and the COSMO polarization charge densities σ, established for an unprecedented chemically diverse sample, can be used for the prediction of hydrogen-bond enthalpies of compounds for which experimental data are not available or even not experimentally accessible, for example, in the case of multiple competing hydrogen-bond acceptors."

The hydrogen-bond enthalpy, assumed to be proportional to the strength of the association was plotted as a function of (MAPE on P^{sat} + MAPE on v_{liq}^{sat}) which is believed to be a good indicator of the accuracy with which the data are correlated. The results can be seen in Figures 4–6 for the PC-SAFT, *I*-PC-SAFT and *tc*-PR EoS. Such figures speak by themselves: regardless of the EoS, there is absolutely no correlation between the strength of association and the EoS accuracy. It is possible to find strongly-associating molecules (for which $-\Delta_{HB}H > 25$ kJ mol^{-1}) that are very accurately correlated. Examples are: L-phenylalanine, 1,4-cyclohexanedicarboxylic acid, and pyridine-3-carboxylic acid. Conversely, slightly-associating molecules ($-\Delta_{HB}H < 3$ kJ mol^{-1}) that exhibit very large deviations can be found. Among others, examples are: ethylene carbonate, nitroethane, or succinic anhydride that are highlighted in Figures 4–6. From Figures 4–6, we can even assert that regardless of the EoS, the component that has the highest hydrogen-bond enthalpy is well-represented, while the SA compound having the smallest hydrogen-bond enthalpy is badly-represented. Such results do not help to decide in which direction efforts have to be devoted to improve SAFT-type and CEoS without association term. It seems thus legitimate to wonder if the addition of an association term is really the most suited solution. Although this question will be addressed in a subsequent paper, it is important to state that so far, numerous studies with different versions of SAFT-type EoS have demonstrated that this addition substantially improved modeling of phase equilibria in mixtures. As highlighted in many papers,[22–24] this is also true for the CPA (Cubic Plus Association) EoS. Regarding the *I*-PC-SAFT EoS, the weak point of which is unsatisfactory liquid phase volumes, a promising direction to improve its accuracy could be a re-evaluation of the PC-SAFT universal parameters matrix. Indeed, both Liang et al.[25] and

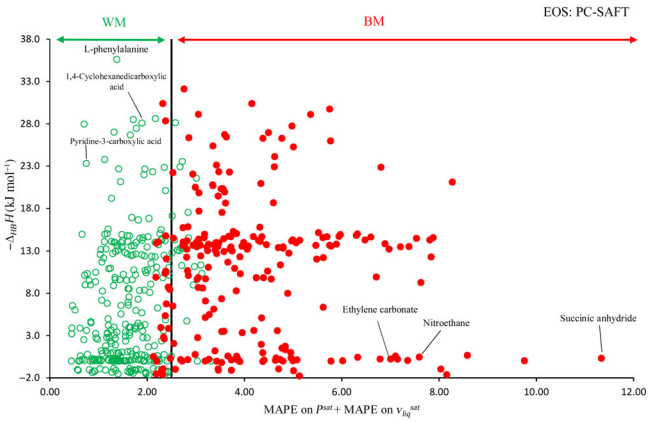

FIGURE 4 Hydrogen-bond enthalpy vs. (MAPE on P^{sat} + MAPE on v_{liq}^{sat}) for the 548 SA compounds modeled with the PC-SAFT EoS. ○: 311 well-modeled components. ●: 237 badly-modeled components. The vertical line is an approximate border between the region where the fluids are well-modeled (WM) and badly-modeled (BM)

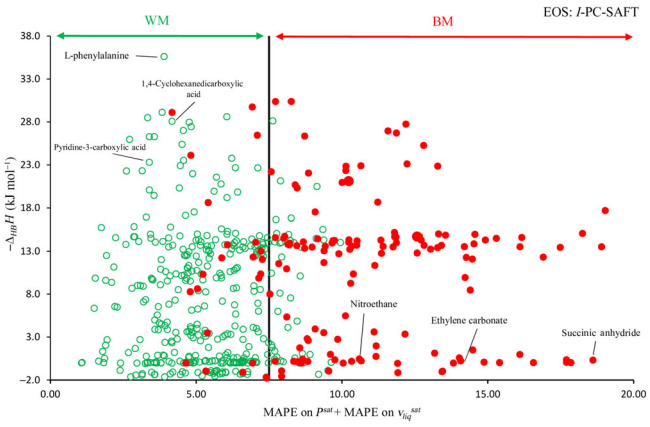

FIGURE 5 Hydrogen-bond enthalpy vs. (MAPE on P^{sat} + MAPE on v_{liq}^{sat}) for the 548 SA compounds modeled with the *I*-PC-SAFT EoS. ○: 377 well-modeled components. ●: 171 badly-modeled components. The vertical line is an approximate border between the region where the fluids are well-modeled (WM) and badly-modeled (BM)

Polishuk,[26] demonstrated that the precision in predicting the liquid phase densities and sound velocities, could be remarkably increased with new parameters.

Finally, a closer inspection across various chemical families (as defined by the DIPPR) is proposed. Table 8 shows the distribution of well-modeled compounds for different chemical families and for the three EoS (PC-SAFT, *I*-PC-SAFT, and *tc*-PR). Once again, the similitude of the results obtained with SAFT-type and cubic EoS can be highlighted. It is possible to observe that the three EoS have a ratio of well-modeled molecules greater than 65% and often close to 80% for alkanes, alkenes, alkynes, aromatics, esters, ethers, ketones, aldehydes, epoxides, peroxides, halogen compounds, amines, amides, sulfur, and silicon compounds. Alcohols have >50% of well-modeled molecules except with the PC-SAFT model which yields a ratio of

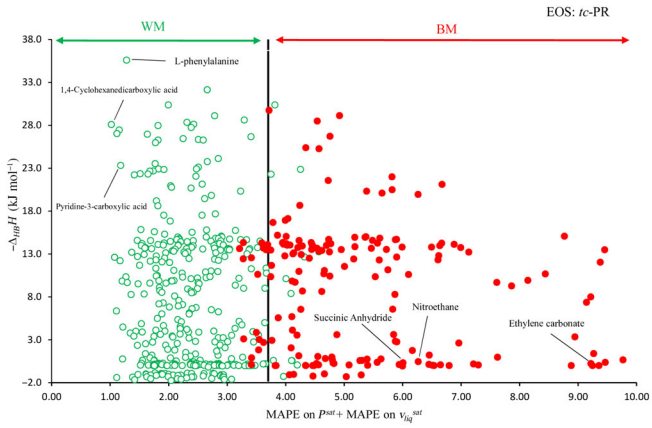

FIGURE 6 Hydrogen-bond enthalpy vs. (MAPE on P^{sat} + MAPE on v_{liq}^{sat}) for the 548 SA compounds modeled with the *tc*-PR EoS. ○: 366 well-modeled components. ●: 182 badly-modeled components. The vertical line is an approximate border between the region where the fluids are well-modeled (WM) and badly-modeled (BM)

TABLE 8 Distribution of well-modeled compounds across different chemical families for the PC-SAFT, *I*-PC-SAFT, and *tc*-PR EoS

Chemical family	PC-SAFT	*I*-PC-SAFT	*tc*-PR[a]
Alcohols	32%	54%	53%
Alkanes	96%	96%	94%
Alkenes	93%	88%	87%
Alkynes	67%	83%	83%
Amines/amides	69%	79%	68%
Aromatics	85%	88%	83%
Epoxides	94%	94%	83%
Esters/ethers	83%	78%	79%
Halogen compounds	74%	84%	80%
Inorganic compounds	60%	69%	60%
Ketones/aldehydes	83%	86%	93%
Nitriles	29%	36%	35%
Nitrogen compounds	69%	72%	75%
Organic acids	59%	65%	79%
Organic salts	54%	62%	46%
Other compounds	56%	78%	44%
Peroxides	73%	91%	73%
Polyfunctional compounds	72%	82%	74%
Silicon compounds	64%	71%	72%
Sulfur compounds	88%	97%	90%

[a]Reproduced from our previous article.[6]

32%. To give proof once again of the absence of correlation between the strength of association and the accuracy of the EoS we can have a closer look at two emblematic families that are the alcohols and the amines. Whatever the linear alcohol (from methanol to docosanol), the COSMOtherm tool calculates a nearly constant hydro-bond

enthalpy which is close to 14 kJ mol^{-1}. However as can be concluded from Table 8, some of them are well-modeled whereas others are badly-modeled. For *normal* amines ranging from methylamine to *n*-tetradecylamine, COSMOtherm returns very similar values, close to 3 kJ mol^{-1} for the hydro-bond enthalpy. However, as shown in Table 8, whatever the EoS the corresponding accuracy is not the same for all the amines: 70% are well-modeled whereas 30% are badly modeled.

4 | CONCLUSION

In this article, two non-associating versions of the popular PC-SAFT EoS were evaluated and contrasted in their performance on the basis of pure-compound property prediction. The first version was the original PC-SAFT EoS with a recently proposed parametrization strategy in which the three molecular parameters m, σ, ε/k_B are fitted to experimental P^{sat} and ρ_{liq}^{sat} data with specific weights assigned to them in the objective function to be minimized. The second version was the *industrialized* PC-SAFT or *I*-PC-SAFT EoS which estimates the three molecular parameters by exactly reproducing the experimental critical coordinates and acentric factor ($T_{c,\text{exp}}$, $P_{c,\text{exp}}$, ω_{exp}). Such an EoS is volume-translated and the volume shift (c) is determined in order to exactly reproduce the saturated liquid molar volume at the reduced temperature of 0.8.

The assessment was performed over 1800 molecules that have accurate P^{sat} and ρ_{liq}^{sat} correlations in the DIPPR databank making possible to generate accurate pseudo-experimental data. Among the 1800 fluids, 1536 also possess an accurate correlation for $\Delta_{vap}H$ and 890 for $c_{P,liq}^{sat}$ making possible to generate 50 data points for such properties. The critical properties (T_c, P_c, and v_c) are available for the 1800 components so that in the end, the resulting database contains 306,700 high-quality pseudo-experimental points. These 1800 molecules were divided into 1252 non-self-associating (NSA) compounds and 548 self-associating (SA) compounds.

Results obtained over the entire database highlight:

- The very high accuracy of both SAFT-type EoS that got an average overall deviation of 2.2% and 3.6% over the 306,700 experimental data points respectively. Deviations on the derived properties ($\Delta_{vap}H$ and $c_{P,liq}^{sat}$) are around 4% which is higher than those observed for vapor pressures and liquid densities. For possible comparison, the *tc*-PR EoS, which was found to be the most accurate cubic EoS got an average deviation of 1.9% over the entire database.
- The strong influence of the parameterization: the PC-SAFT EoS is parameterized in order to minimize the deviations between experimental and calculated P^{sat} and v_{liq}^{sat} data so that such properties are perfectly correlated. The counterpart is a large deviation on the critical pressure. On the other hand, the *I*-PC-SAFT is parameterized in order to exactly reproduce the critical coordinates in a (P,T) plane but the prize is a loss of accuracy in the correlation of liquid densities, especially the critical volume although a volume translation is applied.
- The absence of correlation between the strength of association and the EoS accuracy. Among the 548 self-associating components, the one that has the highest hydrogen-bond enthalpy is well-represented, whereas the one that has the smallest hydrogen-bond enthalpy is badly-represented. In addition, poor results are obtained for more than 15% of the non-self-associating compounds. Such a disappointing result was not expected from molecular-based equations of state. Simultaneously, the PC-SAFT equation is able to correlate with high accuracy (deviations lower than 2%) the vapor pressures and the liquid densities of about 60% of the self-associating compounds. This second result is even less expected since no association term was included in the considered equations of sate. Such results do not help to decide in which direction efforts have to be devoted to improve SAFT-type and cubic EoS that do not embed an association term. Is the addition of an association term really the most suited solution?

Let us also recall that this article is the first one in which molecular parameters suitable for the PC-SAFT and *I*-PC-SAFT EoS are published for 1800 pure compounds. Such parameters can be used immediately in any commercial process simulator.

Finally, the authors hope that the database used in this article and also in a previous one dedicated to cubic EoS will be widely adopted by the scientific community to identify the strengths and weaknesses of a given thermodynamic model to correlate (or predict) the properties of pure compounds.

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AUTHOR CONTRIBUTIONS

Nicolás Ramírez-Vélez: Software (equal); writing – original draft (equal). **Andrés Piña-Martinez:** Software (equal). **Jean-Noël Jaubert:** Conceptualization (equal); supervision (equal); writing – review and editing (equal). **Romain Privat:** Conceptualization (equal); supervision (equal); writing – review and editing (equal).

DATA AVAILABILITY STATEMENT

The data that support the findings of this study were used under license for this study. They are available from DIPPR's Project 801 Database: https://www.aiche.org/dippr

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