Evaluating the performance of well-established cubic and SAFT-type equations of state over thousands of pure-component experimental data points

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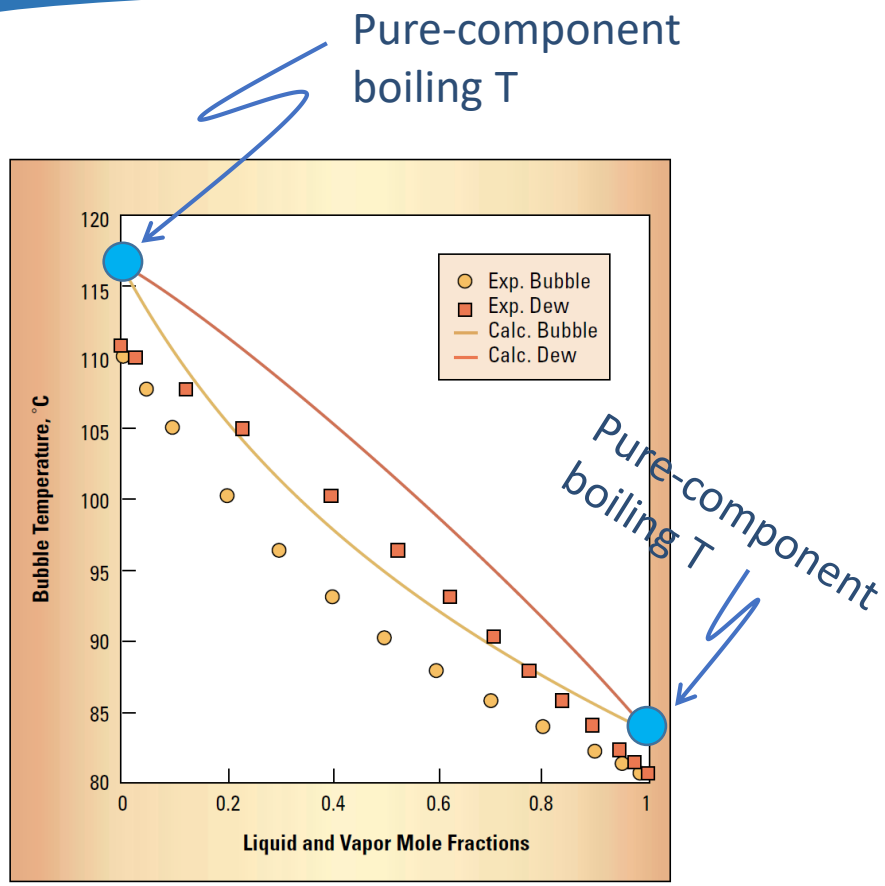
Why EoSs for pure components ?



Presentation devoted to pure components only

"Regardless of the sophistication of your thermodynamic model and the number of parameters in the mixing rule, you are in trouble if the PURE COMPONENTS are inaccurate."

Agarwal et al. 2001: Uncovering the realities of simulation. Part II.

Outline

- Constitution of a pure-component reference database to assess the performances of EoS
- An entirely transparent and universal protocol to parameterize cubic and (non-associating) SAFT-type EoS
- Evaluation of cubic and SAFT-type EoS *performances* over 300 000 data points
- Discussion on the correlation between the strength of association and the model accuracy

PART 1: Constitution of a pure-component reference database to assess the performances of EoS

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- The proposed database is a carefully selected fraction of the:

DIPPR *Design Institute for Physical Properties*

Which properties ?

Critical constants

- Critical temperature
- Critical pressure
- Critical volume

T-dependent

- Vapor pressure
- Liquid density
- Enthalpy of vaporization
- Liquid heat capacity

when available

Part 1. Constitution of a pure-component reference database to assess the performances of EoS

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when available

50 data points per property (T_{tr} < T < T_c)

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Constant

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DIPPR *Design Institute for Physical Properties*

How many components?

All those for which accurate correlations were available

- 1 800 pure components.
- 20 chemical families.

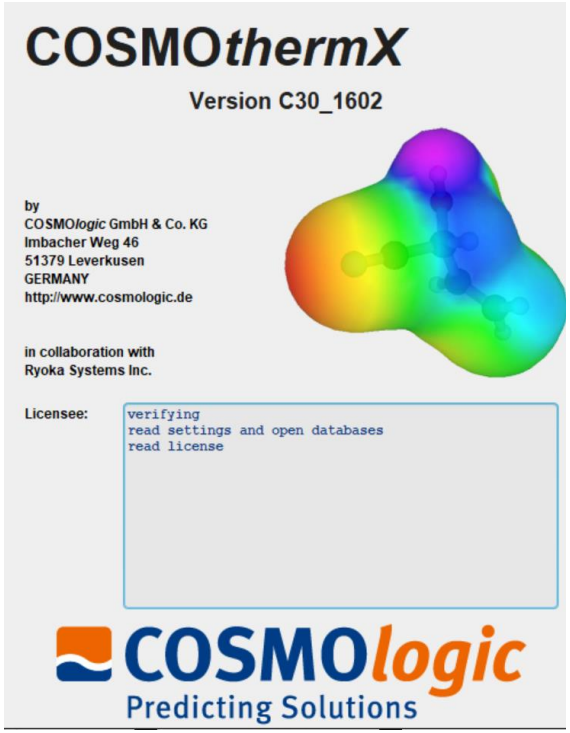
306 700 experimental data points

Part 1. Constitution of a pure-component reference database to assess the performances of EoS

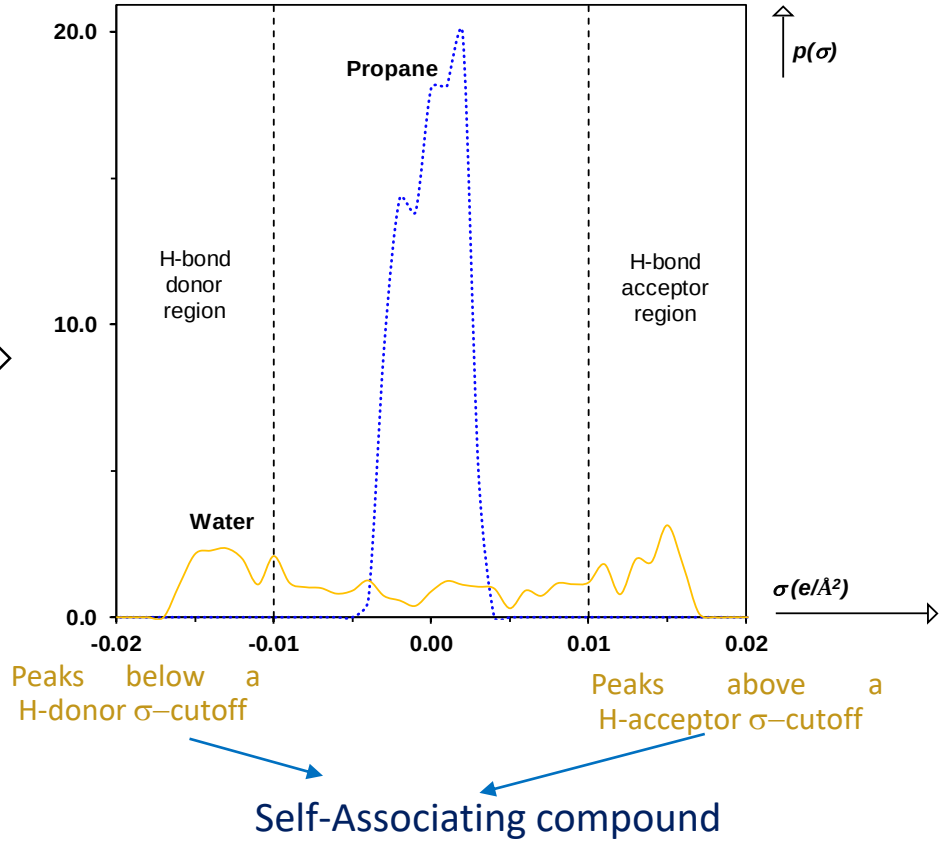
- To better assess the performances of an EoS, the 1 800 pure components were classified as SA and NSA

Self-Associating compounds

Non-Self-Associating compounds



σ-profile



Part 1. Constitution of a pure-component reference database to assess the performances of EoS

Properties

Constant	T-dependent
Critical temperature	Vapor pressure (1800)
Critical pressure	Liquid density (1800)
Critical volume	Enthalpy of vaporization (1536)
	Heat capacity (890)

306 700 experimental data points

DIPPR *Design Institute for Physical Properties*

- 1 800 pure components.
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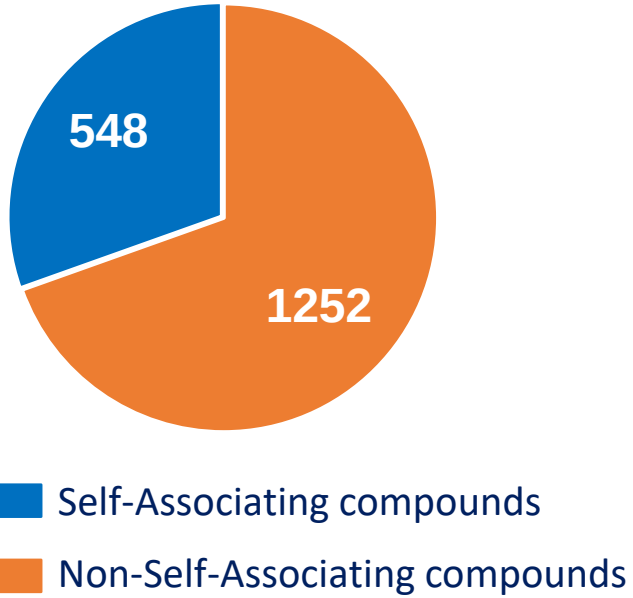

Piña-Martinez, A.; Privat, R.; Jaubert, J.-N. *AIChE J.* 2021.

PART 2: Entirely transparent and universal protocol to parameterize cubic and non-associating SAFT-type EoS

3 EoS are considered:

- *tc*-PR (*translated-consistent* Peng-Robinson)
- PC-SAFT (non-associating)
- *I*-PC-SAFT (*Industrialized*-PC-SAFT)

The *tc*-PR EoS

***translated and consistent (tc)*-PR CEoS**

$$P(T,v)=\frac{RT}{(v+c)-b}-\frac{a_c\cdot\alpha(T_r)}{(v+c)(v+c+b)+b(v+c-b)}$$

$$\begin{cases} a_c = 0.45724\dfrac{R^2T_{c,exp}^2}{P_{c,exp}} \\ b = 0.07780\dfrac{RT_{c,exp}}{P_{c,exp}} \end{cases}$$

Volume-translation parameter

$$c = v_{liq}^{sat,tc-PR}(T_r=0.8)-v_{liq,exp}^{sat}(T_r=0.8)$$

Consistent Twu91 α-function

$$\alpha(T_r)=T_r^{N(M-1)}\exp\left[L\left(1-T_r^{MN}\right)\right]$$

L,M,N determined so that the α-function passes the *consistency test* of Le Guennec et al. (2016)

$$\begin{cases} \alpha(T_r)\geq 0 \text{ and } \alpha \text{ continuous} \\ \dfrac{d\alpha}{dT_r}(T_r)\leq 0 \text{ and } \dfrac{d\alpha}{dT_r} \text{ continuous} \\ \dfrac{d^2\alpha}{dT_r^2}(T_r)\geq 0 \text{ and } \dfrac{d^2\alpha}{dT_r^2} \text{ continuous} \\ \dfrac{d^3\alpha}{dT_r^3}(T_r)\leq 0 \end{cases}$$

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$$P(T,v)=\frac{RT}{(v+c)-b}-\frac{a_c\cdot\alpha(T_r)}{(v+c)(v+c+b)+b(v+\ldots}$$

$$\ldots R^2T_{c,exp}^2 \quad \ldots P_{c,exp} \quad \ldots{}_{exp}$$

Volume-translation parameter

Consi

α continuous

$\frac{d\alpha}{dT_r}(T_r)\le 0$ and $\frac{d\alpha}{dT_r}$ continuous

$\frac{d^2\alpha}{dT_r^2}(T_r)\ge 0$ and $\frac{d^2\alpha}{dT_r^2}$ continuous

$\frac{d^3\alpha}{dT_r^3}(T_r)\le 0$

consistency test of Le Guennec et al. (2016)

Proposed protocol:

L,M,N were fitted on P^{sat} data

$\Delta_{vap}H$, and C_P data were included in the fitting procedure when available.

The *non-associating PC-SAFT* EoS:

On which exp. data m, σ, ε/k_B must be determined?

several combinations of exp. data were considered:

Conclusion

- The PC-SAFT **parameters absolutely need to be fitted** on **vapor pressure** and **liquid density data** (the best weight factors were found to be 3 and 2 respectively). **This is the protocol we decided to use.**

$$\begin{cases} \omega_{P^{sat}} = 3 \\ \omega_{\rho_{liq}^{sat}} = 2 \end{cases}$$

The *I-PC-SAFT* EoS:

- It is a volume-translated version of the PC-SAFT EoS.
- Molecular parameters **m, σ, ε/k_B** are determined to exactly reproduce $T_{c,exp}$, $P_{c,exp}$ and the acentric factor (ω_{exp}).
- The volume translation is determined in order to exactly reproduce $v_{liq,exp}^{sat}(T_r = 0.8)$

.

Parameterization is straightforward

$$\begin{cases} m_i \approx 0.5959\omega_{i,exp}^2 + 7.5437\omega_{i,exp} + 0.9729 \\ \varepsilon_i/k \approx T_{c,i,exp} \Big/ \left(4.7968\cdot10^{-6}m_i^5 - 3.0895\cdot10^{-4}m_i^4 + 7.8649\cdot10^{-3}m_i^3 - 0.10215m_i^2 + 0.75358m_i + 0.63659\right) \\ \sigma_i \approx \left[\varepsilon_i/k \cdot \frac{k}{P_{c,i,exp}} 10^{\left(1.6345\cdot10^{-7}m_i^6 - 1.1346\cdot10^{-5}m_i^5 + 3.1389\cdot10^{-4}m_i^4 - 4.4618\cdot10^{-3}m_i^3 + 3.6282\cdot10^{-2}m_i^2 - 0.22498m_i - 0.77655\right)}\right]^{1/3} \end{cases}$$

PART 3: Evaluation of *tc*-PR, PC-SAFT and *l*-PC-SAFT performance over the 306 700 data points of the developed database

Global results

EoS	MAPE on P^{sat} (1800 fluids)	MAPE on V_{liq} (1800 fluids)	MAPE on $\Delta_{vap}H$ (1536 fluids)	MAPE on $C_{P,liq}$ (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 data points
PC-SAFT	1.18%	0.95%	3.25%	4.17%	2.28%	20.8%	4.38%	**2.2%**
l-PC-SAFT	2.08%	4.60%	4.00%	4.10%	0%	0%	12.4%	**3.6%**
tc-PR	0.98%	2.08%	1.92%	2.53%	0%	0%	19.6%	**1.9%**

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- The parameters of the PC-SAFT are fitted over P^{sat} and v_{liq} data and such properties are reproduced with a deviation close to 1% which is excellent.
- The counterpart is a huge deviation on P_c

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- The *l*-PC-SAFT is parameterized in order to exactly reproduce $P_{c,exp}$ and $T_{c,exp}$
- The counterpart is larger deviation on liquid density

With a SAFT-type EoS it is impossible to simultaneously obtain accurate predictions for v_{liq} and P_c.

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- The *tc*-PR EoS has homogeneous results, around 2% (except for v_c)
- Overall, its accuracy is comparable to that of the PC-SAFT EoS

PART 4: Discussion on the correlation between the strength of association and the model accuracy

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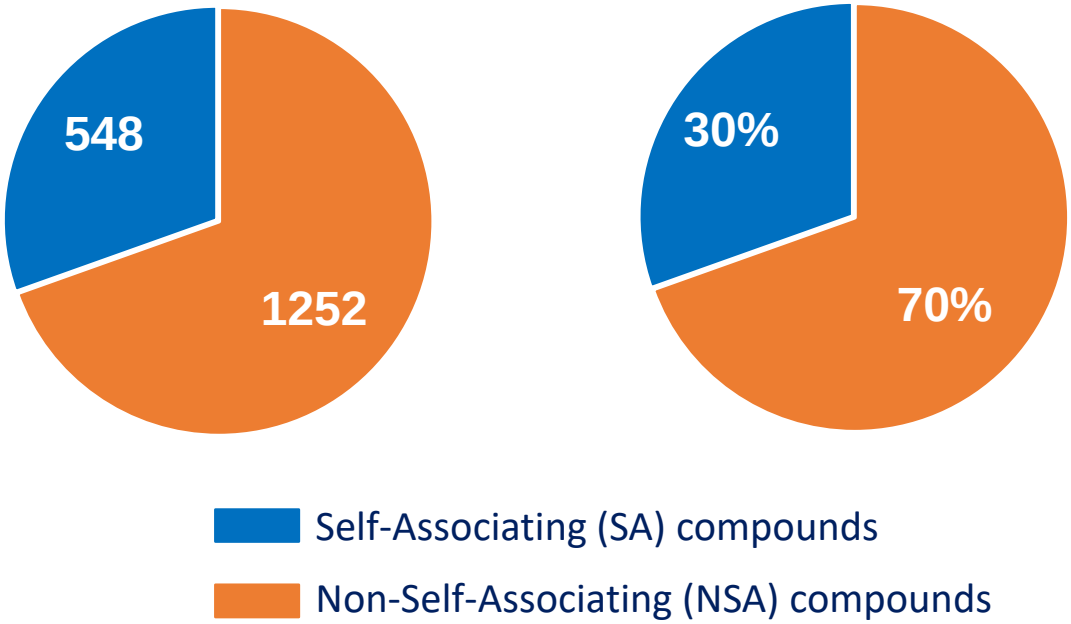
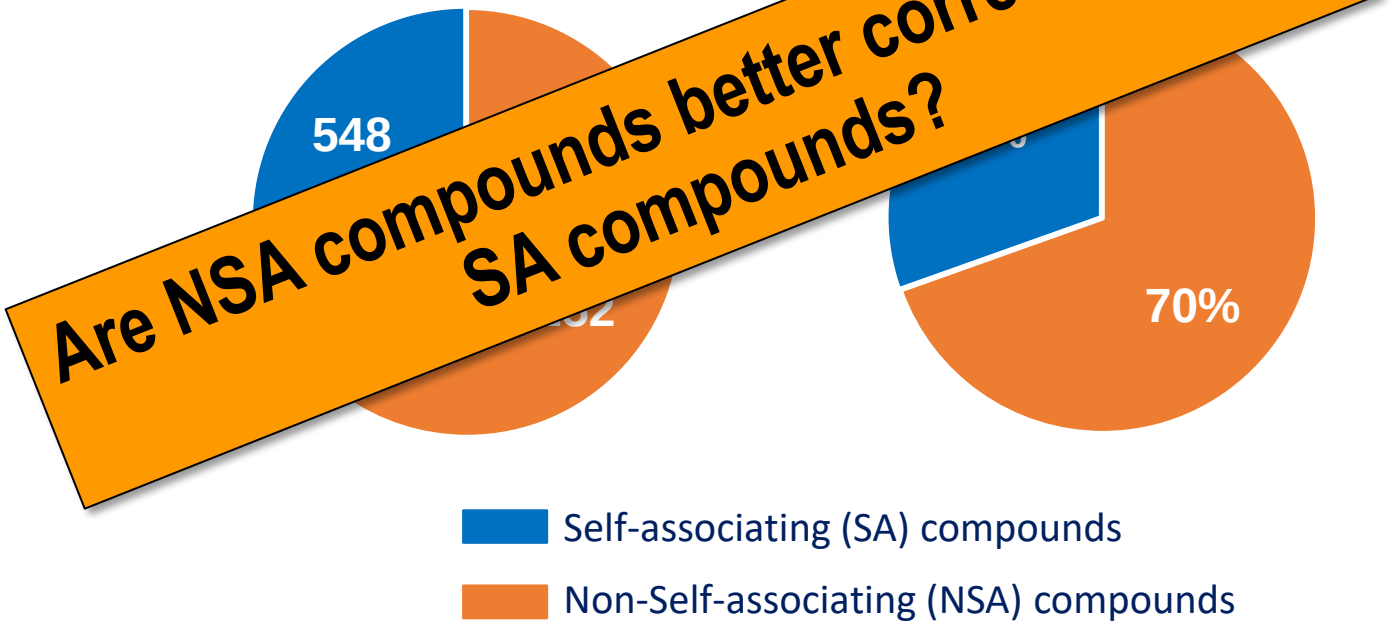
It is recalled that the database contains:



The evaluated EoSs DO NOT CONTAIN an association term.

It is recalled that the database contains:

Are NSA compounds better correlated than SA compounds?



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It is recalled that the database contains:

Are NSA compounds better correlated than SA compounds?

A criterion of modeling quality must be defined

The evaluated EoS DO NOT CONTAIN an association term.

PART 4: Discussion on the correlation between the strength of association and the model accuracy

A pure component *j* will be considered as well-modeled by a given EoS provided:

$$\begin{cases} \left(MAPE_{P^{sat}}^{EoS}\right)_j \leq \overline{MAPE}_{P^{sat}}^{EoS,NSA} + SD_{P^{sat}}^{EoS,NSA} \\ \textbf{\textit{and}} \\ \left(MAPE_{V_{liq}^{sat}}^{EoS}\right)_j \leq \overline{MAPE}_{V_{liq}^{sat}}^{EoS,NSA} + SD_{V_{liq}^{sat}}^{EoS,NSA} \end{cases}$$

$\overline{MAPE}_X^{EoS,NSA}$ = mean MAPE calculated with a given EoS over the 1252 NSA components

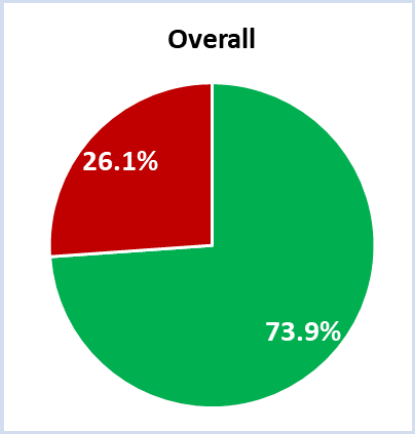
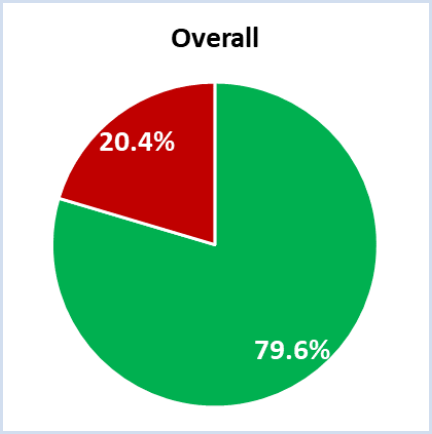
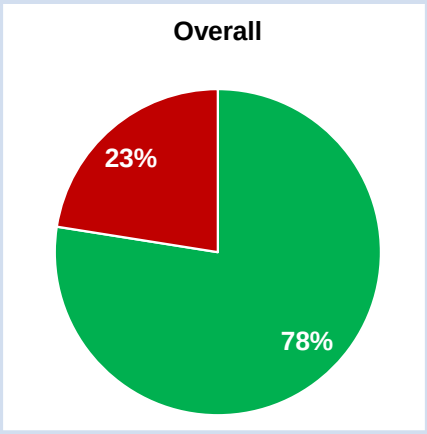
$SD_{P^{sat}}^{EoS,NSA}$ = standard deviation calculated with a given EoS over the 1252 NSA components

If NOT, it will be considered as badly-modeled

PART 4: Discussion on the correlation between the strength of association and the model accuracy

Results:

Well-modeled
Badly-modeled

PC-SAFT EoS:	*l*-PC-SAFT EoS:	*tc*-PR EoS:
		

- Huge similitude between the 3 EoSs: 75% of well-modeled and 25% of badly-modeled

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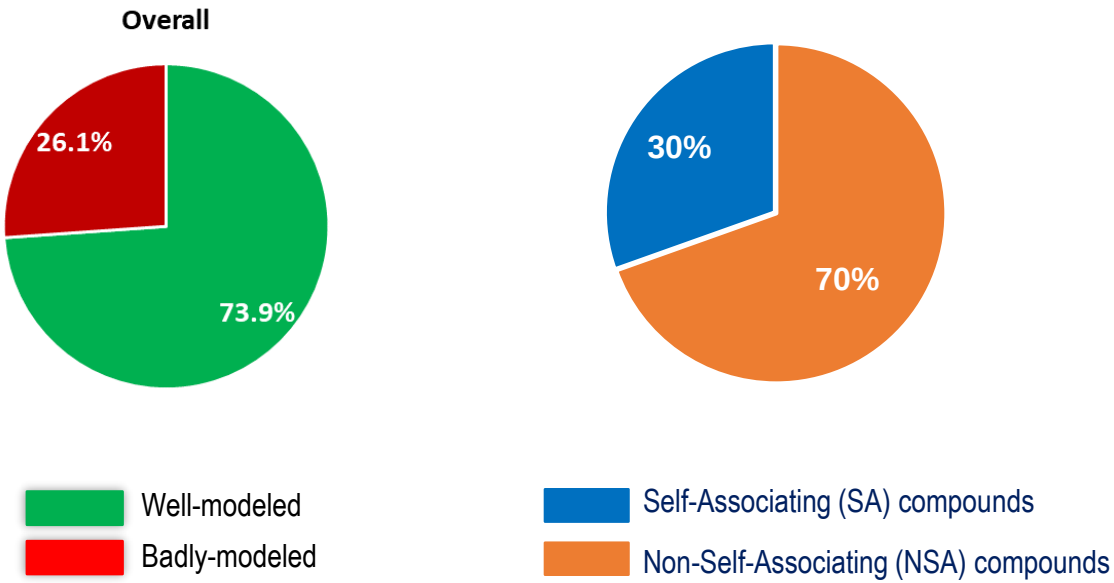

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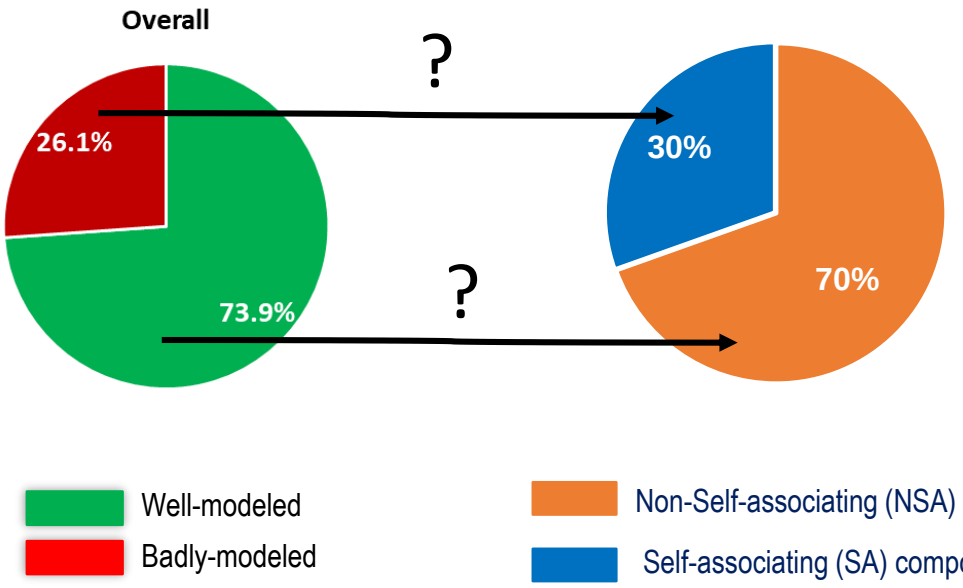

Are the well-modeled molecules essentially the NSA fluids?

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Answer: NOT AT ALL !

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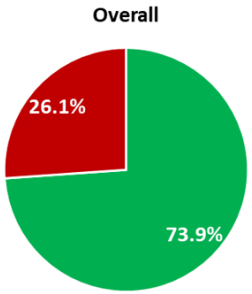
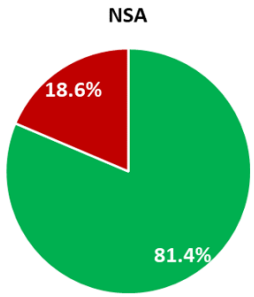
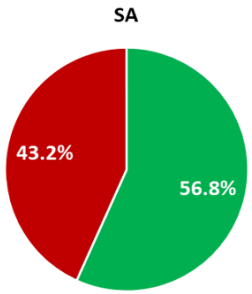
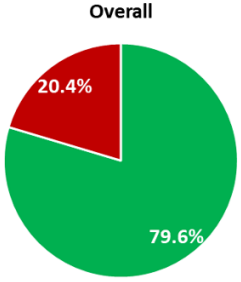
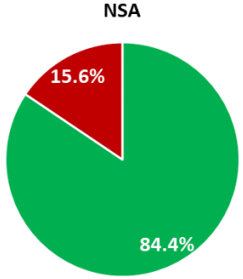


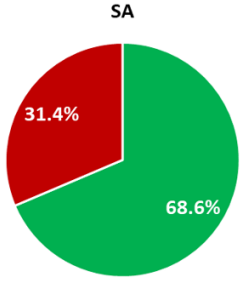




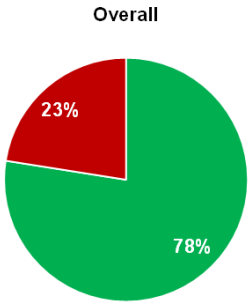
I-PC-SAFT EoS:

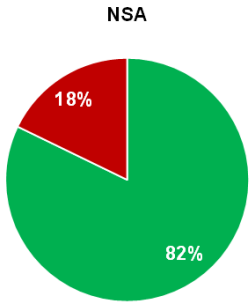


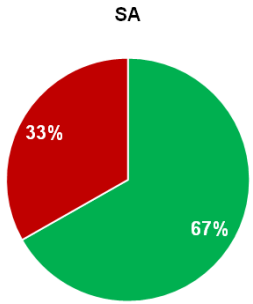




tc-PR EoS:







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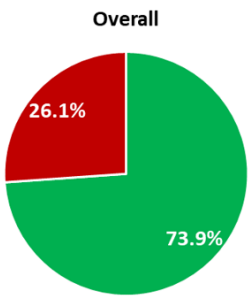
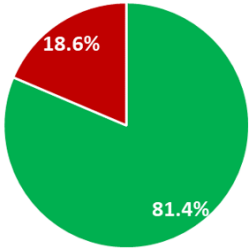
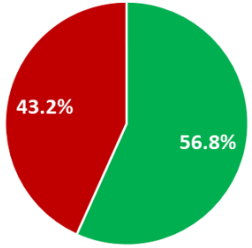
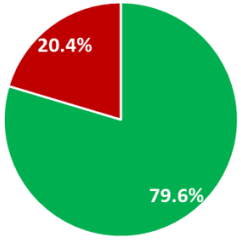
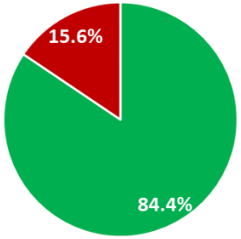


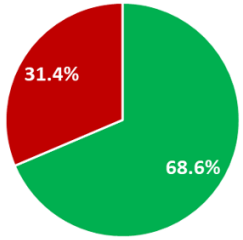




I-PC-SAFT EoS:







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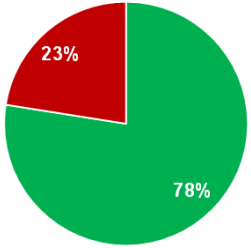

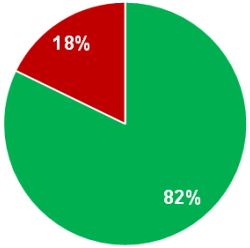

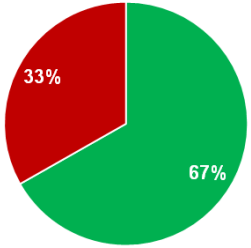

- Huge similitude between the 3 EoS:
- NO ASSOCIATION TERM but **65%** of the SA molecules are well-modeled !

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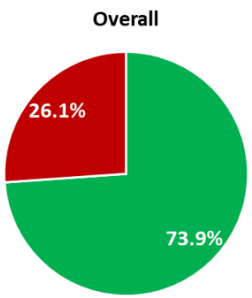

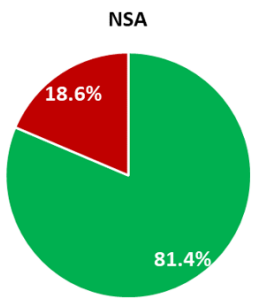

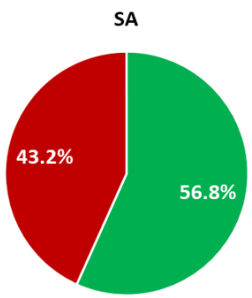

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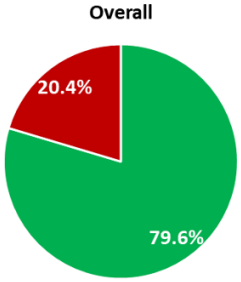
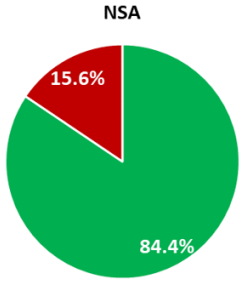
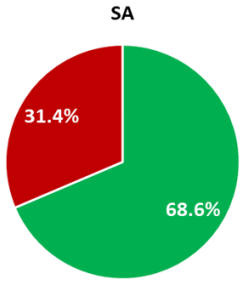
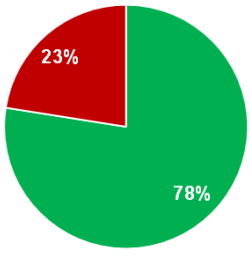
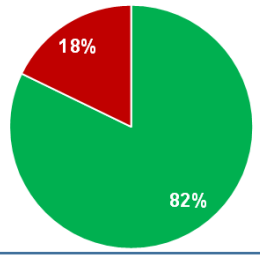


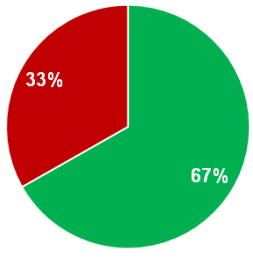




tc-PR EoS:







- Huge similitude between the 3 EoS:
- NO ASSOCIATION TERM but **65%** of the SA molecules are well-modeled !
- 17% of the NSA molecules are badly-modeled !

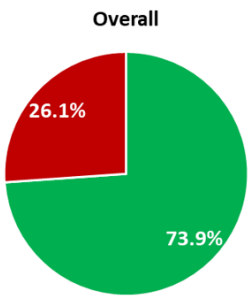
PART 4: Discussion on the correlation between the strength of association and the model accuracy

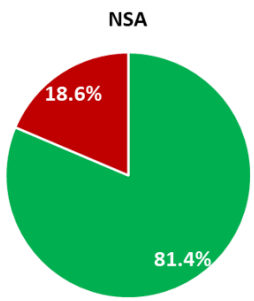
Are the well-modeled molecules essentially the NSA fluids?

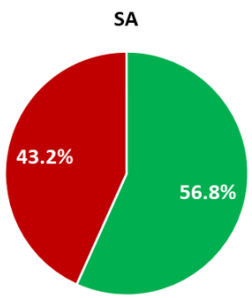
Are the badly-modeled molecules essentially the SA fluids?

Answer: NOT AT ALL !

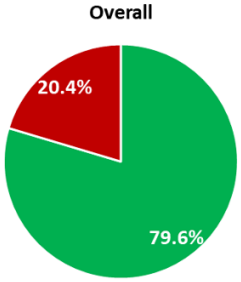
PC-SAFT EoS:

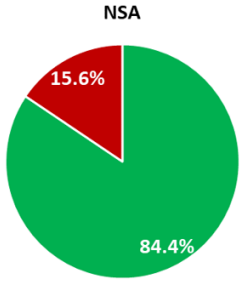


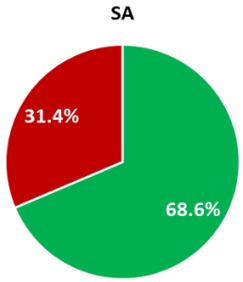




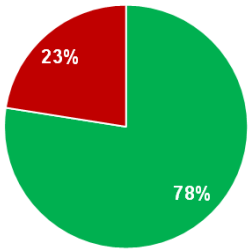
I-PC-SAFT EoS:

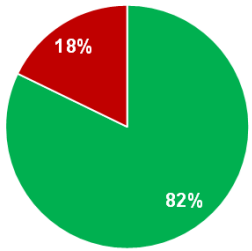


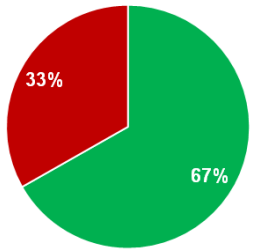




tc-PR EoS:







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- 17% of the NSA molecules are badly-modeled !

Difficult to interpret

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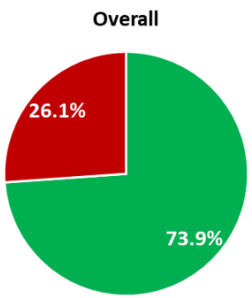
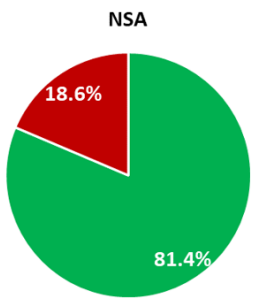
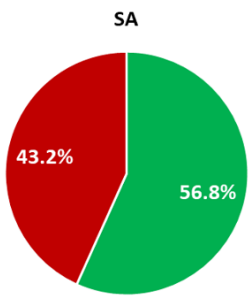
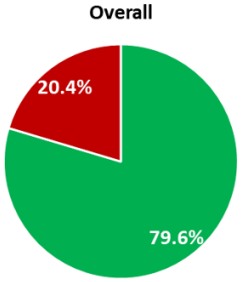
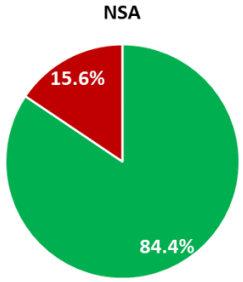


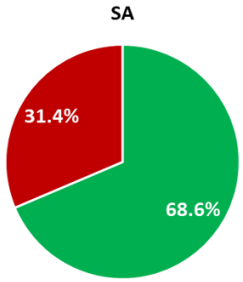




I-PC-SAFT EoS:







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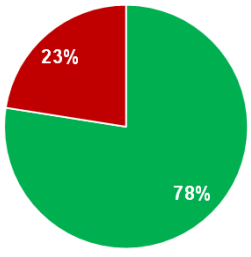
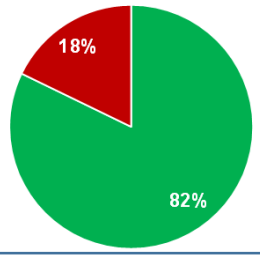
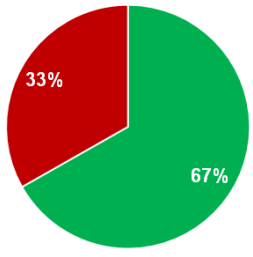






- Huge similitude between the 3 EoS:
- NO ASSOCIATION TERM but **65%** of the SA molecules are well-modeled !
- 17% of the NSA molecules are badly-modeled !

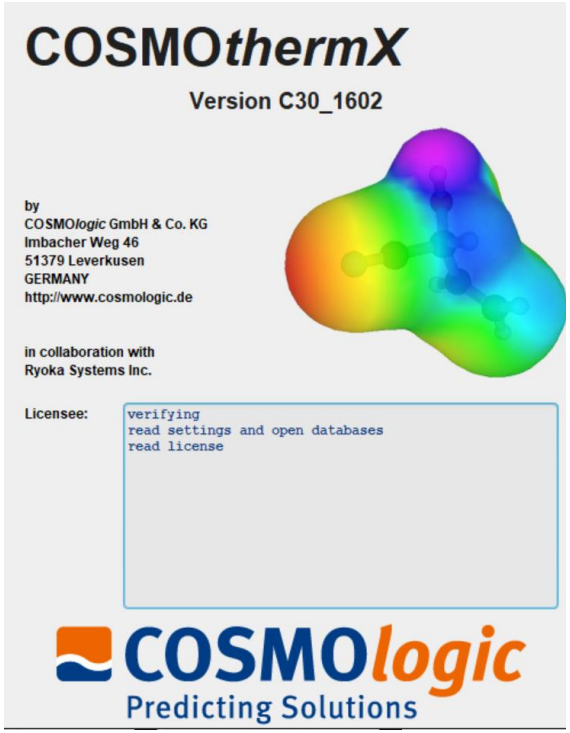
Difficult to interpret

Is the association strength very weak for many SA molecules explaining why they are well-modeled?

Is there a correlation between the strength of the hydrogen bond and the accuracy of the EoS?

PART 4: Discussion on the correlation between the strength of association and the model accuracy

Are weakly-associating molecules better correlated than strongly associated molecules?



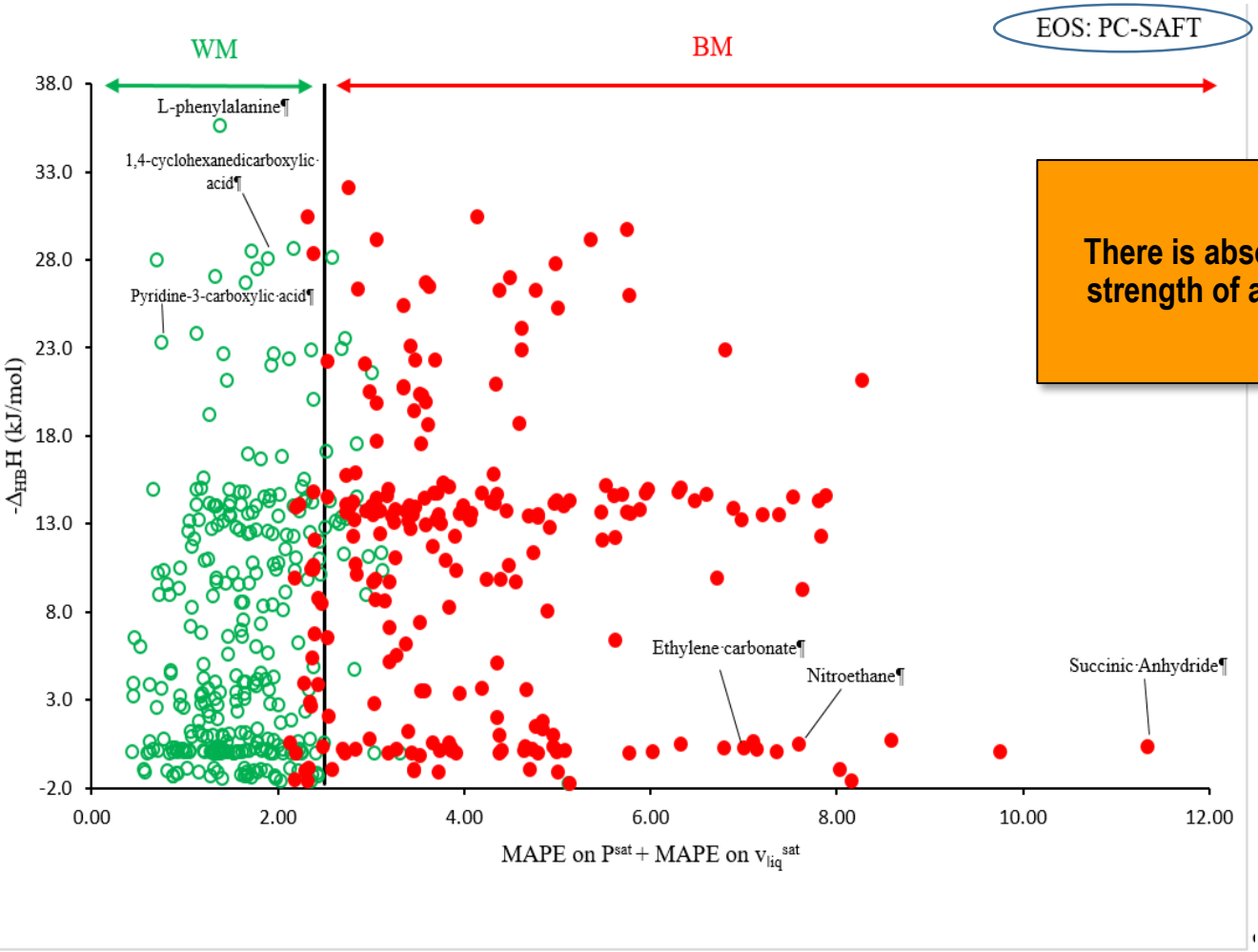
Calculation of the Hydrogen bond enthalpy for the 548 SA fluids

HB strength = HB enthalpy

$$-\Delta_{HB}H$$

PART 4: Discussion on the correlation between the strength of association and the model accuracy

Are weakly-associating molecules better correlated than strongly associated molecules?

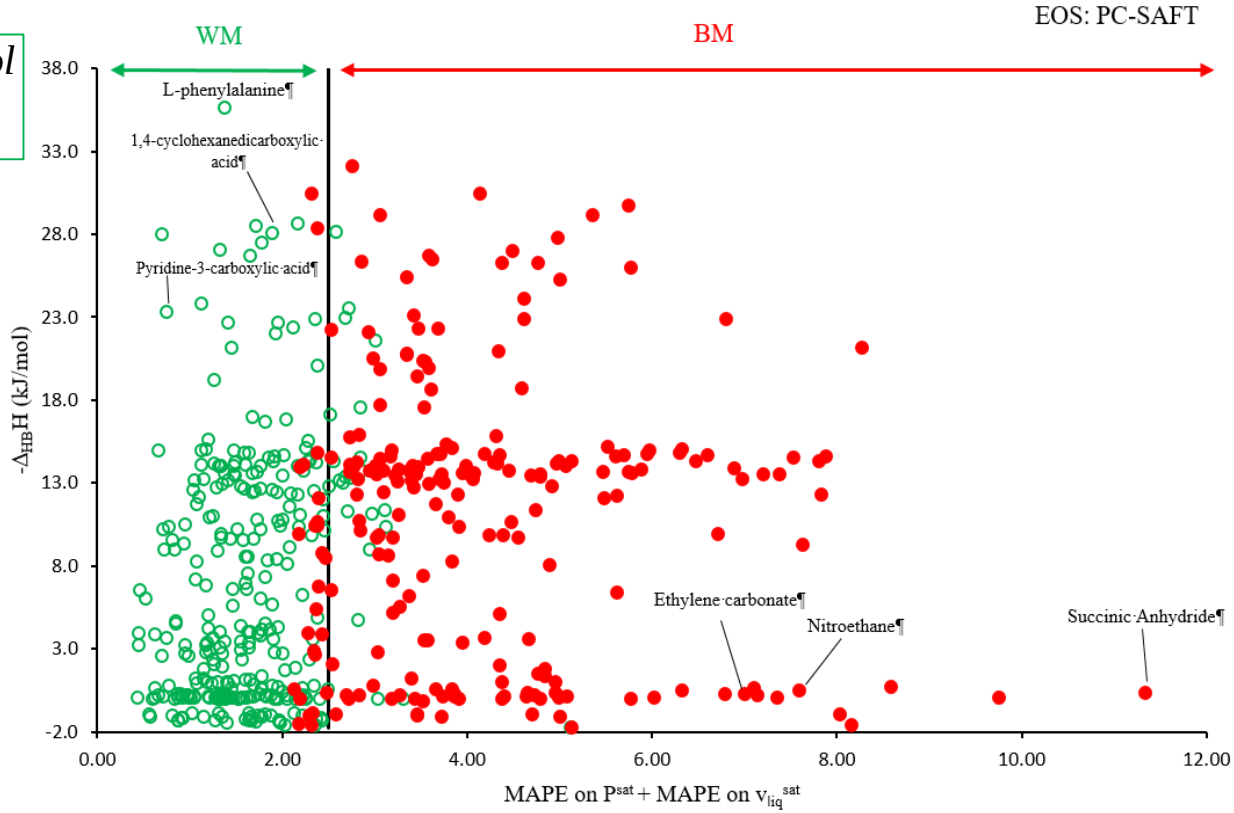


There is absolutely no correlation between the strength of association and the EoS accuracy.

Effect of the HB strength

$-\Delta_{HB}H_{L\text{-}phenylalanine} = 35.6\ kJ\ /\ mol$

(well - modeled)

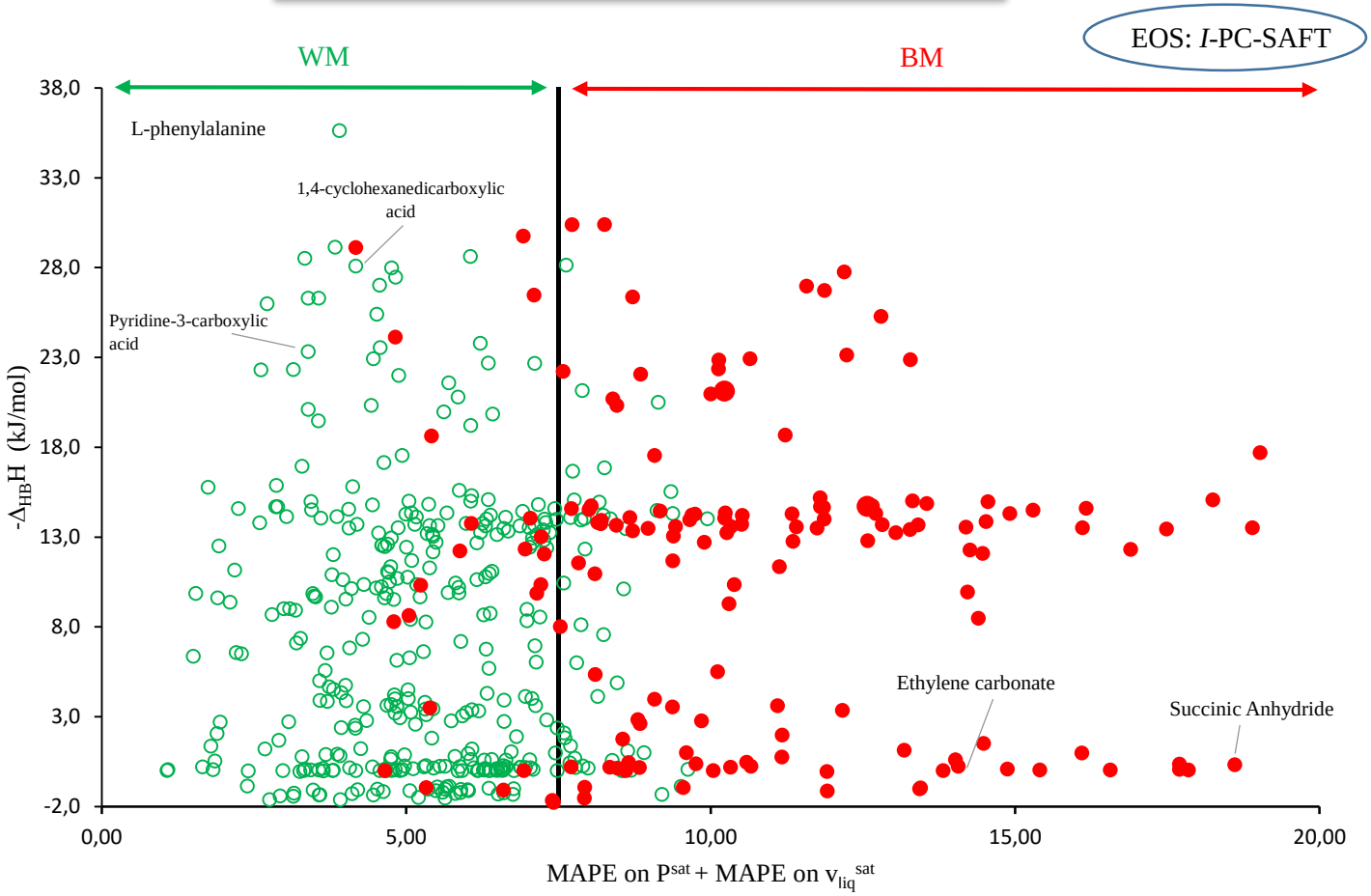


$-\Delta_{HB}H_{Succinic\ Anhydride} = 0.33\ kJ\ /\ mol$

(badly modeled)

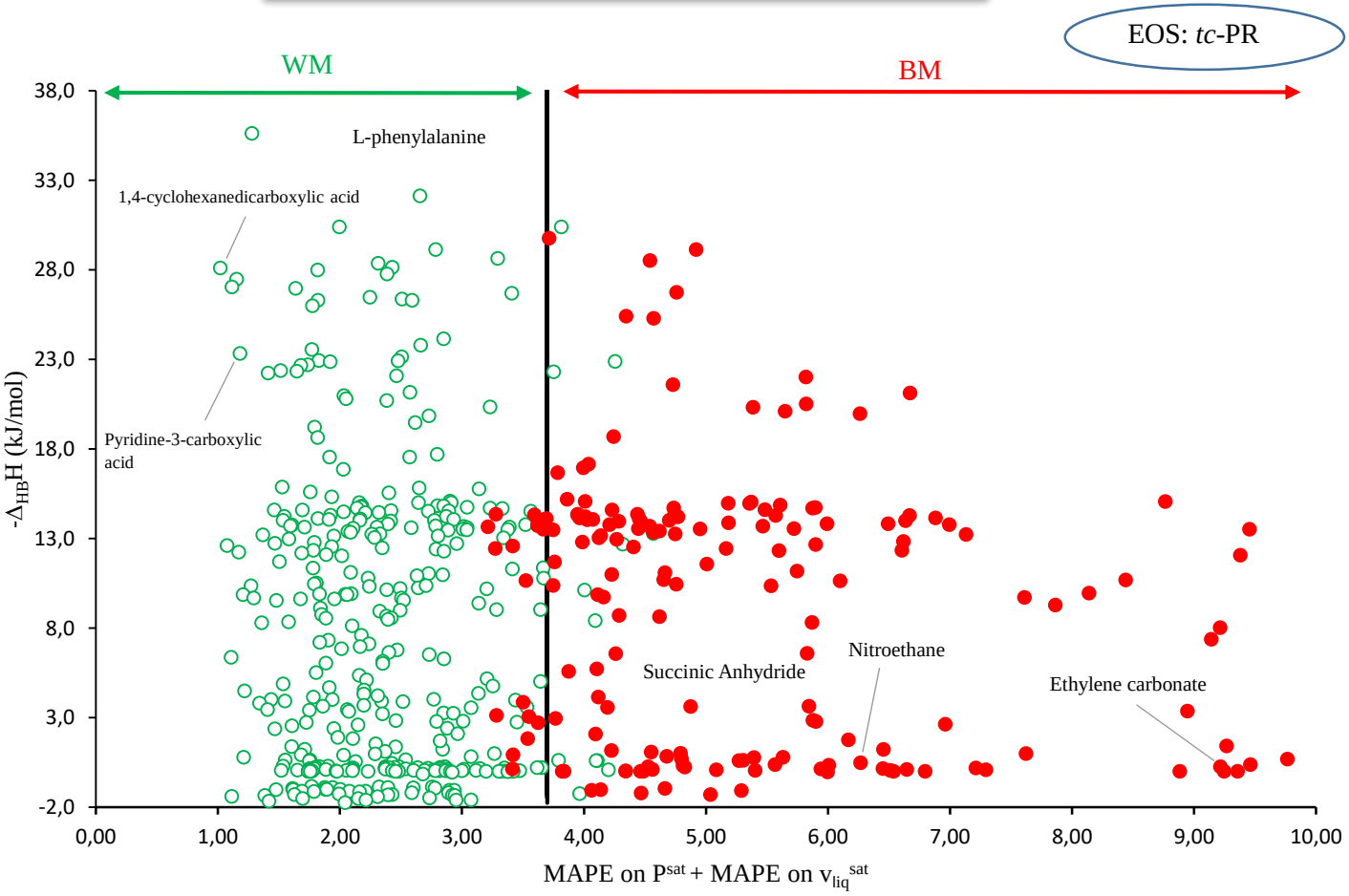
PART 4: Discussion on the correlation between the strength of association and the model accuracy

Similar conclusions with other EoS



PART 4: Discussion on the correlation between the strength of association and the model accuracy

Similar conclusions with other EoS



PART 4: Discussion on the correlation between the strength of association and the model accuracy

Conclusion

- The PC-SAFT, *l*-PC-SAFT and *tc*-PR EoS **without association term a**re able to model **accurately 65%** of the **SA compounds**  **but only 80% of the NSA compounds**  .

- For SA molecules, **there is absolutely no correlation between the strength of association and the EoS accuracy.**

==========

- Such results do not help to decide in which direction efforts have to be devoted to improve SAFT-type and CEoS that do not embed an association term.
- Let's be provocative: is the addition of an association term the most suited solution?


Thank you!