

## **Sensitivity of PPC-SAFT parameters for the prediction of VLE and LLE properties**

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### **Abstract**

The GC-PPC-SAFT model has been shown to be useful for predicting the liquid-liquid equilibrium (LLE) properties [Nguyen, T.-B.; De Hemptinne, J.-C.; Creton, B.; Kontogeorgis, G.M. *Ind. Eng. Chem. Res.*, 2013 (in press)]. In view of improving the accuracy of this model, a sensitivity analysis of the parameters for calculating a number of eight industrially relevant properties (pure component, gas solubilities or Henry constants and liquid-liquid phase split with water and n-octanol) is proposed on a large database containing 290 mono-functional compounds. It reveals the very large sensitivity of the model to the numerical values of its parameters, in particular for the calculation of LLE type properties (equilibrium with water). In view of these results, it is proposed to use a non-additive hard sphere theory, thus introducing a binary interaction parameter  $l_{ij}$  on combining rules for the segment diameter parameter. The binary interaction parameter  $l_{ij}$  is fitted on infinite dilution activity coefficient in water. There are 134 molecules in the regression database. The regressed  $l_{ij}$  values and the average values per family, are subsequently used for predicting water solubility and n-octanol/water partition coefficient. In general, the results obtained are very much improved with respect to the predictive approach discussed previously [Nguyen, T.-B.; De Hemptinne, J.-C.; Creton, B.; Kontogeorgis, G.M. *Ind. Eng. Chem. Res.*, 2013 (in press)]. The global deviation values for infinite dilution activity coefficient in water, water solubility and n-octanol/water partition coefficient are 0.09, 0.22, 0.30, respectively. However, the use of the binary interaction parameter  $l_{ij}$  does not allow representing correctly the solubility minimum.

**Keywords :** GC-PPC-SAFT, oxygenated compounds, VLE, LLE, binary interaction parameter.

### **1. Introduction**

A correct prediction of thermodynamic properties over a wide range of conditions is a starting point, and of great importance, for the design and optimisation of chemical processes. This task becomes more difficult when considering fluids originating from the so-called second generation biomass which covers a large variety of oxygenated compounds (Hubert et al., 2006). Specific interactions (strong association and hydrogen bonding) between molecules, particularly water/oxygenated compounds mixtures, which results in extremely non-ideal fluid behaviour, cause a major challenge for conventional predictive approaches. In order to overcome this problem, it is necessary to use equations of state (EoS) that account explicitly for associating and/or polar interactions between molecules. Many thermodynamic models have been proposed in the literature such as A- $\alpha$ -PACT (Ikonomidou & Donohue, 1986), GCA (Gros et al., 1996), SAFT (Chapman et al., 1989, 1990), CPA (Kontogeorgis et al., 1996).

The Statistical Associating Fluid Theory (SAFT), which was initially proposed by (Chapman et al., 1989, 1990), is an advanced molecular thermodynamic model that takes into account explicitly each type of interactions between molecules. Many SAFT-type versions have been proposed in literature. More details can be found in the recent reviews (Kontogeorgis et al., 2010; Müller & Gubbins, 2001; Economou, 2002; Tan et al., 2008).

In this work, the Group Contribution – Polar Perturbed Chain – SAFT (GC-PPC-SAFT) will be used for predicting some properties of water/oxygenated compounds mixtures. This EoS, coupled with the Group Contribution concept of (Tamouza et al. 2004), is an extension of the PC-SAFT model (Gross & Sadowski, 2001) for polar molecules (Nguyen-Huynh et al., 2008). The performance of this model for predicting pure compounds properties (i.e. vapour pressure and molar liquid volume) and mixture properties (i.e. water solubility, infinite dilution activity coefficient in water, n-octanol/water partition coefficient, Henry's law constants) was evaluated and presented in our previous work (Nguyen et al., 2013). A sensitivity analysis of the PPC-SAFT parameters for predicting properties was also carried out in order to identify which parameters need to be determined with more accuracy. Based on the latter study, it is observed that a very small modification on the segment diameter could lead to very significant changes in solubility. In view of improving the predictive capability of this model for the solubility properties, it is proposed to apply a binary interaction parameter, called  $l_{ij}$ , on the combining rules for the segment diameter. The introduction of this parameter is based on the observation that the non-additivity of hard sphere may have a large impact on liquid-liquid phase split (Santos et al. 2005; Paricaud, 2008), which showed that the use of this character had a large effect on liquid-liquid phase split. This paper will focus essentially on the results of the sensitivity analysis and the use of the new correction parameter on the segment diameter.

First, the description of the GC-PPC-SAFT EoS and the determination of its parameters is introduced. The results of the sensitivity analysis are presented in section 3. In section 4 the results of using  $l_{ij}$  in the prediction of the LLE-type properties are presented and discussed. Our conclusions are presented at the end.

## 2. GC-PPC-SAFT model

The Group Contribution – Polar Perturbed Chain – Statistical Associating Fluid Theory (GC-PPC-SAFT) is the combination of the PPC-SAFT model (Nguyen-Huynh et al., 2008) with the GC concept (Tamouza et al., 2004) in order to determine the three basic molecular parameters, the dispersive energy  $\epsilon/k$ , the segment diameter  $\sigma$  and the chain length  $m$ . This EoS is constructed using the thermodynamic perturbation theory that allows writing the various intermolecular contributions to the Helmholtz free energy at given temperature, volume and composition as a sum of contributions:

$$A^{\text{res}} = mA^{\text{hs}} + A^{\text{chain}} + A^{\text{disp}} + A^{\text{assoc}} + A^{\text{multi-polar}} \quad (1)$$

where  $A^{\text{hs}}$  is the so-called reference term which is based on the hard sphere theory of Boublik, 1970 and Mansoori et al., 1971. The segment diameter  $\sigma$  is the only parameter in for the hard sphere contribution. This term is multiplied by  $m$  which represents the number of segments in the molecular chain. The term  $A^{\text{chain}}$  is used to describe the formation of the chain. It originates in the association term where the association strength is considered infinite. In the PC-SAFT EoS, the reference is in fact the sum of these two terms. The third term is called "dispersive" as it takes into consideration the London-type attractive interactions between segments. It is based on the second order perturbation theory of Barker and Henderson, 1967. This term requires the well-depth energy, often expressed as  $\epsilon/k$  (where  $k$  is the Boltzman constant) with units of temperature. In case of associative and/or polar molecules, we need additional parameters to describe these specific interactions. Therefore the contribution  $A^{\text{assoc}}$  that originates from the Wertheim theory is used to consider the associative interactions, represented by association energy parameter  $\epsilon^{AB}$  and association volume parameter  $K^{AB}$ . The last term  $A^{\text{multi-polar}}$  describes polar characteristics of some segments. Several theories exist. The one chosen here is that of Jog and Chapman, 1999 which was selected by Nguyen-Huynh et al., 2008. Its parameters are the polar moment (dipole  $\mu$  and quadrupole  $Q$ ), and the polar fraction for each type of polarity  $mx^{p\mu}$  and  $mx^{pQ}$ . The details of the group contribution approach for parameterizing this equation of state are described in our previous work (Nguyen et al., 2013).

In order to apply this EoS to mixtures, combining rules must be defined. Regarding the dispersive energy  $\epsilon_{ij}$  and the segment diameter  $\sigma_{ij}$ , the so-called Lorentz Berthelot combining rules are used, as shown in Eqs. (2) & (3):

$$\varepsilon_{ij} = (1 - k_{ij}) \sqrt{\varepsilon_i \varepsilon_j} \quad (2)$$

$$\sigma_{ij} = (1 - l_{ij}) \frac{\sigma_i + \sigma_j}{2} \quad (3)$$

where  $k_{ij}$  and  $l_{ij}$  are binary interaction parameters. In this work, all binary interaction parameters  $k_{ij}$  on the dispersive energy are taken as zero, and we will focus on the use of the non-additivity of the hard sphere diameters. The  $l_{ij}$  values will be regressed as explained in the next section. The reason for taking zero values for  $k_{ij}$  is that its effect has been found negligible, as discussed in (Nguyen et al., 2013). Here, we therefore want to focus on the  $l_{ij}$  parameter, which appears to have a much larger effect on the final result. Using both parameters simultaneously would have not much sense.

In the case of mixtures having two associating components, e.g. water and alcohols, a set of the cross-association parameters ( $w_{\alpha\beta}$ ,  $u_{\alpha\beta}$ ) may be used, as proposed by Nguyen-Huynh et al., 2011. The detail of these cross-parameters can be found in our previous work (Nguyen et al., 2013).

### 3. Results and discussions

#### 3.1. Experimental data

The collection and correlation results of experimental data were described in our previous paper (Nguyen et al., 2013). There are 8 properties considered in this work: vapour pressure  $P^\sigma$ , molar liquid volume  $v^L$ , water solubility  $x_i^{aq}$ , infinite dilution activity coefficients in water  $\gamma_i^{aq,\infty}$ , n-octanol/water partition coefficient  $K_{ow}$ , Henry's law constant of hydrogen  $H_{H_2}$ , of methane  $H_{CH_4}$  and of nitrogen  $H_{N_2}$ . Except for  $P^\sigma$  and  $v^L$ , the data points of the remaining properties are correlated as shown in the following equation:

$$\log X = A_x + \frac{B_x}{T} + C_x \log(T) \quad (4)$$

where  $X$  is the property to be correlated and  $A_x$ ,  $B_x$ ,  $C_x$  are coefficients.

The database used contains 290 molecules belonging to 15 chemical families. Note that all the chemical families used in this work are mono-functional. The number of oxygenated components is 184.

#### 3.2. Sensitivity analysis

The first objective of this work is to analyze the sensitivity of the PPC-SAFT parameters on the calculated values. There are 9 parameters considered in this work: dispersive energy  $\varepsilon^k$ , segment diameter  $\sigma$ , chain length  $m$ , association energy  $\varepsilon^{AB}$ , association volume  $K^{AB}$ , dipole moment  $\mu$ , quadrupole moment  $Q$ , dipole fraction  $mx^{p\mu}$ , quadrupole fraction  $mx^{pQ}$ . Their reference value was obtained from the group contribution approach (Nguyen et al., 2013). Each parameter is modified one at a time by +5%, and then compared to its initial value. Every modification of the parameters is evaluated on 8 properties ( $P^\sigma$ ,  $v^L$ ,  $x_i^{aq}$ ,  $\gamma_i^{aq,\infty}$ ,  $K_{ow}$ ,  $H_{H_2}$ ,  $H_{CH_4}$ ,  $H_{N_2}$ ). The analysis is quantified by the average absolute deviation (AAD), as shown in Eq. (5). The AAD values are averaged over temperatures and components.

$$\overline{AAD}_x = \frac{1}{n_{cpds}} \sum_{i=1}^{n_{cpds}} \left( \frac{1}{n_{pts}} \sum_{j=1}^{n_{pts}} \left( \frac{|X^{5\%} - X^{0\%}|}{X^{0\%}} \right)_j \right) \quad (5)$$

where  $X^{5\%}$ ,  $X^{0\%}$  indicate the values computed with the modified and original parameter value, respectively.  $n_{cpds}$  corresponds to the number of compounds (184 oxygenated molecules for table 1).

$n_{pts}$  indicates the number of data points investigated for each property (11 for all properties except  $K_{ow}$  where a single point was considered at 25°C).

Table 1: Sensitivity analysis (% AAD for a 5% change in each parameter) of PPC-SAFT parameters for the oxygenated compounds.

Properties	PPC-SAFT parameters								
	$\epsilon/k$	$\sigma$	$m$	$\epsilon^{AB}$	$K^{AB}$	$\mu$	$Q^*$	$mx^{pl}$	$mx^{pQ}$
$P^\sigma$	41.7	11.3	26.9	15.5	2.2	6.8	1.8	3.4	0.7
$v^L$	3.0	16.5	4.1	0.6	0.1	0.4	0.2	0.2	0.1
$x_i^{aq}$	36.4	72.1	47.2	14.9	2.0	9.4	5.6	4.6	2.9
$\gamma_i^{aq,\infty}$	25.2	314.4	95	14.9	2.3	8.5	5.5	4.3	2.9
$K_{ow}$	23.8	340.1	96.9	8.2	1.2	12.5	7.5	6.4	3.8
$H_{H_2}$	9.7	25.1	2.7	1.2	0.2	2.7	--	1.3	--
$H_{CH_4}$	9.6	25.6	3.0	0.7	0.1	2.4	--	1.1	--
$H_{N_2}$	19.9	32.8	2.0	1.3	0.2	3.4	--	1.6	--

\* a phenyl-group bearing molecules, included in the oxygenated compounds.

Table 1 shows that the three parameters ( $\epsilon/k$ ,  $\sigma$  and  $m$ ) have most influenced on the pure component properties ( $P^\sigma$  and  $v^L$ ). A 5% modification in  $\epsilon/k$  results in a 41.7% change of  $P^\sigma$  and a 3.0% change of  $v^L$ . Therefore it is important to determine these three parameters accurately.

The prediction of the Henry's law constants appears to be much less sensitive to the parameters than those for the other properties. The largest effect is observed for  $\sigma$  and  $\epsilon/k$  for which a 5% change leads to respectively 33 and 20% modifications.

Regarding the so-called LLE-type properties ( $x_i^{aq}$ ,  $\gamma_i^{aq,\infty}$  and  $K_{ow}$ ), the calculated values are much more sensitive to the parameters. The sensitivity to the molecular size parameters ( $\sigma$  and  $m$ ) is very important: a 5% change of  $\sigma$  leads to almost 300% change of  $\gamma_i^{aq,\infty}$ . It will lead to about 340% change of  $K_{ow}$ . The dispersive energy  $\epsilon/k$  is also sensitive to these properties. Although the effect of the association and polar parameters is less extreme, it is still important as a 5% change of  $\epsilon^{AB}$  will lead to about 15% or so change in  $x_i^{aq}$ . The trend for  $x_i^{aq}$  is less extreme than for the infinite dilution properties. These results are not completely unexpected, as it is well-known that the water solubility decreases very fast with increasing hydrocarbon size.

### 3.3. Regression of $l_{ij}$

Based on the results of the sensitivity analysis, in view of improving the water solubility predictions, it may be pertinent to use a correction on the segment diameter  $\sigma$ . A new correction parameter, called  $l_{ij}$ , will be used to correct the combining rule of the segment diameter (see Eq. (3)).

The  $l_{ij}$  values are regressed for each chemical on its infinite dilution activity coefficients in water  $\gamma_i^{aq,\infty}$  by minimizing the following objective function:

$$OF = \sum_{i=1}^n \left( \log \gamma_{i,calc}^{aq,\infty} - \log \gamma_{i,exp}^{aq,\infty} \right)^2 \quad (6)$$

where the experimental data  $\log \gamma_{i,exp}^{aq,\infty}$  are obtained from Eq. (4), and  $\log \gamma_{i,calc}^{aq,\infty}$  are calculated from the PPC-SAFT model. The database contains here 134 molecules because for a number of compounds investigated earlier no such data was available. The values are estimated within the given range of temperature of experimental data.

In general, the  $l_{ij}$  values estimated is found between -0.03 and 0.01 (see Table 2), which correspond to a change of the segment diameter  $\sigma$  from -1% to +3%. The uncertainty on the  $l_{ij}$  parameter was computed to be 0.0008. For n-alkanes, methyl alkanes and n-alkyl benzenes, the regressed values were often below this limit, indicating that the use of this parameter does not change the result. No trend was observed with molecular weight, but the values vary quite a bit among chemical families. In order to check the sensitivity of the results to  $l_{ij}$ , an average value per family is also used. These values are presented in Table 2.

Table 2: The average values of  $l_{ij}$  per family. Notation:  $N$  is the number of molecules within each family (Total = 134).

Family	N	average $l_{ij}$	min. value	max. value
1-alkenes	4	-0.00237	-0.00306	-0.00158
acetates	13	-0.01577	-0.02276	-0.00518
aldehydes	7	-0.00635	-0.00942	-0.00405
aliphatic ethers	10	-0.02077	-0.02568	-0.01259
alkylcyclohexanes	2	0.00745	0.00606	0.00884
formates	7	-0.01356	-0.02033	-0.00913
ketones	18	-0.01497	-0.02116	-0.00541
methylalkanes	9	0.00031	-0.0039	0.00582
methylalkenes	2	0.00315	0.00113	0.00516
n-alcohols	14	-0.0023	-0.00611	0.00082
n-aliphatic acids	8	-0.01886	-0.02546	-0.01169
n-alkanes	12	-0.00042	-0.00412	0.00448
n-alkylbenzenes	3	0.00006	-0.00296	0.00291
other aliphatic alcohols	15	0.00047	-0.00705	0.01048
propionates/butyrate	10	-0.01736	-0.02106	-0.01441

### 3.4. Evaluation of the LLE-type properties

Using the obtained  $l_{ij}$  values, the performance of the model for predicting the LLE-type properties is evaluated. The evaluation is quantified by using standard error SE which is defined as shown in Eq. (7).

$$SE = \sqrt{\frac{\sum_{i=1}^n (\log X_i^{\text{SAFT}} - \log X_i^{\text{Corr}})^2}{n-1}} \quad (7)$$

where  $\log X_i^{\text{SAFT}}$  and  $\log X_i^{\text{Corr}}$  correspond to the values predicted by the model and calculated from the correlations of the experimental data (Eq. (4)), respectively. Note that exactly the same expression is used for determining the standard error of the correlation ( $SE^{\text{Exp}}$  in the figures below). In that case, it is compared with the true experimental values. The formula (7) is expressed with the logarithmic values because the orders of magnitude of data considered cover a very large range (from  $10^0$  to  $10^{11}$ ). It should be noted that  $SE = 1$  is equivalent to a factor of 10 in deviation between the experimental and model calculated values. For small values, SE values can be compared to the well-known relative deviations by multiplying with 2.3 (e.g.  $SE = 0.04$  is equivalent with a relative deviation of 10%). In next section, the results of this evaluation are presented, for which three different approaches are compared:

- the so-called 'predictive' approach ( $l_{ij} = 0$ ), which uses the group contribution pure component parameters. This approach was already presented in the previous paper (Nguyen et al., 2013).
- the 'regressed  $l_{ij}$ ' approach, where each individual binary system has a different  $l_{ij}$  value. These values are regressed on  $\gamma_i^{\text{aq},\infty}$  and presented in the section 3.3.
- the 'average  $l_{ij}$ ' approach, where an average  $l_{ij}$  value is taken for each chemical family.

#### a) Infinite dilution activity coefficient in water

As expected, the use of the regressed  $l_{ij}$  improved significantly the results as compared to ones without, or even with the predicted  $k_{ij}$  that was discussed in our previous work (Nguyen et al., 2013). The global SE value equals 0.09 (an average of 20% deviation). These results confirm the observations made in our sensitivity analysis that a small modification on  $\sigma$  results in a very large change in property values at infinite dilution in water. The use of the average  $l_{ij}$  values per family also gave very encouraging results (global SE value = 0.22, or 50% of deviation). Figure 1 provides a view of the improvements that have been obtained per chemical family.

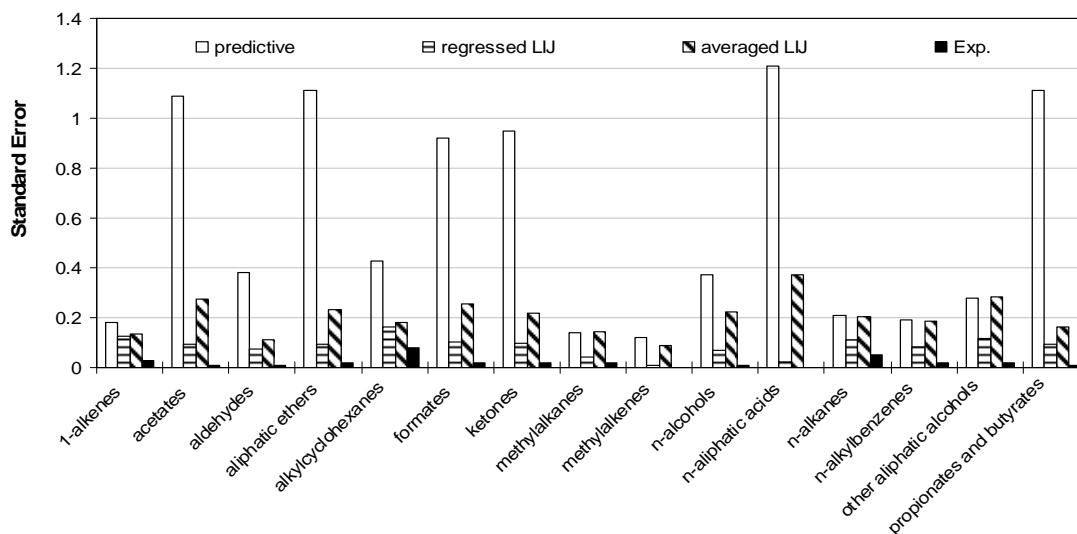


Figure 1: Infinite dilution activity coefficient in water  $\gamma_i^{aq,\infty}$ .

b) Solubility in water

The predictive capability of the GC-PPC-SAFT model on  $x_i^{aq}$  is evaluated with the use of the  $I_{ij}$  values obtained.

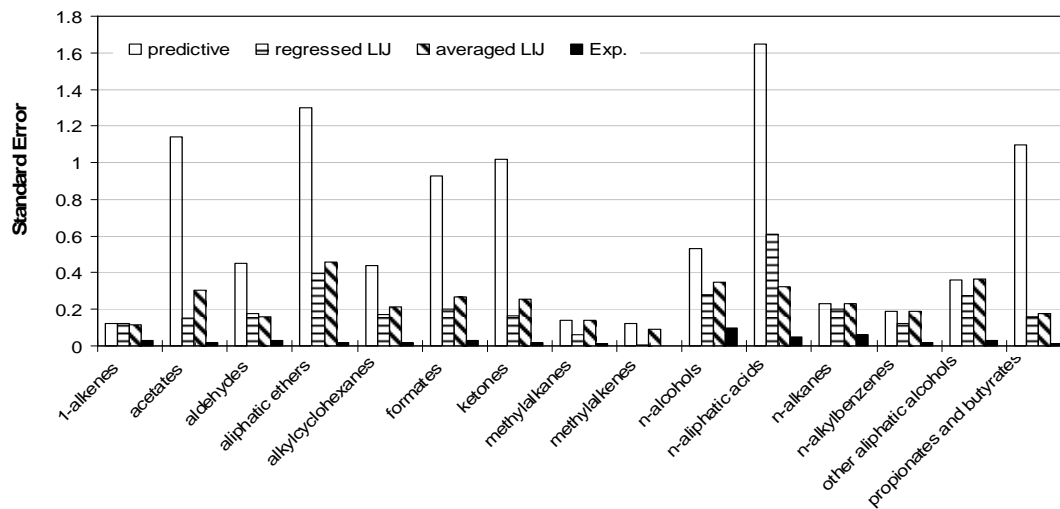


Figure 2: Evaluation of water solubility  $x_i^{aq}$ .

In general, the predictive capability for  $x_i^{aq}$  is better when the regressed  $I_{ij}$  values are used. Some significant improvements are observed, as compared to the predictive approach, for aliphatic acids, ethers, esters, formates and ketones. Figure 2 shows that while the SE value for the majority of molecules is less than 0.4, it remains significant for n-butyl ethyl ether, n-dodecanoic acid and n-tetradodecanoic acid. The large deviations for these molecules may be due to the experimental data.

Figure 3 presents some examples for the prediction of  $x_i^{aq}$  with the use of  $I_{ij}$  values. As for most SAFT models, the GC-PPC-SAFT model can not predict the minimum of the water solubility which is shown in many cases at low temperatures. However, this model is able to capture the order of magnitude of the data, which in itself is already a good result. The reason for this, and in particular for the reversed trend observed for ethers may be related to the cross-association phenomenon that water exhibits with a number

of components, and which could be improved by using corrective parameters on these mixtures (as discussed in (Nguyen et al., 2013), but is not further investigated here.

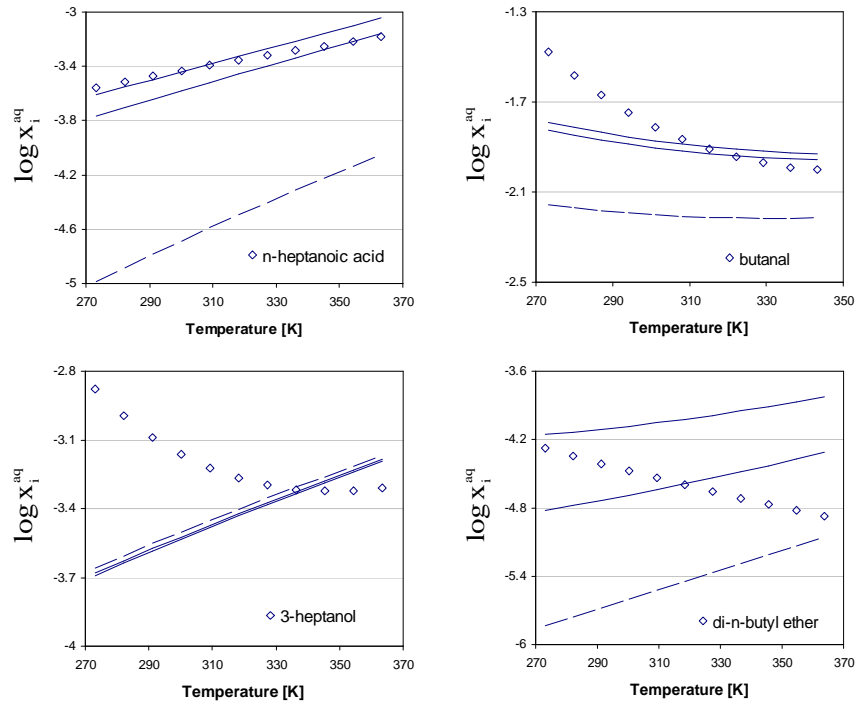


Figure 3: Water solubility for some examples. Notation: Experimental data (points), regressed  $l_{ij}$  (solid line), averaged  $l_{ij}$  (dot-dash line) and predictive approach (dashed line).

c) *n*-octanol/water partition coefficient

The third property considered in this work is *n*-octanol/water partition coefficient  $K_{ow}$ .

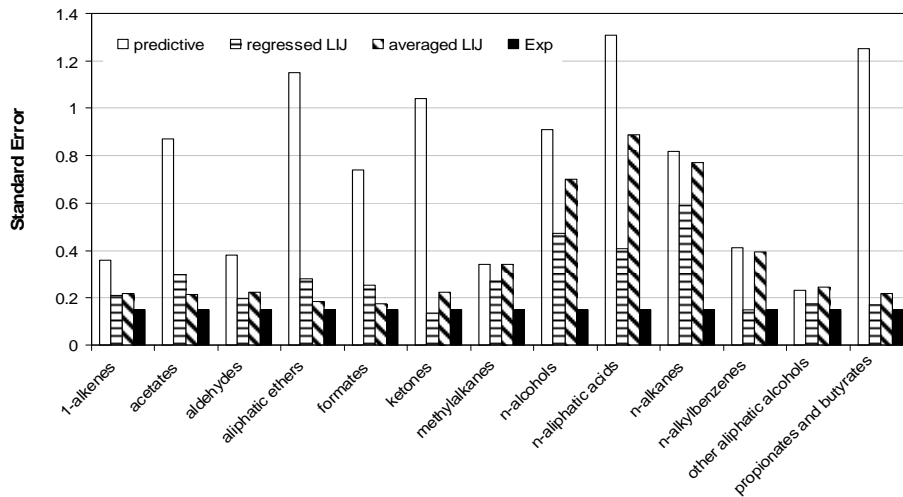


Figure 4: Evaluation of *n*-octanol/water partition coefficients  $K_{ow}$ . The experimental value of SE is that found from the scatter among the experimental data ( $SE = 0.18$ )

The best results are obtained when the regressed  $l_{ij}$  values are used except for acetates, ethers and formates, where the average value is best. The global SE value is 0.3 (using the regressed  $l_{ij}$ ), in comparison to 0.79 in the case of using no  $l_{ij}$ . The prediction is improved a lot (with  $l_{ij}$ ) for some polar chemical families such as formates, acetates, propionates/butyrate, aliphatic ethers, ketones, which are essentially the same as those that showed large improvements for infinite dilution activity coefficient in

water and water solubility. However, some large deviations are observed for some heavy molecules, particularly aliphatic acids, alcohols and alkanes with carbon atoms greater than 10.

## 5. Conclusion

The first objective of this work is to evaluate the performance and especially the predictive capability of the GC-PPC-SAFT model for a wide range of properties and mixtures. The analysis showed a large sensitivity of the model calculations on the parameter values. This is *in se* an significant conclusion in that it illustrates the importance of the quality of the parameter values when using this equation of state. Further mathematical analysis concerning the correlations between parameters may be needed in order to complete the picture.

The conclusion of this first part brought us to propose using a binary interaction parameter  $I_{ij}$ , which is a correction on the combining rule for the segment diameter  $\sigma$ . This is the first time that such a systematic investigation has been carried out for a SAFT-type model. The correlative and predictive capability of the model is studied for three LLE-type properties, i.e. water solubility, infinite dilution activity coefficient in water and n-octanol/water partition coefficient.

The  $I_{ij}$  values are obtained based on infinite dilution activity coefficients in water. Thus, the results for water solubility and n-octanol/water partition coefficients should be considered to be predictions.

As expected, the results are better using the regressed  $I_{ij}$  values but acceptable results are obtained in many cases also when using the average values  $I_{ij}$  which are transferable within a chemical family. These average  $I_{ij}$  values should, however, be used with caution.

In general, the performance of the GC-PPC-SAFT model for water solubilities and n-octanol/water partition coefficients is very encouraging considering the predictive nature of many calculations and the very extensive database used. The results with the GC-PPC-SAFT model are much improved when  $I_{ij}$  is used. Most authors consider that predictive models should be able to give these values within an order of magnitude, which is clearly the case here.

## References

- Barker, J.A., D. Henderson, 1967, Perturbation Theory and Equation of State for Fluids: The Square-Well Potential. *J. Chem. Phys.* 47 (8), 2856-2861.
- Boublik, T., 1970, Hard Sphere Equation of State. *J. Chem. Phys.* 53, 471-473.
- Chapman, W.G., K.E. Gubbins, G. Jackson et M. Radosz, 1989, SAFT: Equation of State Solution Model for Associating Fluids. *Fluid Phase Equilib.* 52, 31-38.
- Chapman, W.G., K.E. Gubbins, G. Jackson et M. Radosz, 1990, New Reference Equation of State for Associating Liquids. *Ind. Eng. Chem. Res.* 29 (8), 1709-1721.
- Economou, I.G., 2002, Statistical Associating Fluid Theory: A Successful Model for the Calculation of Thermodynamic and Phase Equilibrium Properties of Complex Fluid Mixtures. *Ind. Eng. Chem. Res.* 41 (5), 953-962.
- Gros, H.P., S. Bottini et E.A. Brignole, 1996, A Group Contribution Equation of State for Associating Mixtures. *Fluid Phase Equilib.* 116 (1-2), 537-544.
- Gross, J., G. Sadowski, 2001, Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules. *Ind. Eng. Chem. Res.* 40 (4), 1244-1260.
- Hubert, G.W., S. Iborra et A. Corma, 2006, Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chem. Rev.* 106 (9), 4044-4098.
- Ikonomou, G.D., M.D. Donohue, 1986, Thermodynamics of Hydrogen-bonded Molecules: The Associated Perturbed Anisotropic Chain Theory. *AIChE J.* 32 (10), 1716-1725.
- Jog, P.K., W.G. Chapman, 1999, Application of Wertheim's Thermodynamic Perturbation Theory to Dipolar Hard Sphere Chains. *Molec. Phys.* 97 (3), 307-319.
- Kontogeorgis, G.M., E.C. Voutsas, I.V. Yakoumis et D.P. Tassios, 1996, An Equation of State for Associating Fluids. *Ind. Eng. Chem. Res.* 35 (11), 4310-4318.
- Kontogeorgis, G.M., G.F. Folas *Thermodynamic Models for Industrial Applications: From Classical and Advances Mixing Rules to Association Theories*; Wiley: New York, 2010.
- Mansoori, G.M., N.F. Carnahan, K.E. Starling et T.W. Leland, 1971, Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres. *J. Chem. Phys.* 54 (4), 1523-1525.
- Müller, E.A., K.E. Gubbins, 2001, Molecular-Based Equations of State for Associating Fluids: A Review of SAFT and Related Approaches. *Ind. Eng. Chem. Res.* 40 (10), 2193-2211.



- Nguyen, T.-B., J.-C. de Hemptinne, B. Creton et G.M. Kontogeorgis, 2013, GC-PPC-SAFT equation of state for VLE and LLE of hydrocarbons and oxygenated compounds. Part I: Sensitivity analysis. *Ind. Eng. Chem. Res* , 52, 7014-7029
- Nguyen-Huynh, D., J.-P. Passarello, P. Tobaly et J.-C. de Hemptinne, 2008, Application of GC-SAFT EOS to Polar Systems Using a Segment Approach. *Fluid Phase Equilib.* 264 (1-2), 62-75.
- Nguyen-Huynh, D., J.-C. de Hemptinne, R. Lugo, J.-P. Passarello et P. Tobaly, 2011, Modeling Liquid-Liquid and Liquid-Vapor Equilibria of Binary Systems Containing Water with an Alkane, an Aromatic Hydrocarbon, an Alcohol or a Gas (Methane, Ethane, CO<sub>2</sub> or H<sub>2</sub>S), Using Group Contribution Polar Perturbed-Chain Statistical Associating Fluid Theory. *Ind. Eng. Chem. Res* , 50 (12), 7467-7483.
- Paricaud P., 2008, Phase Equilibria in Polydisperse Nonadditive Hard-sphere Systems. *Physical Review E* , 78 (2), 021202.
- Santos, A., M. López de Haro et S.B. Yuste, 2005, Equation of State of Nonadditive d-dimensional Hard-Sphere Mixtures. *J. Chem. Phys.* 122 (2), 024514.
- Tamouza, S., J.-P. Passarello, P. Tobaly et J.-C. de Hemptinne, 2004, Group Contribution Method with SAFT EOS Applied to Vapor Liquid Equilibria of Various Hydrocarbons Series. *Fluid Phase Equilib.* 222-223, 67-76.
- Tan, S.P., H. Adidharma et M. Radosz, 2008, Recent Advances and Applications of Statistical Associating Fluid Theory. *Ind. Eng. Chem. Res* , 47 (21), 8063-8082.

## Sensibilité des paramètres PPC-SAFT dans la prédiction des propriétés d'équilibre liquide-vapeur et liquide-liquide

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### Résumé:

Les travaux de Nguyen et al. [Nguyen, T.-B.; De Hemptinne, J.-C.; Creton, B.; Kontogeorgis, GM *Ind. Chem. Res.*, 2013 (sous presse)] ont montré que l'équation d'état GC-PPC-SAFT est capable de prédire les propriétés de l'équilibre liquide-liquide (ELL). En vue d'améliorer la capacité prédictive du modèle, une analyse de sensibilité des paramètres a été réalisé vis-à-vis du calcul de huit propriétés industrielles importantes (tension de vapeur du corps pur, constantes de Henry d'un certain nombre de gaz et démixtions en présence d'eau et de n-octanol), à partir d'une base de données contenant 290 composés mono-fonctionnels. On y observe une sensibilité très importante de certains paramètres du modèle à la démixtion liquide-liquide. Au vu de ces résultats, il est proposé d'introduire un paramètre d'interaction binaire  $l_{ij}$  sur la règle de combinaison du diamètre de segment, ce qui se fonde par la théorie non-additive de la sphère dure.

Le paramètre d'interaction binaire  $l_{ij}$  est régressé sur le coefficient d'activité à dilution infinie dans l'eau. Il y a 134 molécules dans la base de données de régression. Les valeurs régressé et celles moyennes par famille, sont ensuite utilisées pour prédire la solubilité dans l'eau et le coefficient de partage eau/n-octanol.

En général, les résultats obtenus sont très encourageants par rapport à l'approche prédictive qui est discutée dans les travaux antérieurs [Nguyen, T.-B.; De Hemptinne, J.-C.; Creton, B.; Kontogeorgis, GM *Ind. Chem. Res.*, 2013 (sous presse)]. Les écarts globales pour le coefficient d'activité à dilution infinie dans l'eau, la solubilité dans l'eau et le coefficient de partage eau/n-octanol sont de 0,09, 0,22, 0,30, respectivement. Cependant, l'utilisation du paramètre d'interaction binaire  $l_{ij}$  ne permet pas de représenter correctement le minimum de solubilité.

**Mot-clés :** GC-PPC-SAFT, composés oxygénés, ELV, ELL, paramètre d'interaction binaire.