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PERFORMANCE OF PREDICTIVE MODELS IN PHASE EQUILIBRIA OF COMPLEX ASSOCIATING SYSTEMS: PC-SAFT AND CEoS/GE

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Abstract - Cubic equations of state combined with excess Gibbs energy predictive models (like UNIFAC) and equations of state based on applied statistical mechanics are among the main alternatives for phase equilibria prediction involving polar substances in wide temperature and pressure ranges. In this work, the predictive performances of the PC-SAFT with association contribution and Peng-Robinson (PR) combined with UNIFAC (Do) through mixing rules are compared. Binary and multi-component systems involving polar and non-polar substances were analyzed. Results were also compared to experimental data available in the literature. Results show a similar predictive performance for PC-SAFT with association and cubic equations combined with UNIFAC (Do) through mixing rules. Although PC-SAFT with association requires less parameters, it is more complex and requires more computation time.
Keywords: PC-SAFT; Association term; Cubic equations of state; Gibbs Excess models; Phase equilibria.

INTRODUCTION

Modeling phase equilibria and thermodynamic properties of systems in which molecules exhibit associating interactions is still a challenge for the chemical industry. The sheer number of recent studies on equations of state applied to associating systems points to this fact (Gross and Sadowski, 2002; Derawi *et al*., 2004; Ruffine *et al*., 2006; Kontogeorgis *et al*., 2007; Perakis *et al*., 2007; Grenner *et al*., 2007; Kleiner *et al*., 2009).

Progress regarding equations of state adequate for complex and macromolecular compounds was made by applying principles of statistical mechanics, assuming the molecules to be arranged in a lattice (Sanchez and Lacombe, 1974). Despite its simplicity, this molecular model accounts for size and shape effects of molecules and has been successfully applied to simple species as well as large polymeric fluids and their mixtures (Gross and Sadowski, 2001). Among these equations of state, the SAFT (Statistical Associating Fluid Theory) and PC-SAFT (Perturbed Chain - Statistical Associating Fluid Theory) models stand out.

The SAFT equation of state, suggested by Huang and Radosz (1990) is able to reproduce the thermodynamic properties of several fluids. However, this model still has limitations, especially when modeling more complex systems (such as pharmaceuticals, polymers, detergents and food ingredients). The PC-SAFT equation of state, proposed by Gross and Sadowski (2001), is based on the modification of the SAFT dispersion term. While non-spherical molecules are represented in the SAFT model as chains of freely jointed spherical segments, in PC-SAFT attractive (dispersive) interactions are

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modeled by taking into account the shape and size effects of molecules. PC-SAFT has shown a great application potential, being capable of overcoming most limitations seen in other models and being suitable for various systems of pure fluids or mixtures, including polymers and complex polar mixtures. For polymer systems, the association term is usually neglected, since most systems are non-associating. Compared to the SAFT model, PC-SAFT was found to improve pure-component representation and eliminate systematic errors which occur when the dispersion term does not account for the non-spherical shape of molecules (Gross and Sadowski, 2001; Gross and Sadowski, 2002). A clear improvement over the earlier version of SAFT was also found for mixtures, for which the PC-SAFT model showed predictive strength and revealed precision in the correlation of asymmetric mixtures (Gross and Sadowski, 2001).

Gross and Sadowski (2002) applied the PC-SAFT equation of state to pure associating components as well as to vapor-liquid and liquid-liquid equilibria of binary mixtures of associating substances, such as alcohols, amines, water and acetic acid. Grenner *et al*. (2007) applied PC-SAFT to model liquid-vapor and liquid-liquid equilibria for glycol oligomer systems. Liquid-liquid extraction has been gaining importance in biochemical engineering as a result of the development of aqueous two-phase systems for the purification and isolation of macromolecules (Perumalsamy and Murugesan, 2009). Kleiner *et al*. (2009) have shown that the PC-SAFT equation of state with association can be successfully applied to a whole variety of substances ranging from small gas molecules up to solubility of organic solutes (such as paracetamol) in organic solvents and polymeric systems. In these cases, the authors relied on empirical binary interaction parameters for better model and experiment matching.

The Group Contribution (GC) with Association Equation of State (GCA-EoS) is the first equation of state of the SAFT family (Chapman *et al*., 1989) that uses the GC approach of the Wertheim model (Wertheim 1984a and 1984b). By assuming a value of one for the radial distribution function, it was possible to take into account the association contribution by a GC approach. In the group contribution approach molecules are considered to be formed by segments chosen from a previously established set, which allows the description of a large number of substances in terms of a much smaller number of parameters (Ourique and Telles, 1997). Association and solvation effects play a major role in the properties of pure compounds and mixtures that can form hydrogen bonds. GCA-EoS (Gros *et al*., 1996) explicitly takes into account these strong and highly directed attractive forces via its group contribution association term, which is based on Wertheim's theory as applied in the SAFT equation (Chapman *et al*., 1990).

Other alternatives that are being employed for the phase equilibria prediction of systems with association are cubic equations of state (CEoS) combined with Gibbs Excess models G^E and Cubic Plus Association (CPA) equations. The combination of CEoS with Gibbs Excess models G^E is well known and, since its basic idea was presented by Huron and Vidal (1979), several new mixing rules have been developed to extend the applicability of cubic EoS (e.g., Peng Robinson (PR), Soave-Redlich-Kwong (SRK)) to the prediction of high-pressure, high-temperature vapor-liquid equilibria of polar and/or asymmetric mixtures (Coutsikos *et al*., 1995). More interestingly, CEoS can become powerful predictive tools for a wide range of applications when coupled with predictive G^E models, such as UNIFAC (Weidlich and Gmehling, 1987) variants and COSMO-based models (Klamt *et al*., 1998; Lin and Sandler, 2002). Cubic Plus Association (CPA) is an equation of state that is based on a combination of the Soave-Redlich-Kwong (SRK) equation to describe the "physical" interactions and the association term of the Wertheim theory for the polar/association effects (Kontogeorgis *et al*., 1996). The CPA EoS is not cubic with respect to volume and contains five pure compound parameters. It is applied to complex multicomponent, multiphase equilibria for systems containing associating fluids (Folas *et al*., 2005). However, the CPA EoS and GCA-EoS were not used in this work because their association term is the same as that in PC-SAFT.

The goal of this work is to compare the predictive performance of PC-SAFT with association contribution and PR combined with UNIFAC (Do) through mixing rules, with no additional empirical correction (binary interaction parameters). Binary and multi-component systems involving polar and non-polar substances were studied. Results were also compared to experimental data available in literature.

METHODOLOGY

PC-SAFT Equation of State

The PC-SAFT equation of state (Gross and Sadowski, 2001) was implemented in MATLAB 5.3, according to the usual expression for the residual

Helmholtz free energy:

$$\tilde{a}^{res} = \tilde{a}^{hc} + \tilde{a}^{disp} + \tilde{a}^{assoc} \quad (1)$$

where $\tilde{a}^{hc}$ indicates the molecular chain contribution of the substance, $\tilde{a}^{disp}$ represents the dispersion contribution and $\tilde{a}^{assoc}$ is the association contribution term. These terms were calculated according to the expressions presented by Gross and Sadowski (2001, 2002).

The combining rules used for the three PC-SAFT parameters related to the terms $\tilde{a}^{assoc}$ and $\tilde{a}^{disp}$ are the same presented by Gross and Sadowski (2001). Two pure-component parameters determine the associating interactions between the association sites A_i and B_i of a pure component i: the association energy $\epsilon^{A_iB_i}$ and the effective association volume $\kappa^{A_iB_i}$. It is generally far from trivial to obtain cross-association parameters between two different associating substances i and j. For many systems, however, approximate values for the cross-association parameters can be determined from pure-component association parameters. Simple combining rules for cross-association were used by Gross and Sadowski (2002) from a consideration of gas-phase association in the low-pressure limit, as:

$$\epsilon^{A_iB_j} = \frac{1}{2}(\epsilon^{A_iB_i} + \epsilon^{A_jB_j}) \quad (2)$$

$$\kappa^{A_iB_j} = \sqrt{\kappa^{A_iB_i}\,\kappa^{A_jB_j}}\left(\frac{\sqrt{\sigma_{ii}\,\sigma_{jj}}}{\frac{1}{2}(\sigma_{ii}+\sigma_{jj})}\right)^3 \quad (3)$$

Most associating components are assumed to have two association sites (often referred to as the 2B model according to the methodology proposed by Huang and Radosz (1990)). Although a reasonable assumption for some species (such as alcohols), it is a considerable simplification for other compounds – in particular for water. But there is still room for debate on this subject. For instance, Economou and Tsonopoulos (1997) state that water is best represented by a four-site treatment, whereas Suresh and Elliott (1992) found the two-site model to perform at least as well.

For the cases studied in this work, PC-SAFT parameters for non-associating substances (methane, propane and butane) were taken from Gross and Sadowski (2001). For associating substances, two references were used: Gross and Sadowski (2002) for methanol, 1-butanol, 1-pentanol, 1-octanol, and water and Grenner *et al*. (2007) for the TEG and water system only. Following the selected literature sources for the pure substance parameters, the two-site model were used, except for the binary system between water and triethylene glycol (TEG), where the four-site model presented in Grenner *et al*. (2007) was employed.

Peng-Robinson Combined with UNIFAC (Do)

Most of the cubic EoS available today are special cases of a general cubic equation (Valderrama, 2003), which can be written as:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)} \quad (4)$$

where P is the pressure, T is the temperature, V is the molar volume, ε and σ are constants for all substances and depend on the particular EoS and a(T) and b are, respectively, the attractive and co-volume parameters specific for each substance.

When dealing with mixtures, the expressions for the attractive a and co-volume b parameters should be computed as a function of the pure substance values a_i and b_i through mixing rules.

Using the Universal Mixing Rule (UMR), Voutsas *et al*. (2004) obtained satisfactory results for VLE calculations performed in polar systems and asymmetric alkane systems. More recently, Staudt *et al*. (2010) proposed the Universal and Generic Mixing Rule (UGMR) which is a simple modification of UMR. In these mixing rules, the mixture co-volume parameter b is given by the following empirical rule (Voutsas *et al*., 2004):

$$b = \sum_i \sum_j x_i x_j b_{ij},\ b_{ij} = \left(\frac{b_i^{\frac{1}{2}} + b_j^{\frac{1}{2}}}{2}\right)^2 \quad (5)$$

The attractive parameter a is obtained with the aid of a G^E model as follows:

$$\frac{G^E}{RT} = A_0\left[\frac{a}{bRT} - \sum_i x_i \frac{a_i}{b_i RT}\right] \quad (6)$$

where G^E is then evaluated by any Gibbs free energy model.

In the original proposal of UMR, the Gibbs excess model was UNIFAC but with the Flory-Huggins contribution of the combinatorial part neglected. For UGMR the authors suggest using any

Gibbs excess model, not just UNIFAC variants. In the present work, the modified UNIFAC model was used with the parameter matrix as reported by Gmehling *et al*. (1993) with both UMR and UGMR mixing rules.

RESULTS AND DISCUSSION

This section presents results for calculation of vapor-liquid and liquid-liquid equilibria for binary mixtures and liquid-liquid-vapor equilibria for a quaternary mixture of associating substances obtained using the perturbed-chain SAFT equation of state and Peng-Robinson combined with UNIFAC (Do) through UMR and UGMR mixing rules. Mixtures containing one associating compound (selfassociation) or two associating substances (crossassociation) are discussed in the next section; then a mixture containing four substances is discussed in the last section.

Vapor-Liquid and Liquid-Liquid Equilibria

Figure 1 shows vapor-liquid equilibria for the 1-butanol/n-butane binary mixture at 160 and 200 °C, conditions under which n-butane is above its critical temperature. The experimental data were taken from Deák *et al*. (1995). Two association sites were assigned for 1-butanol (often referred as the 2B model) as proposed by Gross and Sadowski (2002). Mixtures with only one associating substance (self-association) do not require mixing rules for the association term. Calculations for such mixtures are suitable for investigating whether the association term contributes to the total Helmholtz energy (in Equation (1)) at the correct order of magnitude. For both temperatures no binary interaction parameter was used. The results of PR + UMR and PR + UGMR show little deviation from the vapor-liquid equilibrium data at both temperatures, while the PC-SAFT equation of state shows better agreement with the experimental data.

The modeling of mixtures in which associative interactions occur between different substances is particularly demanding for molecular theories. Also, the calculation results for cross-associating systems depend significantly on the combining rules. As stated before, in this work, the combining rules (Eq. (2) and (3)) for the PC-SAFT association term suggested by Gross and Sadowski (2002) were used. Results for three systems (methanol/1-octanol, water/1-pentanol and water/triethylene glycol binary mixtures) where this is an important issue are presented in Figures 2 and 3 and will be described below.

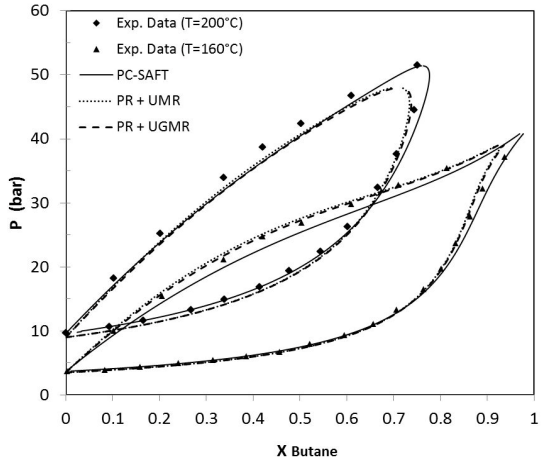

Figure 1: Vapor-liquid equilibria of 1-butanol and n-butane at two temperatures.

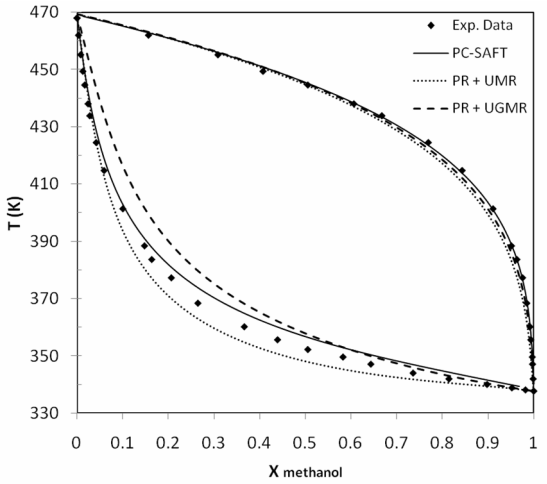

Figure 2: Isobaric vapor-liquid equilibria of methanol and 1-octanol at P = 1.013 bar.

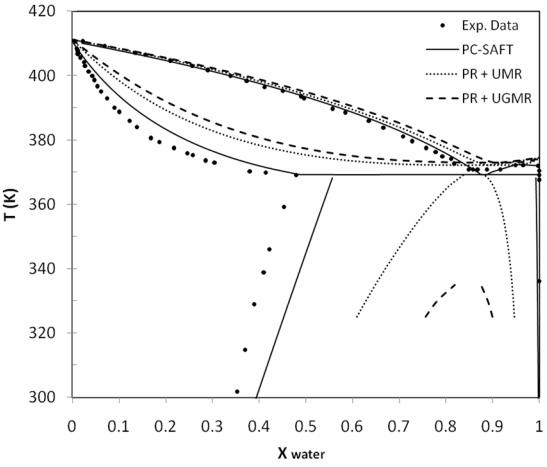

Figure 3: Isobaric, heteroazeotropic vapor-liquid and liquid-liquid equilibria of water and 1-pentanol at P = 1.013 bar.

Figure 2 shows a T-x diagram of the methanol/1-octanol mixture at P = 1.013 bar. For both alcohols two association sites were assigned, according to what was previously described. This model assumes that there are two sites for each component, one being on the hydrogen and the other on the oxygen of the hydroxyl groups. According to this methodology, it is assumed that no association occurs on sites of the same type, while all of the associating sites A will associate with all sites B. In this case, when a site A associates with a site B of the same associating substance, only pure-component parameters are used for the association energy and effective association volume of this substance. When associative interactions occur with different components, mixing rules are used to determine such values. For this system, experimental data were obtained by Arce *et al*. (1995).

As can be seen in Figure 2, good prediction of this vapor-liquid equilibrium was possible with the PC-SAFT equation of state. This result is important because it confirms the accuracy of the two-site model, as well as the efficiency of the combining rules used to determine interaction between sites of different substances. Another possible analysis is that PC-SAFT can also accurately describe the pure components, which lie in the extremes of the curve. This is one of the main improvements in PC-SAFT in comparison with SAFT, as SAFT produced significant deviation in these regions. The results obtained for this system by PR+UMR and PR+ UGMR show a slightly higher deviation from the experimental vapor-liquid data compared to PC-SAFT.

The phase behavior of the water/1-pentanol system at P = 1.013 bar is given in Figure 3 in a T-x diagram. This system shows liquid-liquid equilibrium at lower temperatures and a heteroazeotropic vapor-liquid equilibrium. In this case, when using PC-SAFT, both water and 1-pentanol were represented with the two-site model. Thus, the same associative interactions occur as described in the previous example.

For the vapor-liquid equilibrium, the results in Figure 3 show that all models used present some deviation compared to the experimental data gathered by Cho *et al*. (1984). For the liquid-liquid region, all models predict an enhanced solubility compared with the experimental data of Zhuravleva and Zhuravlev (1970). Again, the experimental observations were better represented by PC-SAFT.

Figure 4 shows the T-x diagram for the water/ triethylene glycol (TEG) mixture at P = 85 kPa. Unlike the previous PC-SAFT results, the ones presented in Figure 4 were calculated using the four-site model and the PC-SAFT parameters presented by Grenner *et al*. (2007). This model assigns four association sites to each molecule, two on hydrogen and two on oxygen. Different saturation temperatures were predicted for TEG by the PR and PC-SAFT equations of state. However, using only the experimental data of Mostafazadeh *et al*. (2009), the correct value could not be verified. All models deviated somehow from the experimental data with similar results.

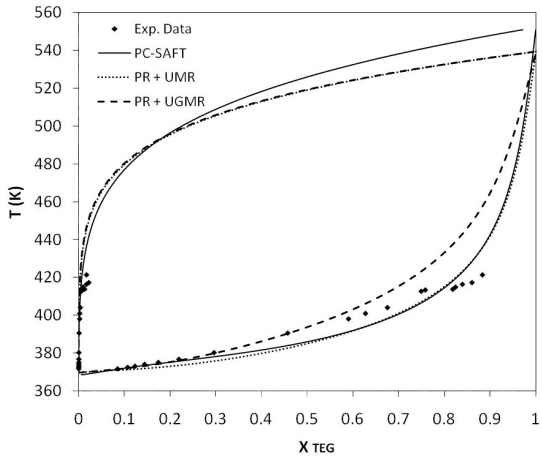

Figure 4: Isobaric vapor-liquid equilibria of water and TEG at P = 85 kPa.

Regarding the two mixing rules used in this section, no significant difference in the results are expected since they are both based on similar simplifications and assumptions. This can be especially seen when symmetric molecules are tested (Figure 1). The elimination of the "double combinatorial effect" of the activity equation and EoS (Kontogeorgis and Economou, 2010) in the UMR model gave a better response for the systems in Figures 2 and 3. The bigger discrepancies between the two mixing rules were always observed for the liquid phase behavior.

VLL Equilibria for Multicomponent Systems

Using experimental data presented by Yan *et al*. (2009) for a quaternary system of methanol, water, methane and propane, a simulation of the vapor-liquid-liquid (VLL) equilibrium was made. Two temperature conditions were simulated: 253.15 K and 265.15 K, both at a pressure of 67 bar.

Table 1 shows the experimental data of Yan *et al*. (2009) and results obtained by the PC-SAFT and Peng-Robinson coupled with UNIFAC (Do) through

the UGMR mixing rule at 253.15 K. The results in Table 1 show great similarity between the results obtained with PC-SAFT and PR+UGMR for this quaternary mixture. PC-SAFT showed an average deviation of 8.7% when compared to experimental data, while the average deviation for PR+UGMR was 7.6%. Again, similar results were obtained with the two models tested, but in this case with slightly better results using the CEoS.

Similarly, Table 2 shows the results for the aforementioned mixture at a temperature of 265.15 K. Once more, similar results were obtained for the models PC-SAFT and PR+UGMR, with average deviations relative to the experimental data of 5.7 % and 4.4 %, respectively.

As it stands, it is important to mention that both SAFT EoS models and CEoS have limitations. Some works have demonstrated that SAFT EoS models might show unrealistic and even non-physical predictions due to the temperature dependencies of the a segment packing fraction and the very high-polynomial orders for volume (Polishuk, 2010). The first factor is responsible for predicting negative values of the heat capacities at very high pressures and the intersections of isotherms at high densities. The very high-polynomial orders of several SAFT EoS models result in the prediction of additional stable but unrealistic critical points and pertinent fictitious phase equilibria. On the other hand, empirical thermal cohesion functions, $\alpha(T_r)$, are frequently used in conventional CEoS for fitting the vapor pressures of pure fluids. Segura *et al*. (2003) demonstrated that, in the case of pure fluids, the $\alpha(T_r)$ function can potentially predict multiple mechanically stable critical points, thus affecting the global topology of phase equilibrium predictions. An analysis based on the consistency of the prediction of the Joule-Thomson inversion curve reveals that these predictions are not reliable from a physical point of view. In the case of conventional CEoS with quadratic mixing rules, another pitfall related to conventional $\alpha(T_r)$ functions is the prediction of nondifferentiable critical lines and equilibrium envelopes for mixtures. Such a physical inconsistency might generate a mechanism that predicts closed loops of immiscibility in van der Waals-type EOS that contain a temperature-dependent parameter. Nevertheless, these numerical pitfalls will be studied in future works.

Table 1: Molar composition experimental data and predicted output currents of the quaternary system (methanol, water, methane, propane) at 67 bar and 253.15K.

Component	Experimental			PC-SAFT			PR+UGMR(*)		
	Aqueous	Organic	Vapor	Aqueous	Organic	Vapor	Aqueous	Organic	Vapor
Methanol	0.536	0.0007	-	0.4905	0.0059	0.0002	0.508	0.0052	3.63E-04
Water	0.447	-	-	0.4139	0.0011	0.0001	0.423	0.0068	9.52E-05
Methane	0.0105	0.540	0.874	0.0409	0.5192	0.9064	0.045	0.527	0.909
Propane	0.0071	0.459	0.126	0.0548	0.4737	0.0934	0.0242	0.461	0.0907

Table 2: Molar composition experimental data and predicted output currents of the quaternary system (methanol, water, methane, propane) at 67 bar and 265.15 K.

Component	Experimental			PC-SAFT			PR+UGMR(*)		
	Aqueous	Organic	Vapor	Aqueous	Organic	Vapor	Aqueous	Organic	Vapor
Methanol	0.545	0.001	-	0.493	0.0099	0.0004	0.519	0.0076	6.95E-04
Water	0.435	-	-	0.3966	0.0021	0.0001	0.412	0.0066	1.64E-04
Methane	0.0105	0.520	0.861	0.0424	0.4678	0.8791	0.0406	0.483	0.882
Propane	0.0098	0.483	0.139	0.0679	0.5202	0.1204	0.0282	0.503	0.1172

CONCLUSIONS

The PC-SAFT equation of state and Peng-Robinson combined with UNIFAC (Do) through UMR and UGMR mixing rules were used to model phase equilibria of mixtures of associating components. The objective was to assess the predictive power of the models, and no additional empirical corrections were made, e.g., binary interaction parameters.

First, a mixture with one associating compound was investigated. For this case, no mixing rules are required for in the association term of the PC-SAFT equation of state. For this class of mixtures, vapor-liquid equilibrium was calculated for 1-butanol and n-butane. Liquid-liquid and vapor-liquid equilibria were also calculated for mixtures with two associating substances. In the PC-SAFT model, simple combination rules were adopted for the cross-associating interactions in this study; no additional binary interaction parameter was thereby introduced. In general, the predictions of all models were similar for all binary cases, with a small advantage for PC-SAFT. For the 1-pentanol/water system, larger deviations from the vapor-liquid data were observed for all models. For the LLE of this system poor results were obtained, but again with an advantage for PC-SAFT.

The liquid-liquid-vapor equilibrium of a quaternary system composed of water, methanol, methane and propane was also investigated. Again all models performed similarly, but now with a small advantage for the cubic equations of state. The determination of the mole fractions of each component present in the three-phase system showed an average deviation from experimental data of 7% at most.

These results indicate that the PC-SAFT predictive performance is similar (in some cases superior) to that obtained with cubic equations combined with UNIFAC (Do) and mixing rules. Although PC-SAFT is more complex and requires more computational time, the number of parameters involved in PC-SAFT with association is much smaller than that required by the UNIFAC (Do) parameter matrices. Further, the use of simplified PC-SAFT models for the number of sites provided good results in all the cases studied. Thus, these simpler models should be preferred, which considerably reduces the computational time involved in these calculations.

Finally, an extended database of parameters for the PC-SAFT association contribution is still missing. Only with a vast collection of parameters will this equation be able to compete in an industrial context.

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