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PC-SAFT parameters from ab initio calculations

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ABSTRACT

We use highly accurate ab initio calculations of binding enthalpies and entropies of gas phase clusters of alcohols to demonstrate how they can be used to obtain association parameters for PC-SAFT. The thermochemical results demonstrate that cooperativity effects and state dependent cluster distributions cause a strongly varying average enthalpy and entropy per bond as function of temperature and density for alcohols. In contrast to this, the two association parameters of PC-SAFT lead to density independent bond enthalpy and entropy and are thus effective parameters. Therefore, we choose to compute the cluster distribution at a universal state point and show that the thus obtained association parameters can be used to reduce the number of adjustable parameters from 5 to 3 with only a marginal loss of accuracy for most of the studied systems, and even an estimation of thermodynamic properties without adjusted parameters is possible. The ab initio calculations suggest that the 2B association scheme is more appropriate for 1-alkanols than the 3B one.

1. Introduction

The rather limited availability of trusted experimental data like thermodynamic pure-component properties leads to a great demand for reliable thermodynamic models for the design of new processes [1]. Many different classes of thermodynamic property prediction models have emerged in the past to fulfill the need for such data. Usually, these models aim to reach several goals that partly contradict each other. These goals include that the model should be able to describe a wide variety of data, for chemically diverse compounds, at high accuracy, with as little input of experimental data as possible. Well-known examples of such models are e.g. structure interpolating group contribution (GC) models [2,3], quantitative structure–property relationships (QSPR) [4], molecular simulations using transferable potentials [5], models for the liquid phase based on quantum mechanics (QM) like COSMO-RS [6] and equation of state (EOS) models. EOS models have the advantage that it is possible to compute any thermodynamic equilibrium property at practically any fluid condition for pure compounds and mixtures, with a single model utilizing a single parameter set. However, until recently EOS models mainly have been used as correlation or extrapolation tools. Exceptions are group contribution models that have been developed for EOS parameters and often provide a high accuracy. Such GC models exist e.g. for lattice models [7] and for cubic EOSs in combination with a G^E model like UNIFAC (predictive Soave–Redlich–Kwong (PSRK) [8] and volume-translated Peng–Robinson (VTPR) [9]). Several GC versions of SAFT-based models (Statistical Associating Fluid Theory) have been proposed recently as well. They include models like GC-SAFT [10] and GC-SAFT-VR [11] that are based on SAFT-VR [12]. SAFT-γ is a GC-SAFT model based on a hetero-nuclear version of SAFT-VR [13]. GC-PC-SAFT [14] and further models [15–17] are based on PC-SAFT [18], GC-PPC-SAFT includes an extension for polar molecules [19] and HS-PC-SAFT [20] one for hetero-segmented chains. There are also models based on simplified PC-SAFT [21,22] and a group contribution with association (GCA) EOS [23] that employs SAFT for the association contribution only.

All GC models have in common that they are always applicable to a relatively small class of compounds for which group additivity parameters have been determined only. Therefore, there are also other approaches to reduce the number of data points required to determine the EOS parameters. Starting with an experimental minimal data set of only three and five experimental data points that allow for a fitting of the pure-component parameters for non-associating and associating components, respectively [24], the experimental effort was already reduced to only one vapor pressure point for non-associating substances using quantum mechanics [25] or parameter correlations [26]. Since modeling of associating components using PC-SAFT requires two additional parameters and therefore a larger amount of experimental data, the parameter estimation for this substance category is of major interest. With regard to this task different approaches have been investigated by now.

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First, Wolbach and Sandler coupled the equilibrium constant of the dimerization in the vapor phase, which can be obtained from quantum mechanically calculated enthalpies and entropies of dimerization, with the association strength of SAFT [27]. In principle, it is possible to calculate both association parameters ab initio by this approach, but Wolbach and Sandler's results have not been completely convincing [27]. Second, parameter correlations have been developed for associating components [28] in analogy to the parameter correlations for non-associating substances [26]. Therefore, the already mentioned approach of Wolbach and Sandler [27] was combined with COSMO-RS calculations [29,30] that give the hydrogen-bonding contribution to the enthalpy of the condensed liquid phase. This promising approach proved the possibility of using quantum mechanical calculations to obtain at least one of the association-specific PC-SAFT pure-component parameters [28] in general. On the other hand, the pure-component modeling results especially of the carboxylic acids pointed out the room for further improvements [28].

Very recently, Ferrando et al. suggested to compute the association parameters for use in PPC-SAFT from the degree of association observed in a Monte Carlo (MC) simulation [31]. Using this method, a good correlation of experimental VLE data with only three parameters adjusted to them is possible but a MC simulation using an interaction potential fitted to additional experimental data is required additionally.

In the present study Wolbach and Sandler's [27] general dimerization approach served as a starting point for the development of an improved quantum mechanically-based approach. Unfortunately, the dimerization approach shows several weaknesses that are mainly due to the limitation of available methods and computational capacity when the approach has been developed by Wolbach and Sandler [27]. First, the quantum mechanical calculations were conducted applying the Hartree–Fock method and density functional theory (DFT) that used Becke's three-parameter functional with the gradient corrected correlation functional of Lee, Yang, and Parr (B3LYP) [32–35]. This method has recently been shown to perform worse than average for hydrogen-bonded complexes compared to other DFT and post HF methods available today [36–38]. Second, a rigid rotor, harmonic oscillator (RRHO) approximation was applied to model the effect of the motion of the nuclei on thermodynamic functions, in which rotations of parts of a molecule or cluster were neglected (internal rotations). Third, only one conformation of each species (monomers and dimers only) was considered and, fourth, cooperativity was thus neglected. Especially the neglect of cooperativity effects shows a major impact on the calculation of the enthalpy change ΔH resulting in a difference of more than 10 kJ/mol per hydrogen bond for methanol clusters [39]. In comparison, for a 10 K standard error in the normal boiling temperature, an accuracy of 1 kJ/mol in Gibbs free energy change, ΔG, is required for short-chain 1-alkanols as demonstrated by a sensitivity analysis described in detail in Section 2.2.1.

The discussion of the methods employed by Wolbach and Sandler showed that these methods were not sufficient to compute thermochemical data of dimerization with the accuracy required to judge the validity of their basic assumption, namely that the transfer of thermochemical gas phase hydrogen bond data into SAFT parameters is possible. Therefore, we investigated in recent work [40,41] whether the required accuracy can be achieved with modern quantum mechanical and statistical thermodynamic methods. A comparison to experimental gas densities shows that this is indeed possible and also demonstrates the relevance of cooperativity at higher densities [40,41]. Hence, an extension of Wolbach and Sandler's method of coupling both models at zero density is required (Section 3.2). The improved approach was applied to estimate the two association parameters for the homologous series of the 1-alkanols from thermochemical data calculated ab initio. The three remaining pure-component parameters were fitted to experimental vapor pressure and liquid volume data. The pure-component modeling results for the so-obtained parameter sets were compared to appropriate modeling results using five fitted pure-component parameters (Section 3.2.1) and to results based on one (Section 3.2.4) and on no fitting parameters (Section 3.2.4).

2. Methods

2.1. PC-SAFT equation of state

The Perturbed Chain-Statistical Associating Fluid Theory (PC-SAFT) equation of state derived by Gross and Sadowski [18,42], is based on a thermodynamic perturbation theory. Its reference state is given by a hard chain consisting of freely jointed hard spheres. Additional contributions account for dispersive and associative interactions. In principle also the consideration of dipolar and quadrupolar interactions is possible due to appropriate extensions [43–46]. In the present study, these extensions were not used since only substances were regarded where association dominates [42]. Hence, the residual Helmholtz energy, a^{res}, can be calculated according to Eq. (1) considering the reference contribution of the hard chain, a^{hc}, and the perturbing contributions due to dispersive, a^{disp}, and associative interactions, a^{assoc}.

$$a^{\text{res}} = a^{\text{hc}} + a^{\text{disp}} + a^{\text{assoc}} \tag{1}$$

Further details concerning the different contributions are given in the literature [18,42,47–50].

According to the substance type a different number of pure-component parameters are required for their description. For non-associating components, three parameters, namely the segment number, m, the segment diameter, σ, and the dispersion-energy parameter, ϵ/k, are required. Associative interactions can be described by two additional parameters. These are the association volume, κ^{AB}, and the association-energy parameter, ϵ^{AB}/k. They are usually adjusted to vapor-pressure and liquid-volume data over broad temperature ranges simultaneously to the three above mentioned parameters. The choice of an adequate association scheme [50] regards the appearance of different association sites. Within this work, the 2B and the 3B association schemes have been considered for the 1-alkanols as will be rationalized later.

The associative contribution to the residual Helmholtz energy a^{assoc} can be calculated by summation over all association sites of a molecule i considering the fraction of molecules that are not bonded at association site A_i X^{A_i} [47].

$$\frac{a^{\text{assoc}}}{kT} = \sum_i x_i \sum_{A_i=1}^{n_i} \left[\ln(X^{A_i}) - \frac{X^{A_i}}{2} + \frac{1}{2} \right] \tag{2}$$

In Eq. (2) x_i gives the molar fraction, n_i the number of association sites of molecule i, T is the temperature, and k the Boltzmann constant. The fraction of molecules that are not bonded at association site A, X^{A_i}, can be calculated according to the implicit Eq. (3) [47].

$$X^{A_i} = \left(1 + \rho \sum_j x_j \sum_{B_j} X^{B_j} \Delta^{A_i B_j} \right)^{-1} \tag{3}$$

ρ gives the total number density of molecules and $\Delta^{A_i B_j}$ the association strength that can be calculated according to Eq. (4) [50].

$$\Delta^{A_i B_j} = g_{ij}^{\text{hs}}(d_{ij}) \kappa^{A_i B_j} \sigma_{ij}^3 \left[\exp\left(\frac{\epsilon^{A_i B_j}}{kT} \right) - 1 \right] \tag{4}$$

The association strength $\Delta^{A_i B_j}$ is a function of the radial pair distribution function g_{ij}^{hs} of the spherical segments of component i and j