On the estimation of water pure compound parameters in association theories

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RESEARCH NOTE

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Abstract

Determination of the appropriate number of association sites and estimation of

parameters for association (SAFT-type) theories is not a trivial matter. Building

further on a recently published manuscript by Clark et al. [1], this work investigates

aspects in parameter estimation for water using two different association theories.

Their performance for various properties as well as against the results presented by

Clark et al. [1] is demonstrated.

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Association schemes for water and degeneracy of parameters

As mentioned in this abstract, Clark et al. [1] have published recently a manuscript about the choice of association sites for water for use in SAFT-type models. The article emphasizes the care that must be exercised when choosing parameters for water and other associating fluids with SAFT-type theories (or other multi-parameter models) as there is a clear degeneracy in the model parameters when these are regressed from pure compound vapour pressures and liquid densities.

It is of interest to investigate whether the same conclusions hold for other SAFT-type approaches.

Indeed, several sets of water and other associating fluid parameters can be obtained from SAFT-type approaches which can represent vapour pressure and liquid density data in a satisfactory manner. We have previously showed this for water and other fluids [2, 3] using the CPA (Cubic-Plus-Association) [4] equation of state (which uses the same association term as SAFT), while in the case of PC-SAFT [5] this is demonstrated in figure 1.

It is useful, as Clark et al. [1] have shown in their figure 2, to investigate the search for optimal parameters by plotting contours of the absolute average deviation with fixed dispersions and hydrogen bonding energy while fitting the remaining pure compound parameters. The water parameters published by Grenner et al. [6] (dispersion energy $\varepsilon=180.3$ K and association energy-$\varepsilon^{HB}=1804.22$ K) are theoretically based values. Errington et al.[7] obtained, based on molecular simulations studied, values between $\varepsilon= 74-160$ K for the dispersion energy of water. Koh et al. [8] report for the association energy a value of 1813 K. These parameters belong to a minimal surface area as shown in figure 1a (dark blue). We did not use parameters with the lowest deviations of figure 1a because we used a third

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constraint. The first two constraints were keeping the ε and ε^{HB} in the range of physically justified values as we point out in [6]. The third constraint was the segment number-m should have a low value, around unity since water is treated as a nearly spherical molecule and a low molecular weight compound. Thus, we choose m=1.5 and this case is shown in figure 1b.

Both the parameters used in figure 1 and our previous investigations for various SAFT-type approaches [2,6,10,11] indicate that the 4C scheme, which represents physical correct two hydrogen donor sites and the two hydrogen acceptor sites (terminology refers to the work of Huang and Radosz [12]), is indeed the best choice for water.

Input from other properties should be used for selecting the optimum set of pure compound parameters. In our view, these should primarily be readily measurable and widely available properties like enthalpies of vaporization and second Virial coefficients. Input from spectroscopy like monomer fractions, as used by Clark et al. [1], is of course valuable although to our knowledge and for pure compounds such data is available only for water and a few alcohols. The choice of the optimum parameter set is discussed in the next section.

Selection of appropriate water parameters

Clark et al. [1] have discussed how appropriate parameters can be selected for association theories like the SAFT-VR [13], in their work. An interesting property, not directly used in the parameter estimation, is the enthalpy of vaporization.

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According to Clark et al. [1] and as showed in their figure 5, the performance of SAFT-VR is essentially the same for the enthalpy of vaporization of water no matter the parameter set (and association scheme) used. The calculated values with SAFT-VR are not in good agreement with the experimental data and the authors [1] conclude that "nothing in or comparisons with … enthalpy of vaporization can be used to select one set of optimal parameters for water".

As figure 2 shows, other association models like PC-SAFT and CPA perform substantially better than SAFT-VR for this property. As the performance of all three models for vapour pressures is essentially equivalent, the improved enthalpies of vaporization must be primarily attributed to the better vapour volumes or compressibilities achieved.

Clark et al. [1] find great sensitivity in the performance of SAFT-VR with various parameter sets for water against the monomer data obtained from spectroscopy and reported by Luck [15] more than 25 years ago. We find a similar sensitivity as shown in figures 3 and 4, although our results are not quite as good as those reported by Clark et al. [1] using the optimum set in their work (W1 in their figure 7).

We have no intention to underestimate the importance of spectroscopic data, as we have ourselves used them for testing the models [11]. Especially such monomer data for mixtures (associating/inert compounds like alcohol-hydrocarbons) are very useful as several mixture data have indeed been reported and new measurements continue to appear in the literature e.g. [16, 17]. However, spectroscopic monomeric

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data for pure compounds are extremely scarce, to our knowledge available only for water and a few alcohols, and –again to the best of our knowledge- the measurements of Luck [15] on water have not been repeated although they are 25 years old. Due to the apparent lack of plentiful data of this type and the –presumably- associated experimental difficulties, we do not feel that such data can indeed be routinely used for testing association parameters.

Nezbeda and co-workers [18,19] point out that the structure and properties of water are determined primarily be short-range intermolecular forces. Thus, they develop a molecular-based equation of state by setting up an expansion about a short-range reference system. This gives a satisfactory performance also for thermodynamic properties not used in the development of the parameters. Their way illustrates a somewhat different approach to solve the problem which could be considered in future studies. However, that equation of state is also not yet tested for mixture data. The importance of those is addressed in the next section.

The use of mixture data in parameter selection

Mixture data are useful but should only be used for parameter evaluation of associating compounds. Clark et al. [1] have used water-methanol VLE data for this purpose but cross-associating systems cannot be considered to be a real test of the parameters of any of the compounds involved. The effect of cross-association with the requirement of combining rules used will obscure judgement. Moreover, water-methanol is not a very non-ideal system. A more useful test is to use more sensitive data for the associating compound in question with an inert compound e.g. n-alkane

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i.e. in this case to use water-alkane LLE data. When this is done, indeed different

sets yield different results and choice of optimum sets and association schemes can

be achieved e.g. as shown in figure 5 for PC-SAFT and CPA.

The use of mixture data especially for associating/inert mixtures is possibly the

ultimate test for selecting optimum parameters, as parameters which are obtained by

optimizing various pure compound properties may not always be the optimum ones

for mixture calculations. This is evident from figure 6 and table 1, where the

published PC-SAFT 4C-water parameters [6] perform better than the ones estimated

here based on all three properties (vapour pressures, liquid densities and enthalpies

of vaporization).

Concluding remarks

Optimal parameter estimation procedures for water are still missing in relation to

molecular theories. Even for rather similar equations of state like SAFT-VR and

PC-SAFT different results were obtained. Especially interesting is the fact that these

models use essentially the same theory to model hydrogen bonds but still rather

different values for the association energy (SAFT-VR [1] e.g. parameter set W1:

$\varepsilon^{HB}/k=1400.00$ K and PC-SAFT [6]: $\varepsilon^{HB}/k=1804.22$ K). These differences may be

due to various reasons, e.g. different experimental data used in the parameter

estimation (especially the temperature range of the data is of great importance),

different constraints for the parameters or different number of parameters (SAFT-

VR: 6 adjustable parameters, PC-SAFT: 5 adjustable parameters). Additionally, it

seems that contributions e.g. of hydrogen bonding or dipole-dipole interactions are

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incorporated in the parameters of different SAFT type models in different ways, e.g. via the two energetic parameters ε (dispersion energy) and ε^{HB} (association energy). All ε values of the 4 different parameter sets of Clark et al. [1] are higher compared to the value of Grenner et al. [6], and the ε^{HB} values of Clark et al. are accordingly all lower than those of Grenner et al. However, Grenner et al. use theoretically confirmed values to constrain their parameters and the applicability for several mixtures with alkanes, amines or glycols [6,23] confirm the validity of this procedure.

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Table 1. PC-SAFT results for water-methanol VLE at 333.15 K. Water pure compound parameter of this work as presented in the caption of figure 4 and Grenner et al. 2006 parameters from [6]. The methanol pure compound parameter by Gross and Sadowski 2002 [20] parameters are used. The experimental data are taken from Broul et al. [22].

water parameters	kij	ΔP^a /%	Δy^b
this work	0	62	0.1687
	-0.106	1	0.0075
Grenner et al. [6]	0	19	0.0681
	-0.050	1	0.0093

[a] deviations as absolute average deviation (AAD). [b] $\Delta y = 1/np \sum \left| y_i^{calcd} - y_i^{exptl} \right|$ where np is the number of data points.
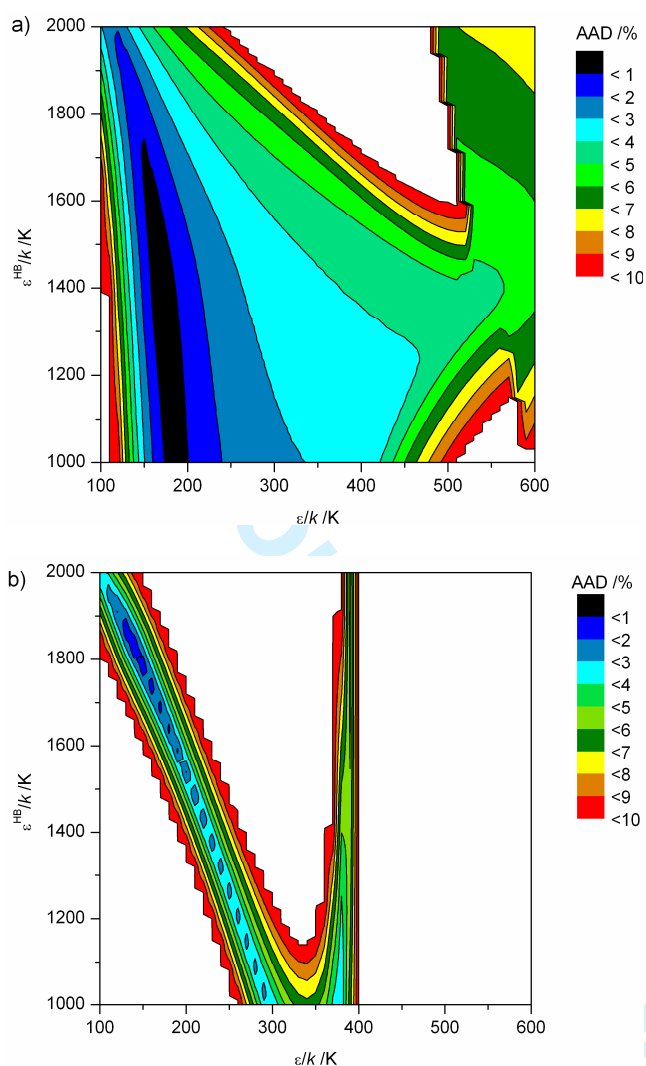
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Figure 1. Contour plot for the percentage absolute average deviation (AAD /%) of the vapour pressure and liquid density predicted by PC-SAFT of water with the 4C scheme. a) The dispersion energy ε/k and the hydrogen bonding energy ε^{HB}/k were fixed at each point. The three other pure compound parameters segment diameter-σ, segment number-m and association volume-κ^{HB} were optimized on vapour pressure and liquid density data from NIST [9] in a reduced temperature range of 0.5-0.9. b) Similar to plot a) but the segment number-m was fixed to m=1.5. The parameters published by Grenner et al. [6] use theoretically justified values m=1.5, ε=180.3 K and ε^{HB}=1804.22 K.
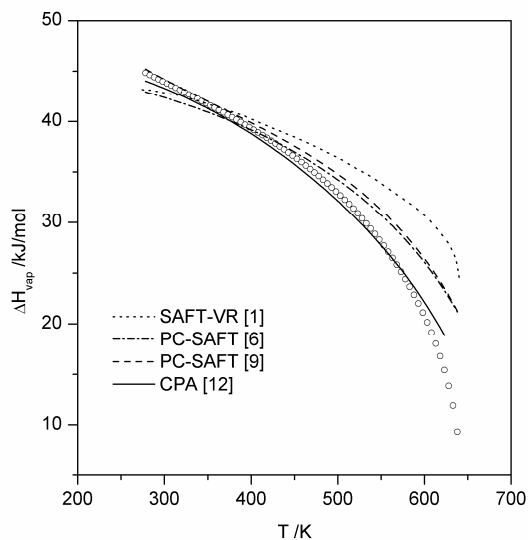
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Figure 2. Enthalpy of vaporization of water with CPA parameter taken from Kontogeorgis et al. [14], PC-SAFT using parameters from [6] and [11]. SAFT-VR results are from [1]. All parameters use a 4C scheme. Experimental data are taken from NIST [9]

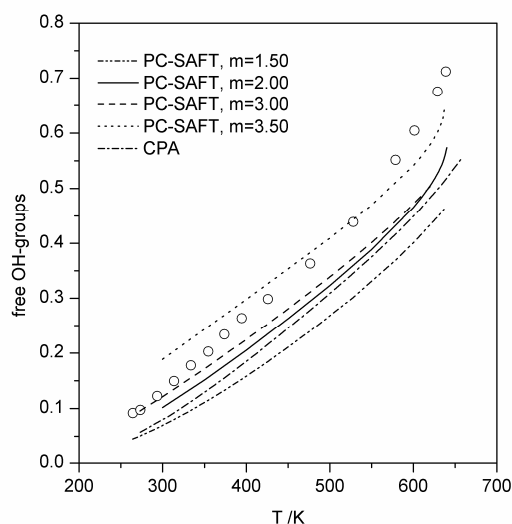**Deleted:** 2

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Figure 3. Free-OH groups (X^A) of water vs. temperature. The lines represent calculations with PC-SAFT and CPA with different parameter sets. CPA parameters are from [14]. and PC-SAFT (m = 2 - 3.5) results are taken from [11]. PC-SAFT with m=1.5 are taken from [6]. All parameters use the 4C scheme. Experimental data are taken from Luck [15].

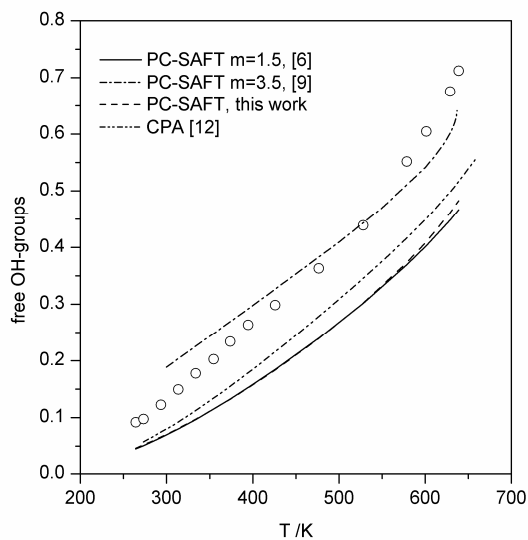**Deleted:** 12

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Figure 4. Free-OH groups (X^A) of water vs. temperature using CPA and PC-SAFT with the 4C association scheme. PC-SAFT parameters are from [6] and [11] and CPA parameters are from [14]. PC-SAFT water parameters of this work are obtained from simultaneous fitting of vapour pressures, liquid density and enthalpy of vaporization data (segment diameter-σ=2.0772 Å, dispersion energy-ε/k=140.39 K, segment number-m=2.61008, association energy-ε^{HB}/k=1694.77 K, association volume-κ^{HB}=0.5879). The results with PC-SAFT of Grenner et al. 2006 [6] and with the parameter set estimated here are almost identical. Experimental data are taken from Luck [15].
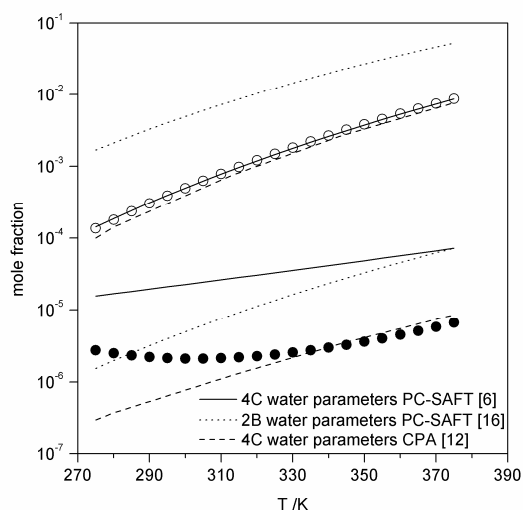
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Figure 5. Water-hexane LLE with PC-SAFT (k_{ij}=0) using two published sets of water parameters from [6] (4C scheme), [20] (2B scheme) and CPA (k_{ij}=0) with parameters form [14] (4C scheme). The experimental data are taken from Tsonopoulos [21].

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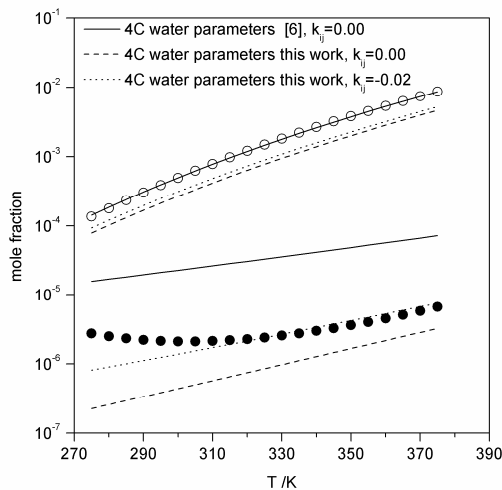
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Figure 6. LLE water + hexane with PC-SAFT using the water 4C scheme and various parameter sets for water, from [6] and the ones presented here (caption of Figure 4). The experimental data are taken from Tsonopoulos [21].

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