



# Uncertainty analysis of the CPA and a quadrupolar CPA equation of state – With emphasis on CO<sub>2</sub>



Martin G. Bjørner<sup>a, \*</sup>, Gürkan Sin<sup>b</sup>, Georgios M. Kontogeorgis<sup>a</sup>

<sup>a</sup> Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, DK-2800 Kgs. Lyngby, Denmark

<sup>b</sup> CAPEC-PROCES Research Center, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 227, DK-2800 Kgs. Lyngby, Denmark

## ARTICLE INFO

### Article history:

Received 14 October 2015

Received in revised form

17 December 2015

Accepted 19 December 2015

Available online 23 December 2015

### Keywords:

Equation of state

CPA

Quadrupole

CO<sub>2</sub>

Parameter estimation

Propagation of uncertainty

## ABSTRACT

The parameters of thermodynamic models, such as the cubic plus association (CPA) equation of state, are subject to uncertainties due to measurement errors in the experimental data that the models are correlated to. More importantly as the number of adjustable parameters increase, the parameter estimation problem becomes more complicated due to parameter identifiability issues. In this work the uncertainties in the pure compound parameters of CO<sub>2</sub> are investigated using several different CPA approaches, including a new quadrupolar CPA. The uncertainties are estimated using both least squares estimation and the bootstrap method for parameter estimation. The uncertainties in the parameters estimated from the bootstrap method are propagated to physical property and vapor liquid equilibrium predictions using Monte Carlo simulations.

The results indicate that both the pure compound parameter uncertainty and the propagated uncertainty are negligible for the modeling approaches which employ three adjustable parameters. For modeling approaches with more than three adjustable parameters, however, there may be significant uncertainties in the pure compound parameters, as well as a high degree of correlation between the adjustable parameters. This results in significant propagated errors for certain output properties. To reduce the uncertainty in the adjustable model parameters the heat of vaporization was included as additional correlation data. This resulted in parameter distributions which followed a normal distribution more closely, however, the correlation between the adjustable parameters remained high. Overall the results indicate, that it is important to report parameter uncertainties together with their correlation matrix when a model is developed, so that better informed decisions can be made, for instance about which model extension, or association scheme should be employed.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The pure compound parameters of advanced thermodynamic models such as the cubic plus association (CPA) equation of state (EoS) [1] and the Statistical Association Fluid Theory (SAFT) [2] are typically correlated to the saturated vapor pressure and saturated liquid densities using a least squares (LSQ) minimization approach in which, presumably, unique parameters are estimated. Even the most accurate experiments, however, are subject to measurement errors. Moreover the parameters may be correlated, so that a change in one parameter can be compensated by a change in

another. Consequently the pure compound parameters will be associated with some degree of uncertainty, which is typically assumed insignificant in the majority of studies thus far. Even small errors in the parameters, however, may significantly affect the result of a simulation [3,4]. While several researchers have drawn attention to this problem [4–10] surprisingly little work has been done on analyzing and quantifying the uncertainty of parameters in thermodynamic models and their effect on physical property and equilibrium calculations.

The work of Whiting and co-workers [3,11–16] is perhaps one of the most notable contributions to uncertainty estimates of thermodynamic models. Using a Monte Carlo approach the authors analyzed the effect of uncertainties in thermodynamic data and their effect on process design. More recently Mathias and co-

\* Corresponding author.

E-mail address: [mgabj@kt.dtu.dk](mailto:mgabj@kt.dtu.dk) (M.G. Bjørner).

workers [17–19] also investigated the importance of uncertainty propagation for processes such as CO<sub>2</sub> capture. Hajipour and co-workers [20–22] estimated the critical properties for a large number of hydrocarbons. The authors took both the experimental uncertainty in the data as well as the correlation between thermodynamic model parameters into account. Subsequently the uncertainties of the binary interaction parameters for 87 binary mixtures were estimated by use of the pure compound uncertainties.

Most research has focused on the propagated error from a thermodynamic model to various unit operations such as distillation columns (e.g. Refs. [5,6,17,23]). Uncertainty analysis, however, can also be used for model development and comparison; by comparing the uncertainties of selected physical properties and equilibria for different models, we can compare the models more objectively. For instance when models such as CPA and SAFT are compared, they often perform almost identically and what differences are present may, in many cases, be due to statistical uncertainties in the pure compound parameters of the models, rather than due to one model being superior to the other.

In an effort to improve the performance of models such as SAFT and to obtain a physically more correct model, additional terms are often added to the base EoS. The addition of an extra term typically leads to an increase in the number of adjustable parameters. This may make it difficult to estimate unique pure compound parameters due to high correlations between parameters as well as the possible presence of multiple local minima. One reason for this is that the data used for parameter estimation is too limited in relation to the model complexity, which must be able to predict a wide range of properties besides those its parameters are fitted to. This may be particularly relevant for a molecule such as CO<sub>2</sub>, for which the vapor pressure curve is very short. Both SAFT and CPA can for instance correlate the saturated vapor pressure and liquid density of CO<sub>2</sub> almost within experimental error, using only the three pure compound parameters commonly employed for non-associating molecules.

Unfortunately neither EoS can predict (i.e.  $k_{ij} = 0$ ) the unusual phase behavior of mixtures containing CO<sub>2</sub> very well. The reason for this is believed to be, that CO<sub>2</sub> has a large quadrupole moment, which the traditional approaches do not account for. The large quadrupole moment is, for instance, believed to be the reason for the liquid–liquid equilibrium between CO<sub>2</sub> and heavy hydrocarbons. During the past decade several quadrupolar terms have been added to the SAFT framework [24–27]. Unfortunately the new terms are often parametrized by using an additional pure compound parameter (such as an ‘effective’ quadrupolar moment). Other more pragmatic approaches tend to treat CO<sub>2</sub> as a self-associating or solvating molecule. Tsvintzelis et al. [28], for instance, demonstrated that such an approach often works quite well, at the cost of two additional pure compound parameters. If the uncertainties in parameters are significant, however, it may be difficult to compare the performance of various modeling approaches, as their differences may be due to the parametrization, rather than the superiority of one model over the other.

In this work, the uncertainties in the pure compound parameters of CO<sub>2</sub> are systematically evaluated, when different modeling approaches are employed with CPA as the base model. The uncertainty estimates are obtained from either a linear approximation of the covariance matrix of parameters estimated from nonlinear regression (LSQ) or using the Bootstrap method [29]. A Monte Carlo procedure (with latin hypercube sampling (LHS) and Iman–Conover correlation control) is employed to quantify the effect of parameter uncertainty by propagating the uncertainties to various derivative properties and binary equilibrium calculations.

## 2. Methods

### 2.1. Parameter estimation – uncertainty and correlation

The pure compound parameters in CPA are typically fitted to saturated pressures and saturated liquid densities using a weighted LSQ objective function. Ideally experimental data should be used for such correlations, however, more often than not, pure compound correlations, such as that of Span and Wagner [30], as implemented in the Reference Fluid Thermodynamic and Transport Properties (REFPROP) program [31] and as disseminated through the National Institute of Standards and Technology (NIST) Chemistry Webbook [32] are employed as pseudo-experimental data, since their correlations are accurate to within experimental error for many compounds. While such pseudo-experimental data are a convenient way of quickly obtaining quite accurate data for many compounds, the measurement errors present in the experimental data is lost. Moreover as the number of model parameters is increased and the closeness of fit improves, there is a clear risk of over-fitting.

In this work we investigate and compare the uncertainty when CO<sub>2</sub> is treated as either an inert (non-associating, non-quadrupolar) molecule, an associating molecule, and as a quadrupolar molecule. In the first two cases regular CPA is employed with and without association (with focus primarily on scheme 4C). In the latter case we employ the quadrupolar CPA (qCPA) which is a recent extension of CPA to quadrupolar fluids suggested by Bjørner and Kontogeorgis [33]. Equations for CPA and qCPA can be found in appendix Appendix A or in the literature [1,33–36]. Two cases are evaluated when CO<sub>2</sub> is considered to be a quadrupolar molecule, one where no additional adjustable parameter is employed and one where an additional volumetric parameter is employed. Table 1 summarizes the various approaches and the adjustable parameters involved in each approach.

#### 2.1.1. The least squares method

The LSQ method is a frequentist approach, in which the underlying model parameters are assumed to have true fixed values. However, since experimental data are subject to measurement errors these values can only be estimated by probability distributions of the measurement errors with the aid of statistical estimators [38,39]. That is, the model parameters are not random but the estimators are, since they depend on the measurements. If it is assumed that the experimental error can be described by a normal distribution with mean equal to the experimental measurement, then the LSQ method is equivalent to minimizing the weighted sum of squares of the difference between measurements (exp) and mathematical model (m):

$$\min \chi^2(\theta) = \sum_{i=1}^N \left( \frac{y_i^{\text{exp}} - y_i^{\text{m}}(\theta; T_i)}{\sigma_i^{\text{exp}}} \right)^2 \quad (1)$$

where  $N$  is the number of experiments,  $y_i^{\text{exp}}$  is the  $i$ th experimental value of an output property, such as the saturated density or saturated pressure,  $y_i^{\text{m}}(\theta; T_i)$  represent the results from the model at temperature,  $T_i$ , where  $\theta$  is a vector of adjustable parameters which depends on the modeling approach. The weight of the  $i$ th term is given as the inverse variance of the  $i$ th measurement, ( $\sigma_{\text{exp},i}^2$ ). In principle  $\sigma$  is the total standard deviation including both the uncertainty in dependent and independent variables. In this work, however, we assume that the uncertainty in the independent variables is insignificant, which greatly simplifies the data fitting problem.

Under a linear approximation the covariance matrix of

Download English Version:

<https://daneshyari.com/en/article/200897>

Download Persian Version:

<https://daneshyari.com/article/200897>

[Daneshyari.com](https://daneshyari.com)