



# Vapor pressure predictions of multi-functional oxygen-containing organic compounds with COSMO-RS



Bernd Schröder <sup>a,\*</sup>, Michal Fulem <sup>b</sup>, Mónia A.R. Martins <sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal

<sup>b</sup> Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28, Prague 6, Czech Republic

## HIGHLIGHTS

- Review of available vapor pressures of oxygenates as used in (UNIFAC- $p_L^0$ .1) with TDE.
- Vapor pressure estimation with COSMO-RS on compounds with reliable experimental data.
- Evaluation of COSMO-RS prediction behaviour on title compounds.

## ARTICLE INFO

### Article history:

Received 22 August 2015

Received in revised form

11 March 2016

Accepted 14 March 2016

Available online 17 March 2016

### Keywords:

ThermoData Engine

Data evaluation

COSMO-RS

Vapor pressure prediction

Oxygenated compounds

Semi-volatile organic compounds

## ABSTRACT

Given the recent interest in multi-functional oxygen-containing organic compounds and the need of accurate and consistent data, a complete review and systematic analysis of available experimental vapor pressure data, as published in the original work of (Asher et al., 2002), was performed with the ThermoData Engine (TDE). A revised set of critical evaluated vapor pressure data, including their uncertainties based on the principles of dynamic data evaluation, is here recommended for a total of 58 compounds. COSMO-RS was further used for vapor pressure estimations for these compounds. The quality of the results is discussed in terms of the chemical functionalities of the molecules. To illustrate the partition behaviour of the title compounds under ambient conditions, a simple comparison of volatility binning between estimates and measurements was performed. Since the encountered vapor pressures are rather high, with respect to pressure range of semi-volatile organic compounds (SVOC), a large fraction is expected to stay in the atmosphere rather than to form secondary organic aerosol.

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## 1. Introduction

The knowledge of organic aerosol (OA) formation is important for the understanding of certain aspects of climate change and for human health issues (Fuzzi et al., 2006). The gas/particle partitioning process of a given organic compound  $i$  in the atmosphere depends on its (sub-cooled) liquid vapor pressure,  $p_{iL}$ : if it decreases, the extent of the partitioning to a particulate material (PM) phase increases. When volatile organic compounds (VOCs) are oxidized, a variety of different oxygen-containing compounds covering an intermediate-to-low volatility range is formed. These compounds have an increased number of functionalities

compared to their respective parent VOC compounds and, due to the resulting lower volatilities, may condense to form a secondary organic aerosol (SOA). Partitioning to the PM phase tends to increase with decreasing  $p_{iL}$ . The amount of SOA condensing in this process is quantifiable when applying gas/liquid equilibrium partitioning models using  $p_{iL}$  as the most important model input (Pankow, 1994). Correct vapor pressure data is hence a key parameter in the characterization of partitioning patterns of biogenic SOA, which is estimated to be a major contributor to organic aerosol (Hallquist et al., 2009), considering, for instance, SOA formed in oxidation processes altering ubiquitously occurring molecules in nature, such as isoprenes or terpenes. Few reliable literature vapor pressure data are commonly found for compounds with oxygenated functionalities and  $p_{iL}$  values down to ( $10^{-5}$ – $10^{-7}$ ) kPa which roughly illustrates the range of potential formation of SOA products of interest. On the other hand, highly

\* Corresponding author.

E-mail address: [bschroder@ua.pt](mailto:bschroder@ua.pt) (B. Schröder).

volatile compounds ( $p_L > 0.01$  kPa) are not expected to be significantly present in the SOA phase. As a rule of thumb, to meet the requirement of sufficiently low (subcooled) vapor pressures for SOA formation, parent VOC compounds are equipped with six or more carbon atoms (Pankow et al., 2001). Low (sub-cooled) liquid vapor pressures, as frequently encountered at ambient temperatures, are difficult to measure (Růžicka et al., 2012). Usually, data are of differing quality or not readily available for many low-volatility compounds that are of interest in research on atmospheric processes (Barley and McFiggans, 2010).

As experimental determinations can never keep pace with the data demand, a reliable and robust methodology for the prediction of vapor pressures for low-volatility compound is highly desirable (Capouet and Müller, 2006). Performance evaluation on available vapor pressure prediction methods is helpful in its concise choice with respect to a suitable volatility range and additional data requirements, e.g. Compennolle et al. (2010). In a systematic approach, Asher et al. (2002), Asher and Pankow (2006), as well as Pankow and Asher (2008) developed a UNIFAC-based group contribution method for the prediction of (sub-cooled) liquid vapor pressures, extending the work of Jensen et al. (1981). This approach assumes that a given compound can be split into constituent groups, and that the (sub-cooled) liquid vapor pressure is determined by group-group interaction parameters. These interaction parameters can be obtained by training the method on a basis set of structurally related compounds with accurately known (sub-cooled) liquid vapor pressure data and the prerequisite of equilibrated basis and test sets. In general, these highly parameterized models give good results, but intrinsically, they are not able to differentiate between differences of certain isomers. In some cases, data for more exotic compounds maybe sought after (e.g., cyclic carbonyl containing compounds in SOA formed during ozone oxidation of common monoterpenes). Hence, besides accurate experimental determinations, reliable and (on a molecular level) versatile prediction methods are of utmost interest. With more and more new vapor pressure data on low-volatile organic substances becoming available, updated and new estimation methods appear (e.g., Barley and McFiggans, 2010; Compennolle et al., 2011; Maadani et al., 2015; O'Meara et al., 2014).

Traditional methods for correlating or predicting thermodynamic properties are primarily based on dividing the molecules into various groups (group-contribution methods – GCMs). COSMO-RS, the conductor-like screening model for realistic solvation, follows a different approach while combining quantum chemistry, dielectric continuum models, electrostatics surface interactions and statistical thermodynamics and can predict thermodynamic properties of neutral and charged molecules in the liquid phase. The method is based on a very small number of adjustable parameters, which are completely independent of any molecular or structural information (Klamt, 2005).

The work of Asher et al. (2002) on the title compounds comprised 43 compounds in the basis set and 33 compounds in the test set. The main objectives of this work are two-fold: to establish a consistent set of vapor pressure data of multi-functional oxygen-containing organic compounds at ambient temperatures using the NIST ThermoData Engine (TDE), starting from the fore-mentioned work. Furthermore, the vapor pressure prediction capability of COSMO-RS on the title compounds against this newly created database of reliable vapor pressure data is evaluated, considering the quantum chemical BP-TZVP and BP-TZVPD-FINE levels of theory, setting-up vapor pressure estimations with the most stable

individual conformer as well as with respective sets of the most relevant conformers.

## 2. Methods

### 2.1. The reference data set of critically evaluated experimental vapor pressures

Establishing a consistent reliable data base of experimentally based vapor pressure data is key to the success of development and verification of predictive models. In this work, the vapor pressure data used by Asher et al. were revised with the aid of the NIST ThermoData Engine 103b (TDE), which provides recommended critically evaluated thermodynamic data including their uncertainties based on the principles of dynamic data evaluation (Frenkel, 2005; Frenkel et al., 2005). In the enforcement of thermodynamic consistency of vapor pressure data, the following concepts are included in TDE i) ensuring the consistency of vapor pressure data with heat capacity differences between the liquid and gas phases at low pressures (for details on this technique, see Růžicka and Majer (1994, 1996), and ii) ensuring the consistency of phase boundary lines and thermophysical properties at the solid-liquid-gas triple points  $T_{tp}$  (i.e. the liquid-vapor and solid-vapor curves must converge to the same triple-point pressure and the difference between the enthalpies of sublimation and vaporization derived from the vapor pressure equations at  $T_{tp}$  must yield the enthalpy of fusion).

A distinguishing feature of the TDE is that recommended data include estimates of uncertainties which are obtained as part of the dynamic critical evaluation based on partial uncertainties estimated at NIST for each experimental data point. Uncertainties developed by TDE represent estimates of the combined expanded uncertainty (level of confidence 0.95) for the property value, as defined in Chirico et al. (2003). More details about foundations of TDE, enforcement of thermodynamic consistency, and uncertainty evaluation can be found in Frenkel et al. (2005).

The compounds gathered in Asher's data set from 2002 exert relatively high vapor pressures at ambient conditions, in almost all the cases, hence the assessment of this work is not regarding compounds with a high condensable fraction under ambient conditions.

### 2.2. COSMO-RS

In our work, we utilized the built-in vapor pressure estimation capability of COSMO-RS in its COSMOtherm implementation (Eckert and Klamt, 2014; Nakajoh et al., 2009; Schröder et al., 2010) on the same compounds as Asher et al. (2002) did with their model (UNIFAC- $p_L^o$ .1).

Extending the prediction of the chemical potential of liquids, COSMO-RS provides an *a priori* estimate of a pure compound's chemical potential in the gas phase, as described in Eq. (1):

$$\mu_i^{\text{Gas}} = E_i^{\text{Gas}} - E_i^{\text{COSMO}} - \omega^{\text{Ring}} n_i^{\text{Ring}} + \eta_{\text{Gas}} \quad (1)$$

where  $E_i^{\text{Gas}}$  and  $E_i^{\text{COSMO}}$  are the total energies of the molecule in the gas phase and in the COSMO conductor, as obtained from quantum chemical calculations. The remaining contributions consist of the following terms: the correction for ring shaped molecules with  $n_i^{\text{Ring}}$  being the number of ring atoms in the molecule and  $\omega^{\text{Ring}}$  an adjustable parameter, as well as  $\eta_{\text{Gas}}$ , providing the link between

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