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**Solid state and
sub-cooled liquid
vapour pressures**

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Solid state and sub-cooled liquid vapour pressures of substituted dicarboxylic acids using Knudsen Effusion Mass Spectrometry (KEMS) and Differential Scanning Calorimetry

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Abstract

Solid state vapour pressures of a selection of substituted dicarboxylic acids have been measured using Knudsen Effusion Mass Spectrometry (KEMS). Enthalpies of fusion and melting points obtained using Differential Scanning Calorimetry (DSC) were used to obtain sub-cooled liquid vapour pressures. They have been compared to estimation methods used on the E-AIM website. These methods are shown to poorly represent -OH groups in combination with COOH groups. Partitioning calculations have been performed to illustrate the impact of the different estimation methods on organic aerosol mass compared to the use of experimental data.

1 Introduction

Atmospheric aerosols influence climate directly via the scattering, reflection and absorption of solar radiation, and indirectly by acting as cloud condensation nuclei. The errors associated with aerosols are one of the greatest uncertainties in our understanding of radiative forcing (Solomon et al., 2007). Organic components comprise a major fraction of the sub-micron particulate mass in the ambient lower atmosphere in all locations where they have been sampled (Zhang et al., 2007; Hallquist et al., 2009). The organic fraction may comprise many tens to hundreds of thousands of compounds (Goldstein and Galbally, 2007). A significant proportion of these components are thought to arise from gas to particle partitioning. Organic aerosol (OA) formation from volatile organic compounds (VOC) is frequently described by an equilibrium based absorptive partitioning model (Barley et al., 2009; Pankow et al., 1994). This requires knowledge of pure component vapour pressures. There are many methods of estimating pure component vapour pressures but most of the experimental data collected to date has been for intermediate or high vapour pressures and the proportion of experimental data for low vapour pressures (<100 Pa) has been very small. Some of the estimation methods can give errors in vapour pressure of several orders

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of magnitude for multifunctional compounds at ambient temperatures (Makar, 2001; Camredon et al., 2006; Pankow and Asher, 2008; Barley and McFiggans, 2010). The testing of vapour pressure estimation methods for use in atmospheric applications is severely limited by the relatively small number of multifunctional compounds for which experimental vapour pressure are available at ambient temperatures. This requires a reliable method of determining vapour pressures of low volatility compounds at ambient temperatures. Knudsen Effusion Mass Spectrometry (KEMS) is a well-established technique for measuring the vapour pressures of very low volatility compounds at high temperatures (up to 2500 K) such as metals and ceramics (Hilpert, 1991, 2001). It has also recently been used to measure the solid state vapour pressure at ambient temperature of straight chain dicarboxylic acids; oxalic, malonic, succinic, glutaric and adipic acid (Booth et al., 2009a). Carboxylic acids have been well established as components of atmospheric aerosols (Bilde et al., 2003; Cappa et al., 2007), although there is a high level of uncertainty in the formation mechanisms of multifunctional oxygenated organics (Hallquist et al., 2009). Substituent functional groups of dicarboxylic acids have been isolated and identified in laboratory SOA studies and atmospheric aerosols; methyl (Sempere and Kawamura, 1994) keto (Kawamura et al., 1996) and alcohol (Gao et al., 2003; Kawamura et al., 2005) have all been observed. Understanding how such groups affect vapour pressure is therefore important. These dicarboxylic acids are solids at room temperature and pressure, however, in the atmosphere they can exist as components of a sub-cooled liquid aerosol (Riipinen et al., 2007; Koponen et al., 2007). The sub-cooled liquid state is a hypothetical liquid, which would exist if solidification did not occur at the triple point. On a P, T phase diagram it is a line that forms an extension to the liquid phase vapour pressure line below the triple point temperature. Additionally, current gas/particle partitioning models use the sub-cooled reference state, as do activity models. KEMS however cannot directly measure the sub-cooled liquid vapour pressure. The solid state vapour pressure can be corrected to the sub-cooled state value using thermochemical properties obtained by other means such as Differential Scanning Calorimetry (DSC)(Prausnitz et al., 1986). In this work we com-

bine results from KEMS and DSC to obtain solid state and sub-cooled liquid vapour pressures for the following di- and tri-carboxylic acids: oxalic, malonic, methyl-malonic, tartronic, succinic, malic, tartaric, keto-succinic, methyl-succinic, aspartic, citramalic, glutaric, 2-methyl-glutaric, 3-methyl-glutaric, 2-keto-glutaric, 3-keto-glutaric, glutamic, citric and adipic acid.

2 Theory

2.1 Sub-cooled correction

The sub-cooled vapour pressure is derived from the value measured above the solid state using the following equation (Prausnitz et al., 1986):

$$\ln \frac{p_l}{p_s} = \frac{\Delta H_{\text{fus}}}{RT_m} \left(\frac{T_m}{T} - 1 \right) - \frac{\Delta c_{p,sl}}{R} \left(\frac{T_m}{T} - 1 \right) + \frac{\Delta c_{p,sl}}{R} \ln \frac{T_m}{T} \quad (1)$$

where p is the vapour pressure with the subscript s referring to the solid and l to the sub-cooled liquid phase, ΔH_{fus} is the enthalpy of fusion (J mol^{-1}), $\Delta c_{p,sl}$ denotes the best estimate of the underlying change in heat capacity between the liquid and solid state at the melting point ($\text{J mol}^{-1} \text{K}^{-1}$), T is the temperature (K) and T_m is the melting point (K), which is commonly used instead of the triple point, T_m is typically within 1 K of T_t for small organic acids. The sub-cooled liquid vapour pressure also allows easier comparison with theoretical vapour pressure estimation methods which predict the sub-cooled state.

2.2 Vapour pressure estimation

Many predictive methods exist for vapour pressure. Barley and McFiggans (2010) recently evaluated several methods using a basis set of 45 multifunctional low-volatility compounds for which experimental vapour pressures were available. Here we compare our experimental results with the methods available on the E-AIM (Extended

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Aerosol Inorganics Model) website, <http://www.aim.env.uea.ac.uk/aim/aim.php> (Wexler and Clegg, 2002; Clegg et al., 2008). These methods use a normal boiling point (T_b) from which the vapour pressure at the required temperature is extrapolated using a vapour pressure equation (referred to here as the vapour pressure method).

The three vapour pressure methods available are the Nannoolal et al. (2008) and the Moller et al. (2008) methods both with T_b by Nannoolal et al., 2004), and the Myrdal and Yalkowsky (1997) method with T_b by Stein and Brown (1994). Additionally, boiling points were calculated using the Joback et al. (1987) method (Dortmund data bank) and used with each of the three vapour pressure methods.

The Nannoolal et al. (2004) estimation method uses group contribution calculations using primary and secondary groups and group interactions (207 groups). It was used to calculate both normal boiling points (Nannoolal et al., 2004) and the slope of the vapour pressure line (Nannoolal et al., 2008). The normal boiling point T_b is given by:

$$T_b = \frac{\sum_i N_i C_i}{n^a + b} + c \quad (2)$$

where N_i is the number of groups of type i , C_i the group contribution of group i [K], a , b , c are adjustable parameters from a linear regression ($a = 0.6583$, $b = 1.6868$, $c = 84.3395$), and n is the total number of atoms in the molecule (except hydrogen). The vapour pressure is given by:

$$\log_{10} P_i^0 = (4.1012 + dB) \left[\frac{T_{rb} - 1}{T_{rb} - 0.125} \right] \quad (3)$$

where $T_{rb} = T/T_b$. dB adjusts the slope of the vapour pressure curve and is calculated using group contributions.

$$dB = \left(\sum N_i C_i + GI \right) - 0.176055 \quad (4)$$

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where the first term in the brackets is the sum of the primary and secondary group contributions, and the second term is the group interaction:

$$GI = \frac{1}{n} \sum_{i=1}^m \sum_{j=1}^m \frac{C_{i-j}}{m-1} \quad (5)$$

where $C_{i-j} = C_{j-i}$ and m, n are the total number of interacting groups and the number of (non-hydrogen) atoms in the molecule respectively.

The Moller et al. (2008) method is a refinement of the Nannoolal et al. (2008) method. It features an additional term to improve predictions for aliphatic alcohols and carboxylic acids, new size dependent groups to improve predictions for several functional groups, and new hydrocarbon groups. Re-writing Eq. (3) and adding the extra term gives:

$$\log_{10} P_i^0 = B' \frac{T - T_b}{T - C(T_b)} + D' \ln \left(\frac{T}{T_b} \right) \quad (6)$$

where D' is the new term for carboxylic acids and alcohols which is set to zero when they are not present. In the Nannoolal et al. (2008) method, $C = T_b/8$, but this is replaced with the following term:

$$C(T_b) = -2.65 + \frac{T_b^{1.485}}{135} \quad (7)$$

All group contributions were refitted to the above equations. Several new hydrocarbon groups were added to account for specific structural effects, and size dependent corrections for alkene and alkyne molecules were also introduced to improve predictions.

The Myrdal and Yalkowsky (1997) method requires a source of boiling point (T_b) estimations. In this work the group contribution method of Stein and Brown, 1994) (85 groups), which is adapted from an earlier method (Joback and Reid, 1987), was used to provide T_b . This was then used with the equations of Myrdal and

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Yalkowsky (1997) which uses the flexibility of the molecular structure and hydrogen bond number to estimate the entropy of vapourisation ΔS_{vap} :

$$\Delta S_{\text{vap}} = 86 + 0.4\tau + 1421 \times \text{HBN} \quad (8)$$

where τ is the effective number of torsional bonds and HBN is the number of hydrogen bonds. This is then used with a vapour pressure equation:

$$\log_{10} P_i^0 = \frac{\Delta S_{\text{vap}}(T_b - T)}{19.1T} - \frac{[90.0 + 2.1\tau]}{19.1} \left(\frac{T_b - T}{T} - \ln \frac{T_b}{T} \right) \quad (9)$$

where the P_i^0 is the vapour pressure (Atm).

2.3 Equilibrium gas to aerosol partitioning

The partitioning model follows the approach described in Barley et al. (2009). This approach is based upon earlier models (Pankow, 1994; Pankow et al. 2001) with minor modification. The semi-volatile compounds are partitioned according to their saturation concentration (C_i^*) value:

$$C_i^* = \frac{10^6 \gamma_i P_i^0}{RT} \quad (10)$$

where P_i^0 is the saturated vapour pressure of component i in atmospheres, γ_i is the activity coefficient of component i and C_i^* is the saturation concentration in $\mu\text{mol m}^{-3}$. The amount of condensed material (C_{OA}) is then calculated by summing over all components i ensuring mole balance between the two phases for each component considered. Defining a partitioning coefficient ξ for compound i given its saturation concentration C_i^* :

$$\xi_1 = \left(1 + \frac{C_i^*}{C_{\text{OA}}} \right)^{-1} \quad (11)$$

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where both C_i^* and C_{OA} have units of $\mu\text{mol m}^{-3}$. The total number of moles of organic aerosol is the sum of the products of the individual component concentrations (C_i) and their partitioning coefficient (ξ_i):

$$C_{OA} = \sum_i C_i \xi_i \quad (12)$$

Equation (12) will thus quantify the amount of each component in the condensed phase in $\mu\text{mol m}^{-3}$ and is readily converted into mass based amounts by multiplying by the appropriate molecular weight. Summing the mass based condensed quantities for all the compounds provides the total condensed OA in mass based units.

3 Experimental

Samples of oxalic, malonic, methyl-malonic, tartronic, succinic, malic, tartaric, keto-succinic, methyl-succinic, aspartic, citramalic, glutaric, 2-methyl-glutaric, 3-methyl-glutaric, 2-keto-glutaric, 3-keto-glutaric, glutamic, citric and adipic acid were purchased from Sigma-Aldrich with purities of 99% or higher and used with no further preparation. Solid state vapour pressures were determined using a custom built Knudsen Effusion Mass Spectrometer. Solid state vapour pressures have been previously reported for oxalic, malonic, succinic, glutaric and adipic acid (Booth et al., 2009a). The system (Fig. 1) consists of two chambers connected via an all metal gate valve (VAT-valves). Each chamber is separately pumped by 70 ls^{-1} pumping speed V-81-T turbo pumps (Varian) on CF 63 flanges with a SH-110 dry scroll backing pump. Pressure is measured using convector gauges (Varian) for atmospheric pressure down to 10^{-3} mbar, and IMG-100 inverted magnetron ion gauges for $<10^{-4}$ mbar (Varian).

Briefly, a sample of known vapour pressure is placed in a temperature controlled cell. The cell has a chamfered effusing orifice with a size $\leq 1/10$ the mean free path of the gas molecules in the cell. This ensures the orifice does not significantly disturb

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the thermodynamic equilibrium of the samples in the cell (Hilpert, 2001). The resulting molecular beam is ionised by electron impact, then sampled by a Balzers-Pfeifer quadrupole mass spectrometer which was used with a QMS 410 mass analyzer, a QMH 410 RF-box connected to a QMG 422 controller. This produces a signal proportional to the vapour pressure. After calibration a sample of unknown vapour pressure is put in the cell. During sample change the second chamber is isolated via the gate valve and vented to air allowing the ioniser filament to be left on. After this calibration, unknown vapour pressures can be determined from the intensity of the mass spectrometer signal of the compound in question. The system can be used to determine partial pressures of mixed systems. The pressure of the i^{th} component in the KEMS instrument P_i in Pascals, is given by:

$$P_i = \frac{kI_iT}{\sigma_i} \quad (13)$$

where I_i is the ion intensity measured in the mass spectrometer, σ_i is the ionisation cross section and T is the temperature of the Knudsen cell in Kelvin. k is the machine constant which incorporates information on the geometry of the system, Clausing factor of the effusion orifice and any other correction factors, k and is determined by using reference samples of known vapour pressure. σ_i is calculated by summing the ionisation cross section from constituent atoms or groups in the molecule at the ionisation energy (70 eV) (Hilpert, 2001) using data obtained from the NIST electron impact database (Kim and Irikura, 2000). In all cases, the accommodation coefficient is assumed to be identical between samples. Such an assumption may introduce unquantifiable errors, but it is expected that they are minimized by appropriate choice of similar reference and sample compounds. KEMS directly measures the steady state vapour pressure but the equilibrium vapour pressure is desired. If the Knudsen number is high enough then effusing gas does not significantly disturb the equilibrium in the cell (Booth et al., 2009a; Hilpert 1991, 2001) making the steady state pressure measured as close as possible to equilibrium conditions (negligible perturbation of condensation/evaporation equilibrium). There was no systematic difference between hole size for our dicarboxylic

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acid in Booth et al. (2009a) determinations so the steady state vapour pressure is indistinguishably close to the equilibrium vapour pressure. Pressures reported are the average of two runs. Based on repeat runs of several compounds over a temperature range of 20 K we estimate the error to be $\pm 40\%$. Enthalpies and entropies of sublimation were obtained from a linear fit of the Clausius-Clapeyron equation.

Melting points (T_m) and Enthalpies of Fusion (ΔH_{fus}) were measured using a TA instruments Q200 Differential Scanning Calorimeter (DSC) using a heating rate of 10 C min^{-1} . 5–10 mg of sample was measured out and recorded using a microbalance, the sample was then pressed into a hermetically sealed aluminium DSC pan. A purge gas of N_2 was used with a flow rate of 30 ml min^{-1} . The reference was an empty sealed pan of the same type. Data processing was performed using the “Universal Analysis” software supplied with the instrument. $\Delta c_{p,sl}$ is frequently estimated using three assumptions, based on empirical evidence; $\Delta c_{p,sl}=0$ (Yalkowsky et al., 1981; Prausnitz et al., 1986), $\Delta c_{p,sl}=0.5\Delta S_{fus}$ (Tsonopoulos, 1970) and $\Delta c_{p,sl} = \Delta S_{fus}$ (Mauger et al., 1972; Grant et al., 1984) which is used in this work.

4 Results and discussions

4.1 Solid state vapour pressures

The dependency of certain solid state properties, such as solubility (Booth et al., 2009b) or sublimation pressure (Booth et al., 2009a; Bilde et al., 2003), of dicarboxylic acids on carbon chain parity is well known and has been attributed to crystalline structure. Hydrogen bonds formed from carboxylic end groups line up with neighbouring molecules in either a *cis*- (Odd) or *trans*- (Even) configuration which makes the crystal structure less or more stable, respectively. Interestingly this property also influences the effect of substitutions on the carbon chain. For diacids with an odd carbon number and a relatively less stable crystal structure, the addition of extra groups seems to always lower the vapour pressure (Fig. 2, Table 1). A factor of ~ 0.5 for methyl-malonic

and tartronic compared to malonic, and 0.4 to 0.1 for glutaric depending on the group. With succinic acid (an even carbon number) most group additions raise the solid state vapour pressure by factors of 2 to 6 (excepting a single alcohol or ketone group).

Mønster et al. (2004) have studied methyl and dimethyl substituted dicarboxylic acids using a HTDMA system. They also note that additional groups give an increase in solid state vapour pressure for even numbered dicarboxylic acids. They see an even greater increase in solid state vapour pressure for succinic substitutions. Knudsen mass loss (da Silva et al., 2001) has also been used to study methyl substitutions (Table 2). Mass loss data extrapolated down to 298 K from a higher temperature shows good agreement with our data (within 1σ , except for methyl malonic with is within 2σ). Frosch et al. (2010) have recently published results on keto substituted diacids using by the HTDMA technique (Table 3). We both observe reductions in the solid state vapour pressure for keto substitutions, including a vapour pressure for 3-keto glutaric ~50% lower than for 2-keto glutaric. They observe a greater reduction in vapour pressure for all keto substitutions. Solubility or surface tension effects could possibly explain the differences in the size of the keto and methyl substitution effects compared to Frosch et al. (2010) and Mønster et al. (2004). This could be tested by intercomparing the two techniques on both a very soluble compound (e.g. citric acid) and an insoluble, strongly surfactant compound (e.g. pinonic acid).

4.2 Sub-cooled liquid vapour pressures

Sub-cooled liquid vapour pressures (Fig. 2) were derived using Eq. (1) and the thermochemical data in Table 4. The odd-even effect is noticeable in the melting point and enthalpy of sublimation of the straight chain diacids. The corrected sub-cooled liquid vapour pressures for the unsubstituted diacids show no odd-even effect. There is a significant difference, by up to three orders of magnitude, between the two pressures. This arises as a result of the sub-cooled liquid vapour pressure diverging from the solid vapour pressure at the melting point. As the P_{298K} is measured at a temperature much lower than T_m (A minimum of 71 K lower for glutaric acid and a maximum of 238 K for

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the glutamic acid estimate) a large difference is expected.

Riipinen et al. (2007) and Koponen et al. (2007) were able to directly observe malonic, succinic, glutaric and adipic acid aerosols in the sub-cooled liquid state (Table 5). Our data for those 4 diacids show higher values than those of Riipinen et al. (2007) and Koponen et al. (2007). The discrepancy between our results is far larger at short chain lengths; a factor of 6.5 out for malonic, 4 for succinic, 2 for glutaric, and adipic acid is in agreement within experimental error. The HDTMA method requires a model of the thermodynamic activity, the choice of which will impact upon the results obtained. Riipinen et al. (2007) used Dortmund modified UNIFAC. This may explain the differences observed which seem especially prominent for malonic acid. Koponen et al. (2007) used two different activity models (Dortmund modified UNIFAC and Van Laar), and observed differences between them of two orders of magnitude in the calculated solid state vapour pressure for malonic acid, and the differences between the different activity models decreases with increasing chain length. A comparison of oxalic acid (C_2) could confirm if it is an activity model dependent difference especially prominent for smaller molecules. This opens up the possibility of combining KEMS and HDTMA TDMA to validate activity models, or if the activity coefficients are known, to evaluate the accommodation coefficients required for the TDMA technique.

Malonic acid shows an increase (factor of ~ 1.7) in sub-cooled liquid vapour pressure for methyl and alcohol additions. Glutaric acid shows a decrease by 0.5 for extra methyl groups, amino and keto groups in the 2-position have no discernable effect as the magnitude of the sub-cooled correction cancel out the lower solid state vapour pressure. Interestingly the 3-keto acid and citric acid (an extra OH and COOH on the third carbon) show an increase by a factor of 1.6. Succinic acid shows a greater sensitivity to substitutions; single -OH and methyl groups decrease the vapour pressure (by a factor of ~ 0.2) but 2-methyl, 2-ol and 2,3-diol substitutions show increases by a factor of 2 and 80, respectively. 2-amino and 2-keto also show an increased vapour pressure with respect to succinic acid, by factors of 6.6 and 4, respectively. Increasing vapour pressure by adding polar groups is a counter intuitive result. Chattopadhyay

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and Ziemann (2005) have used thermal desorption particle beam mass spectrometry to obtain solid state vapour pressures of OH- substituted carboxylic and dicarboxylic acids and observed similar effects. They note that group position is highly important; for glutaric acid they observe a 2-ol substitution increasing the vapour pressure by a factor of 4, and 3-ol substitution decreasing the vapour pressure by a factor of 66. Adipic and azelaic OH substitutions were shown to have similar positional effects. Two possible reasons for the unusual behavior of additional polar groups are; intra-molecular hydrogen bonding between the extra group and one of the carboxylic acid groups (Chattopadhyay and Ziemann, 2005), or an inductive effect reducing the polarity of the acid group. Either could reduce inter-molecular bonding and raise the vapour pressure.

The thermochemical parameters used in Eq. (1) determine the difference between the two states. In the literature, reported T_m values lie within a range of 4 K for malonic and succinic, and 7 K for glutaric and adipic. The extremes of these values give differences of 5% and 12% respectively for the sub-cooled liquid vapour pressure. Similarly, ΔH_{fus} values lie in a range of $\sim 7 \text{ kJ mol}^{-1}$ for malonic and adipic and $\sim 4 \text{ kJ mol}^{-1}$ for succinic and glutaric; leading to variations of up to 80% and 40%, respectively. The assumption of $\Delta C_{p;sl} = \Delta S_{\text{fus}}$ leads to an overestimate of sub-cooled liquid vapour pressure compared with literature values of $\sim 10\text{--}20\%$. Combining this with the uncertainties in the solid state vapour pressure ($\sim 40\%$) we estimate a maximum uncertainty of $\pm 75\%$ for our sub-cooled liquid vapour pressures.

4.3 Vapour pressure estimates

As many vapour pressure methods are based predominantly on data for more volatile compounds, low-volatility compound data is essential to verify which methods are best suited for atmospheric applications. The subset of vapour pressure estimation methods shown here are those from the E-AIM (Extended Aerosol Inorganics Model) website, <http://www.aim.env.uea.ac.uk/aim/aim.php> (Wexler and Clegg, 2002; Clegg et al., 2008). The estimation methods used here first require a boiling point. Barley and

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McFiggans (2010) found the Nannoolal et al. (2004) boiling points to give the best results when comparing estimated boiling points for those with experimental data for low volatility compounds. In this data set the Nannoolal et al. (2004) and Stein and Brown (1994) boiling points (Table 6) are in fairly good agreement with differences ~10 K except for citric and tartaric acid (2,3-dihydroxy-succinic acid) where the difference is ~20 K. The Joback et al. (1987) method gives much higher boiling points than those of Nannoolal et al. (2004), an average of 56 K higher and up to 160 K for citric acid.

Table 7 shows the estimated vapour pressures. The Moller et al. (2008), Nannoolal et al. (2008) and Myrdal and Yalkowsky (1997) methods give the best results over this range of compounds when combined with Nannoolal (2004) and Stein and Brown (1994) boiling points, on average 1–2 orders of magnitude out. When using Joback et al. (1987) boiling points the Moller et al. (2008) and Nannoolal et al. (2008) methods perform worse, respectively 4 and 3 orders of magnitude out on average. Interestingly the Myrdal and Yalkowsky (1997) method, when combined with Joback et al. (1987) boiling points gives one of the better results, with the overestimating bias of Joback et al. (1997) boiling points being cancelled out by an opposing bias from the vapour pressure method. The main cause of inaccuracy for the Moller et al. (2008) and Nannoolal et al. (2008) methods are the -OH containing compounds, without these they provide the best match to the experimental data. The Moller et al. (2008) specifically includes extra terms for both COOH and OH so additional experimental data from these sorts of compounds is more likely to help improve this method more than any other.

4.4 Partitioning calculation

In order to assess the impact of estimates of vapour pressures on secondary organic aerosol (SOA) formation, the partitioning calculation method described by Barley and McFiggans (2010); Barley et al. (2009) was used. The base case used the sub-cooled liquid vapour pressure derived from the KEMS with the abundance of all 19

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components set to a value which gave $10.6 \mu\text{g m}^{-3}$ of OA as in the Barley and Mc-Figgans (2010) study. Figure 4 shows a box-whisker plot of the effect on OA yield of substituting a single estimated vapour pressure values for each compound, in turn. As expected, methods using Joback et al. (1987) boiling points tend to overestimate the OA yield, with median overestimates by approximately 12, 8 and $2 \mu\text{g m}^{-3}$ for Moller et al. (2008), Nannoolal et al. (2008) and Myrdal and Yalkowsky (1997), respectively. Myrdal and Yalkowsky (1997) with Stein and Brown (1994) boiling points gives the best results with these compounds, with a narrow spread and a median within $1 \mu\text{g m}^{-3}$ of the target yield. The Nannoolal et al. (2008) method with Nannoolal et al. (2004) boiling points also shows a similar result with the median within $1 \mu\text{g m}^{-3}$ of the target yield although over a larger range. The Moller et al. (2008) method with Nannoolal et al. (2004) boiling points tends to cause over estimates in the OA yield, with a median value $10 \mu\text{g m}^{-3}$ greater than the base case, with a very asymmetric spread towards lower OA yields. This will be greatly influenced by this method's tendency to underestimate the vapour pressure of OH containing compounds.

5 Conclusions

KEMS solid state vapour pressures combined with melting points and enthalpies and entropies of fusion have been used to obtain sub-cooled liquid vapour pressures for a selection of multifunctional compounds based on dicarboxylic acids. The sub-cooled liquid vapour pressures have been compared with a series of vapour pressure estimation methods. The methods underestimate the vapour pressure of dicarboxylic acids substituted with OH groups, possibly due to intramolecular hydrogen bonding between COOH and OH groups. Myrdal and Yalkowsky (1997), combined with Stein and Brown (1994) boiling points gives the best estimates. Partitioning calculations illustrate the impact of this for OA yields. The Moller et al. (2008) and Nannoolal et al. (2008) methods with Nannoolal et al. (2004) boiling points do not match the data as closely. They do however include parameters for group interactions, and the Moller et al. (2008)

method in particular includes extra terms specifically for COOH and OH groups. As the interaction between these two groups causes most of the discrepancies, we expect further experimental data will be able to improve this method disproportionately more than the any other.

- 5 *Acknowledgements.* The authors thank NERC for financial support on grant NE/E018181/1 and the EU-funded European Integrated project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI) under contract number/break 036833-2.

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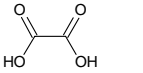
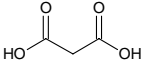
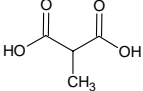
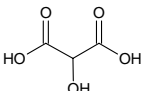
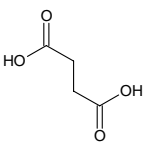
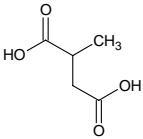
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Table 1. KEMS determined solid state vapour pressures, enthalpies of sublimation and entropies of sublimation.

Structure	Name	P_{298} (Pa)	ΔH_{sub} (kJ mol ⁻¹)	ΔS_{sub} (J mol ⁻¹ K ⁻¹)
	Oxalic	2.15×10^{-2}	75	213
	Malonic	5.73×10^{-4}	92	238
	2-methyl	3.34×10^{-4}	87	225
	2-ol	2.50×10^{-4}	69	162
	Succinic	1.13×10^{-4}	93	222
	2-methyl	2.54×10^{-4}	100	268

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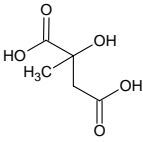
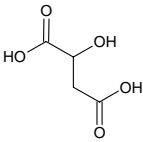
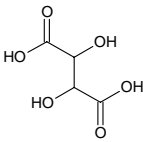
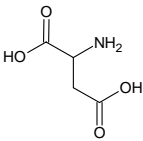
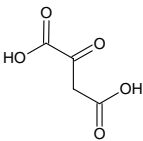
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Table 1. Continued.

Structure	Name	P_{298} (Pa)	ΔH_{sub} (kJ mol ⁻¹)	ΔS_{sub} (J mol ⁻¹ K ⁻¹)
	2- methyl,2- ol	4.90×10^{-4}	104	286
	2-ol	6.37×10^{-5}	81	192
	2,3-diol	1.79×10^{-4}	68	157
	2-amino	6.71×10^{-4}	53	116
	2-keto	8.23×10^{-5}	81	195

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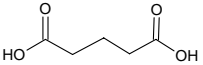
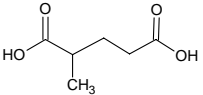
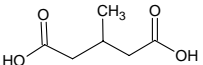
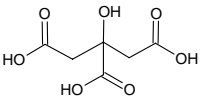
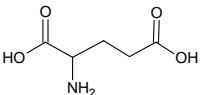
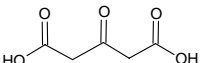
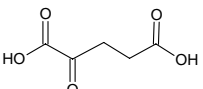
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Table 1. Continued.

Structure	Name	P_{298} (Pa)	ΔH_{sub} (kJ mol ⁻¹)	ΔS_{sub} (J mol ⁻¹ K ⁻¹)
	Glutaric	4.21×10^{-4}	123	208
	2-methyl	1.85×10^{-4}	82	204
	3-methyl	1.77×10^{-4}	86	215
	citric	3.79×10^{-5}	64	129
	2-amino	3.60×10^{-5}	63	128
	2-keto	1.23×10^{-4}	53	103
	3-keto	5.96×10^{-5}	89	217

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Table 2. Comparison of methyl substituted dicarboxylic acid solid state vapour pressures.

	P_{298} (Pa) this work	P_{298} (Pa) Mønster et al. (2004)	P_{298} (Pa) da Silva et al. (2001)
2-methyl-malonic	$3.34 \pm 1.34 \times 10^{-4}$	9.10×10^{-4}	5.70×10^{-4}
2-methyl-succinic	$2.54 \pm 1.01 \times 10^{-4}$	1.60×10^{-3}	2.90×10^{-4}
2-methyl-glutaric	$1.85 \pm 0.74 \times 10^{-4}$	n/a	2.30×10^{-4}

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Table 3. Comparison of keto substituted dicarboxylic acid solid state vapour pressures.

	P_{298} this work	P_{298} Frosch et al. (2010)
succinic	$1.13 \pm 0.452 \times 10^{-4}$	3.90×10^{-5}
keto succinic	$8.23 \pm 3.29 \times 10^{-5}$	1.00×10^{-5}
glutaric	$4.21 \pm 1.72 \times 10^{-4}$	6.70×10^{-4}
2-keto glutaric	$1.23 \pm 0.49 \times 10^{-4}$	3.60×10^{-5}
3-keto glutaric	$5.96 \pm 2.38 \times 10^{-5}$	1.60×10^{-5}

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Table 4. Sub-cooled liquid vapour pressures, melting points, enthalpies and entropies of fusion. * denotes thermochemical data was unobtainable, Joback et al. (1987) estimates were used instead.

	P_{298} (Pa)	T_m (K)	ΔH_{fus} (J mol ⁻¹)	ΔS_{fus} (J mol ⁻¹ K ⁻¹)
Oxalic	2.74×10^{-2}	370	3424	9
Malonic	3.19×10^{-3}	406	18 739	46
2-methyl	5.34×10^{-3}	403	30 746	76
2-ol	5.64×10^{-3}	428	30 619	72
Succinic	3.86×10^{-3}	458	31 259	68
2-methyl	5.58×10^{-4}	383	9980	26
2-methyl,2-ol	7.48×10^{-3}	379	35 697	94
2-ol	8.72×10^{-4}	403	29 031	72
2,3-diol	3.23×10^{-1}	480	62 723	131
2-amino	2.56×10^{-2}	524	28 076*	114
2-keto	1.67×10^{-2}	437	50 382	115
Glutaric	1.96×10^{-3}	369	22 043	60
2-methyl	9.63×10^{-4}	349	30 259	87
3-methyl	9.19×10^{-4}	356	27 351	77
citric	3.10×10^{-3}	427	43 455	102
2-amino	2.05×10^{-3}	536	30 666*	105
2-keto	2.02×10^{-3}	386	34 693	90
3-keto	3.22×10^{-3}	397	45 895	116
Adipic	2.14×10^{-4}	423	35 891	85

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Table 5. Comparison of dicarboxylic acid sub-cooled liquid vapour pressures.

	P_{298} (Pa) this work	P_{298} (Pa) + Riipinen et al. (2007), * Koponen et al. (2007)
Oxalic	$2.74 \pm 1.92 \times 10^{-2}$	n/a
Malonic	$3.19 \pm 2.23 \times 10^{-3}$	$+ 4.90 \times 10^{-4}$
Succinic	$3.86 \pm 2.70 \times 10^{-3}$	$* 9.90 \times 10^{-4}$
Glutaric	$1.96 \pm 1.37 \times 10^{-3}$	$* 7.10 \times 10^{-4}$
Adipic	$2.14 \pm 1.49 \times 10^{-4}$	$+ 1.70 \times 10^{-4}$

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Table 6. Normal boiling points by the estimation methods, in K.

	Joback	Nannoolal	Stein and Brown
Oxalic	536.38	529.636	520.084
Malonic	559.30	544.60	537.30
2-methyl	581.70	548.53	543.87
2-ol	651.00	595.02	580.91
Succinic	582.14	559.40	553.60
2-methyl	604.58	563.54	559.80
2-methyl,2-ol	693.97	602.79	596.46
2-ol	673.88	607.13	594.65
2,3-diol	765.62	651.83	629.01
2-amino	654.23	590.00	584.15
2-keto	636.01	593.11	582.81
Glutaric	605.00	573.80	570.00
2-methyl	627.46	578.06	574.84
3-methyl	627.46	578.06	574.84
citric	862.36	700.97	680.33
2-amino	677.11	603.44	597.69
2-keto	658.89	606.60	596.44
3-keto	658.89	606.60	596.44
Adipic	627.9	587.9	583.5

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Table 7. Vapour pressure results for estimation methods, all P_{298K} are in the sub-cooled liquid state.

	Moller (J)	Nannoolal (J)	Myrdal and Yalkowsky (J)	Moller (N)	Nannoolal (N)	Myrdal and Yalkowsky (S&B)
Oxalic	3.85×10^{-3}	4.35×10^{-1}	2.99×10^{-1}	6.69×10^{-3}	6.45×10^{-1}	7.90×10^{-1}
Malonic	1.48×10^{-3}	7.00×10^{-2}	9.30×10^{-2}	4.91×10^{-3}	1.73×10^{-1}	3.46×10^{-1}
2-methyl	4.79×10^{-4}	1.29×10^{-2}	3.11×10^{-2}	7.33×10^{-3}	1.06×10^{-1}	2.94×10^{-1}
2-ol	1.99×10^{-9}	7.63×10^{-6}	2.76×10^{-4}	1.94×10^{-6}	5.67×10^{-4}	2.19×10^{-2}
Succinic	4.10×10^{-4}	1.08×10^{-2}	2.70×10^{-2}	2.77×10^{-3}	4.71×10^{-2}	1.50×10^{-1}
2-methyl	1.01×10^{-4}	1.91×10^{-3}	8.59×10^{-3}	3.37×10^{-3}	2.94×10^{-2}	1.25×10^{-1}
2-methyl, 2-ol	2.18×10^{-11}	1.15×10^{-7}	2.73×10^{-5}	3.16×10^{-6}	1.92×10^{-4}	1.18×10^{-2}
2-ol	1.57×10^{-10}	7.23×10^{-7}	7.49×10^{-5}	8.61×10^{-7}	1.52×10^{-4}	1.06×10^{-2}
2,3-diol	1.09×10^{-16}	5.88×10^{-12}	1.72×10^{-7}	6.77×10^{-9}	3.34×10^{-7}	1.18×10^{-3}
2-amino	3.65×10^{-7}	2.48×10^{-5}	2.53×10^{-4}	1.89×10^{-4}	2.57×10^{-3}	1.98×10^{-2}
2-keto	2.89×10^{-6}	3.75×10^{-4}	1.36×10^{-3}	1.67×10^{-4}	6.64×10^{-3}	3.37×10^{-3}
Glutaric	8.56×10^{-5}	1.59×10^{-3}	7.33×10^{-3}	1.30×10^{-3}	1.30×10^{-2}	6.51×10^{-2}
2-methyl	1.60×10^{-5}	2.69×10^{-4}	2.23×10^{-3}	1.32×10^{-3}	8.21×10^{-3}	5.37×10^{-2}
3-methyl	1.60×10^{-5}	2.69×10^{-4}	2.23×10^{-3}	1.32×10^{-3}	8.21×10^{-3}	5.37×10^{-2}
3-hydroxy acid	4.18×10^{-21}	6.47×10^{-16}	4.45×10^{-10}	5.34×10^{-9}	9.32×10^{-9}	6.58×10^{-5}
2-amino	4.25×10^{-8}	2.77×10^{-6}	6.44×10^{-5}	8.00×10^{-5}	6.99×10^{-4}	9.42×10^{-3}
2-keto	3.75×10^{-7}	4.35×10^{-5}	3.49×10^{-4}	6.84×10^{-5}	1.70×10^{-3}	1.57×10^{-2}
3-keto	3.75×10^{-7}	4.35×10^{-5}	3.49×10^{-4}	6.84×10^{-5}	1.70×10^{-3}	1.57×10^{-2}
Adipic	1.34×10^{-5}	2.19×10^{-4}	1.89×10^{-3}	5.18×10^{-4}	3.66×10^{-3}	2.86×10^{-2}

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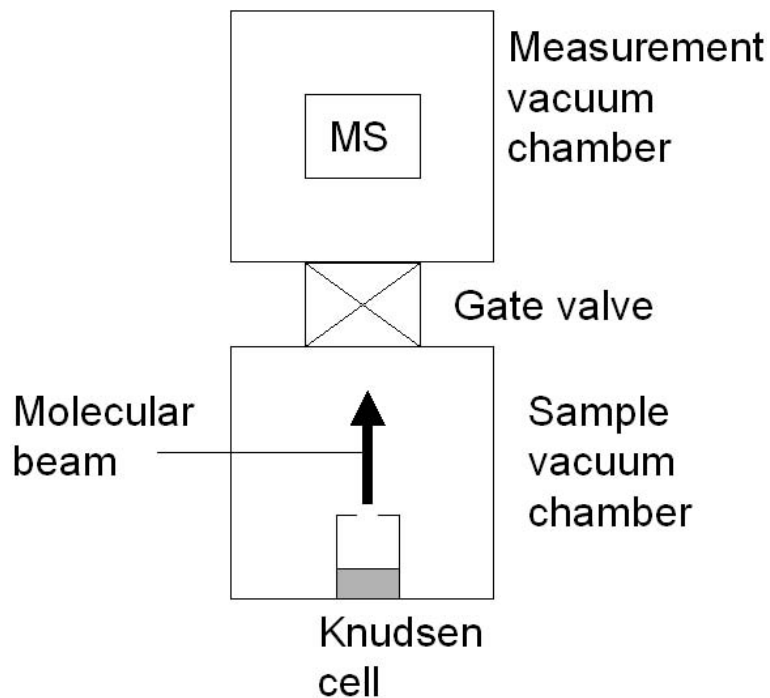


Fig. 1. Schematic of KEMS system. Reproduced from Booth et al. (2009a).

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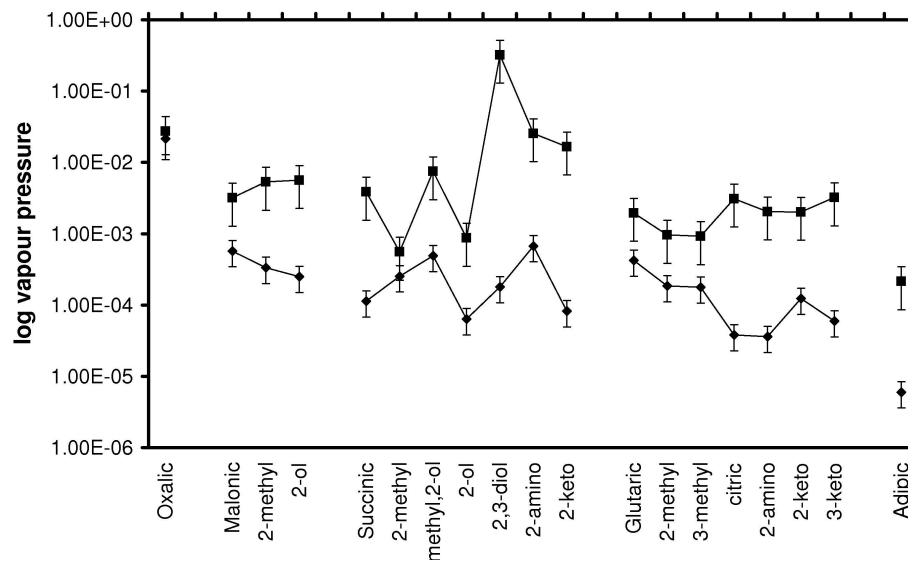


Fig. 2. Vapour pressures at 298 K. \diamond solid state, \blacksquare sub-cooled liquid.

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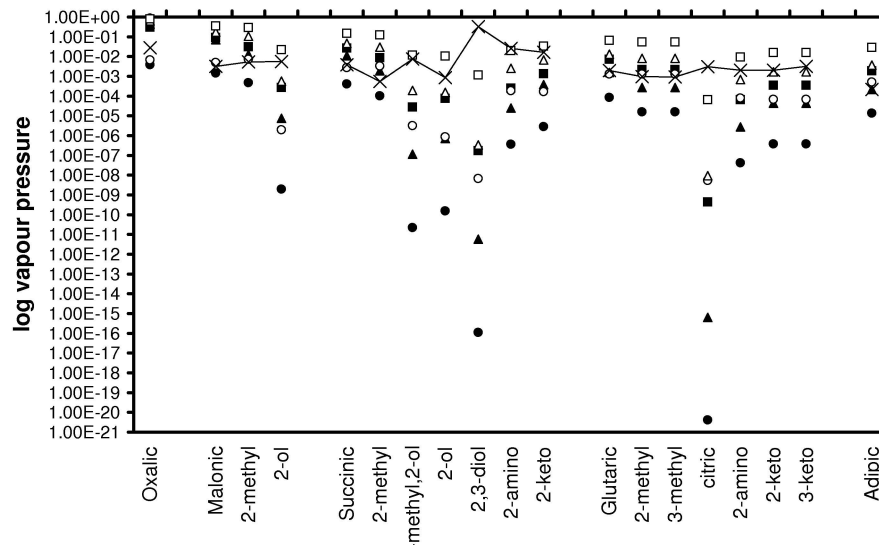


Fig. 3. Sub-cooled liquid vapour pressures at 298 K. Symbols: \times KEMS; \circ Moller with Nannoolal T_b ; \bullet Moller with Joback T_b ; \square Myrdal and Yalkowsky with Stein and Brown T_b ; \blacksquare Myrdal and Yalkowsky with Joback T_b ; Δ Nannoolal with Nannoolal T_b ; \blacktriangle Nannoolal with Joback T_b .

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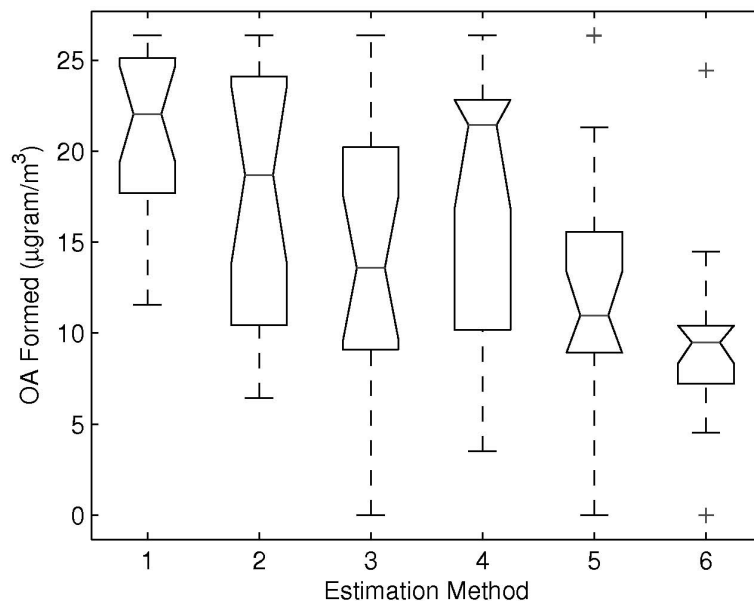


Fig. 4. Box-whisker plots of the predicted amount of OA formed by the partitioning model using estimated vapour pressures for a single compound out of the 19 reported. The base case uses experimental vapour pressure values with the concentration of all components set the value that gives $10.6 \mu\text{g m}^{-3}$ OA. Estimation methods are: 1) Moller with Joback T_b ; 2) Nannoolal with Joback T_b ; 3) Myrdal and Yalkowsky with Joback T_b ; 4) Moller with Nannoolal T_b ; 5) Nannoolal with Nannoolal T_b ; 6) Myrdal and Yalkowsky with Stein and Brown T_b .

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