

Solid state and sub-cooled liquid vapour pressures of cyclic aliphatic dicarboxylic acids

A. M. Booth¹, W. J. Montague², M. H. Barley¹, D. O. Topping¹, G. McFiggans¹, A. Garforth³, and C. J. Percival¹

¹School of Earth, Environmental and Atmospheric Science, University of Manchester, UK

²School of Chemistry, University of Manchester, UK

³School of Chemical Engineering and Analytical Science, University of Manchester, UK

Received: 19 August 2010 – Published in Atmos. Chem. Phys. Discuss.: 6 October 2010

Revised: 13 January 2011 – Accepted: 17 January 2011 – Published: 21 January 2011

Abstract. Knudsen Effusion Mass Spectrometry (KEMS) has been used to measure for the first time the solid state vapour pressures of a series of aliphatic cyclic dicarboxylic acids with increasing ring size. Additionally the atmospherically important compounds; *cis*-pinonic acid and levoglucosan were also measured. Differential Scanning Calorimetry (DSC) was used to measure melting points, enthalpies and entropies of fusion, which were used to determine sub-cooled liquid vapour pressures for the compounds. The sub-cooled liquid vapour pressure of straight chain, branched and cyclic dicarboxylic acids was compared to a selection of estimation methods.

1 Introduction

The direct and indirect impacts of atmospheric aerosols are one of the greatest uncertainties in our understanding of radiative forcing (Solomon et al., 2007). Organic compounds in aerosols are ubiquitous (Zhang et al., 2007; Hallquist et al., 2009) and incredibly varied, with possibly hundreds of thousands of compounds (Goldstein and Galbally, 2007). Gas (volatile organic compounds, VOC) to particle partitioning is responsible for a considerable fraction of organic aerosols (OA), and is frequently described by an equilibrium based absorptive partitioning model (Pankow, 1994). The vapour pressures of the components making up the OA are an important parameter in absorptive partitioning (Pankow, 1994). Accurate vapour pressure estimation methods and

experimental data to test them against are important in improving our understanding of the OA fraction in atmospheric aerosols.

Significant emissions of volatile organic compounds (VOC) arise from biogenic sources and global rates have been estimated at $\sim 800 \text{ Tg C y}^{-1}$ (Fowler et al., 2009). About 50% of the biogenic VOC emissions are thought to be isoprene (Guenther et al., 2006), monoterpenes contribute 10–15%, and sesquiterpenes are also emitted in small quantities (Fowler et al., 2009). The vast emissions of isoprene in particular, and terpenes in general means that if they yield a small amount of aerosol, then the effect on the global organic aerosol budget would be substantial (Henze and Seinfeld, 2006). Products from terpene oxidation such as pinic and pinonic acid have been found in atmosphere aerosols (e.g. Boy et al., 2004; Fu et al., 2009).

There are many methods of estimating pure component vapour pressures, but most of the experimental data collected for fitting these methods are from intermediate or high vapour pressure compounds. Some of the estimation methods can give errors in vapour pressure of several orders of magnitude for multifunctional compounds at ambient temperatures (Barley and McFiggans, 2010; Booth et al., 2010). There are several experimental methods available for very-low vapour pressure measurements including Tandem Differential Mobility Analysis (TDMA) (Bilde and Pandis, 2001; Bilde et al., 2003; Mønster et al., 2004; Koponen et al., 2007; Riipinen et al., 2007; Froesch et al., 2010; Salo et al., 2010), White light resonance spectroscopy (Zardini et al., 2006), Temperature Programmed Desorption (TPD) (Cappa et al., 2007; Chattopadhyay and Ziemann, 2005), Electrodynamic Balance (EDB) (Pope et al., 2010; Soonsin et al., 2010), Optical tweezers (Pope et al., 2010), Knudsen



Correspondence to: A. M. Booth
(alastair.booth@manchester.ac.uk)

Effusion Mass-loss (Riberio da Silva et al., 1999, 2001) and Knudsen Effusion Mass Spectrometry (KEMS) (Booth et al., 2009). They have been previously used to study straight chain (Riberio da Silva et al., 1999; Bilde et al., 2003; Chattopadhyay and Ziemann 2005; Zardini et al., 2006; Koponen et al., 2007; Riipinen et al., 2007; Cappa et al., 2007; Salo et al., 2010; Pope et al., 2010; Soonsin et al., 2010), branched (Riberio da Silva et al., 2001; Mønster et al., 2004; Booth et al., 2010), cyclic (Bilde and Pandis, 2001) and substituted (Chattopadhyay and Ziemann 2005; Froesch 2010; Booth et al., 2010) dicarboxylic acids which have been identified in the atmosphere (Hallquist et al., 2009; Kawamura et al., 1996; Sempere and Kawamura, 1994; Gao et al., 2004; Kawamura et al., 2005) as likely products of VOC oxidation. These dicarboxylic acids are solids at room temperature and pressure; however, current gas/particle partitioning models use the sub-cooled liquid reference state, as do activity models (Booth et al., 2010; Riipinen et al., 2007). The sub-cooled liquid is the metastable liquid which exists if solidification does not occur at temperatures below that of the triple point. On a pressure-temperature (P, T) phase diagram, it is a line that forms an extension to the liquid phase vapour pressure line below the triple point temperature.

In this work KEMS combined with Differential Scanning Calorimetry (DSC) has been used to measure solid state vapour pressures and determine, using a thermodynamic relationship, sub-cooled liquid vapour pressures. As part of a larger data set, measurements have been made here for the first time of a systematic series of cyclic dicarboxylic acids with increasing ring sizes. Cyclic acids and diacids are possible SOA products of biogenic terpeneoid VOC oxidation where the cyclic moiety has been retained. These results will also determine the skill of the estimation methods for compounds with cyclic backbones. In addition, the vapour pressure of levoglucosan, a tracer for biomass burning (Simoneit et al., 1999), has also been measured.

2 Theory

2.1 Sub-cooled correction

The sub-cooled liquid 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 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). Strictly speaking the triple point T_t should be used as per the definition of sub-cooled liquid in Sect. 1,

but T_m is more commonly used and is typically within 1 K of T_t for small organic acids. The sub-cooled liquid vapour pressure also allows more direct comparison with theoretical vapour pressure estimation methods which predict the sub-cooled state (e.g. Nannoolal et al., 2008; Moller et al., 2008).

2.2 Vapour pressure estimates

Many predictive methods exist for vapour pressure (Barley and McFiggans, 2010). Here we use three methods which have previously been used in estimating vapour pressure for atmospheric compounds (Barley and McFiggans, 2010; Booth et al., 2010). The 3 methods have been chosen as they were reported to be the best methods for a test set of 45 low volatility compounds by Barley and McFiggans (2010) and they have been used in conjunction with KEMS measurements previously (Booth et al., 2010). The vapour pressure equations (referred to here as the vapour pressure methods) describe the vapour pressure, which varies exponentially with temperature, (see Eq. 2) as a function of several inputs, such as group contribution parameters, or the vapourisation entropy. All the methods here also require the normal boiling point, T_b , to be calculated separately. Together they described the vapour pressure from 1 atmosphere at the normal boiling point down the pressure at the required temperature, in this case 298 K. The three vapour pressure methods used 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). The methods are briefly outlined here, for more detailed descriptions see Barley and McFiggans (2010) or Booth et al. (2010).

The Nannoolal et al. (2004) estimation method uses group contribution calculations with primary and secondary groups and group interactions (207 groups). It was used to calculate both normal boiling points (Nannoolal et al., 2004) and then the slope of the vapour pressure line (Nannoolal et al., 2008). 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. 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 Yalkowsky (1997) which uses the flexibility of the molecular structure and hydrogen bond number to estimate the entropy of vapourisation ΔS_{vap} .

3 Experimental

3.1 Knudsen effusion mass spectrometry

Samples of 1,1-cyclopropane dicarboxylic acid (>97%), *cis*-pinonic acid (>98%), 1,1-cyclobutane dicarboxylic acid (>99%), 1,2-cyclopentane dicarboxylic acid (>98%), 1,3-cyclohexane dicarboxylic acid (>99%) and levoglucosan (>99%) were purchased from Sigma-Aldrich and used with no further preparation. Solid state vapour pressures were determined using a custom built Knudsen Effusion Mass Spectrometer (Booth et al., 2009) consisting of two separately pumped chambers, connected via a gate valve. The first chamber holds the Knudsen cell and the second chamber holds a Balzers-Pfeifer quadrupole mass spectrometer.

The KEMS system is discussed in more detail in Booth et al. (2009), a brief overview of the experimental method is included here. To calibrate, a sample of known vapour pressure is placed in the temperature controlled Knudsen cell (in this case malonic acid, using vapour pressure values of $\ln P(\text{Pa}) = 29.54 - 11058.97/T(\text{K})$ Booth et al., 2009). 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 the thermodynamic equilibrium of the samples in the cell (Hilpert, 2001). The resulting molecular beam is ionised by 70 eV electron impact, then sampled by the mass spectrometer. After correcting for the ionization cross section of the calibration compound, this produces a signal proportional to the vapour pressure.

After this calibration a sample of unknown vapour pressure can be measured. During sample change the first chamber with the Knudsen cell is isolated via the gate valve and vented to air allowing the ioniser filament to be left on. The unknown vapour pressures can be determined from the intensity of the mass spectrometer signal of the compound in question. If the Knudsen number, the ratio of the mean free path of molecules to the size of the effusion orifice, is high enough then effusing gas does not significantly disturb the equilibrium in the cell (Booth et al., 2009; Hilpert, 1991, 2001) making the steady state pressure, as measured by the KEMS, as close as possible to the equilibrium vapour pressure.

Once the vapour pressure, P , has been determined at a number of different temperatures further thermodynamic data can be obtained using the Clausius-Clapeyron equation (Hilpert, 2001);

$$\ln P = \frac{\Delta H_{\text{sub}}}{RT} + \frac{\Delta S_{\text{sub}}}{R} \quad (2)$$

where T is the temperature, R is the ideal gas constant and ΔH_{sub} and ΔS_{sub} are the enthalpies and entropies of sublimation respectively. P was obtained over a range of 20 K in this work, starting at 298 K. The reported solid state P_{298} vapour pressures are calculated from the linear fit of $\ln P$ vs. $1/T$ used in the Clausius-Clapeyron equation.

3.2 Differential scanning calorimetry

The thermochemical data was obtained using the same procedure as in Booth et al. (2010) and is repeated here: Melting points (T_m) and enthalpies of fusion (ΔH_{fus}) were measured using a TA instruments Q200 DSC with a heating rate of 10 C min^{-1} up to $200 \text{ }^\circ\text{C}$. 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. $\Delta c_{p,\text{sl}}$ is frequently estimated using one of three assumptions, based on empirical evidence; $\Delta c_{p,\text{sl}} = 0$ (Yalkowsky, 1981; Prausnitz et al., 1986), $\Delta c_{p,\text{sl}} = 0.5\Delta S_{\text{fus}}$ (Tsonopoulos, 1970) and $\Delta c_{p,\text{sl}} = \Delta S_{\text{fus}}$ (Mauger et al., 1972; Grant et al., 1984). $\Delta c_{p,\text{sl}} = \Delta S_{\text{fus}}$ is used in this work, which is calculated using DSC measurements and $\Delta S_{\text{fus}} = \Delta H_{\text{fus}}/T_m$. Booth et al. (2010) compared this assumption with literature values of $\Delta c_{p,\text{sl}}$ for the C_3 – C_6 straight chain diacids and it can lead to differences of 10–20% in the sub-cooled liquid vapour pressure. The $\Delta c_{p,\text{sl}} = 0.5\Delta S_{\text{fus}}$ assumption leads to differences of 15–70%, and $\Delta c_{p,\text{sl}} = 0$ gives differences between 35 and 260% for the C_3 – C_6 diacids vs. literature $\Delta c_{p,\text{sl}}$.

4 Results and discussions

4.1 Experimental vapour pressures

Table 1 shows the $P_{298 \text{ solid}}$, ΔH_{sub} and ΔS_{sub} obtained by fitting Eq. (2) to the vapour pressure data in Table 2 measured using KEMS. The data are shown in Figs. 1 and 2. Table 1 also shows literature results for some related compounds, included for comparison with our results. The Table 1 compounds include literature straight chain and branched diacids with the same O/C ratios as those measured in this study. Where possible we have used previous KEMS (Booth et al., 2009, 2010) and Knudsen mass loss data from Riberio da Silva et al. (2001), the remaining literature measurements are using TDMA by the Bilde group which tend to agree well with KEMS results, this is to ensure as much consistency as possible when comparing the relative differences between cyclic and straight chain diacids. Table 3 shows the thermochemical data obtained from DSC and the sub-cooled liquid vapour pressure determined from them and the KEMS results. Table 3 also shows sub-cooled liquid vapour pressures calculated in this work from available literature data and the vapour pressures in Table 1. The difference between the solid state and sub-cooled liquid, which are dependant on T_m and ΔH_{fus} are illustrated in Fig. 3. The error on the solid state is based on repeated measurements of the straight chain diacids in Booth et al. (2009), the sub-cooled liquid error is from Booth et al. (2010) and is the total error from the solid state

Table 1. Solid state vapour pressure, enthalpies and entropies of sublimation measured in this work. Estimated maximum error on $P_{298 \text{ solid}} \pm 40\%$. Also shown, literature solid state vapour pressures (P_{298}) and calculated ΔH_{sub} , ΔS_{sub} (where available) for straight chain, branched and cyclic diacids. ^a HTDMA, Bilde and Pandis (2001) ^b KEMS, Booth et al. (2009) ^c KEMS, Booth et al. (2010) ^d HTDMA, Bilde et al. (2003) ^e HTDMA, Mønster et al. (2004) [◇] Knudsen Mass-loss, Riberio da Silva et al. (2001) extrapolated to 298 K.

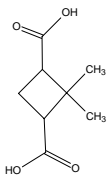
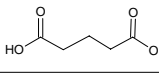
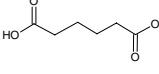
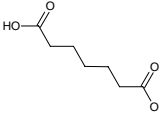
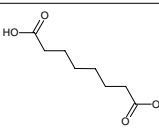
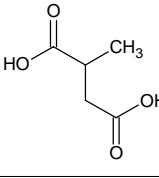
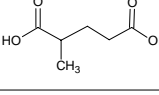
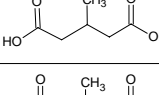
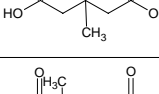
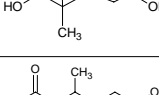

Structure	Name	$P_{298 \text{ solid}}$ (Pa) solid state	ΔH_{sub} (kJ mol ⁻¹)	ΔS_{sub} (J mol ⁻¹ K ⁻¹)
	1,1-cyclopropane dicarboxylic acid	5.95×10^{-4}	126	362
	1,1-cyclobutane dicarboxylic acid	1.13×10^{-4}	84	207
	1,2-cyclopentane dicarboxylic acid	5.97×10^{-5}	66	138
	1,3-cyclohexane dicarboxylic acid	1.17×10^{-4}	67	148
	<i>cis</i> -pinonic acid	1.29×10^{-4}	109	291
	Levoglucosan	4.65×10^{-5}	68	148
	<i>cis</i> -pinonic acid ^a	7.00×10^{-5}	–	–
	<i>trans</i> -norpinic acid ^a	1.41×10^{-4}	42	–

vapour pressure, the assumption of $\Delta C_{p,sl} = \Delta S_{\text{fus}}$, and the change from using the highest and lowest values for ΔH_{fus} and T_m in the literature.

4.1.1 C₅ diacids

The aliphatic C₅ diacids; 1,1 cyclopropane dicarboxylic, glutaric and 2-methyl succinic acid, decrease in solid state vapour pressure by a factor of 1.4 for cyclic to straight chain and 1.7 for straight to branched, these are similar to the

Table 1. Continued.

Structure	Name	P_{298} solid (Pa) solid state	ΔH_{sub} (kJ mol ⁻¹)	ΔS_{sub} (J mol ⁻¹ K ⁻¹)
	pinic acid ^a	4.27×10^{-5}	109	–
	glutaric acid ^b	4.21×10^{-4}	123	208
	adipic acid ^b	3.28×10^{-6}	119	231
	pimelic acid ^d	5.10×10^{-5}	147	–
	suberic acid ^d	1.20×10^{-6}	184	–
	2-methyl succinic acid ^c	2.54×10^{-4}	100	268
	2-methyl glutaric acid ^c	1.85×10^{-4}	82	204
	3-methyl glutaric acid ^c	1.77×10^{-4}	86	215
	3,3-dimethyl glutaric acid ^e	2.30×10^{-3}	60	–
	2,2-dimethyl glutaric acid ^c	1.63×10^{-4}	125	347
	3-methyl adipic acid ^e	1.30×10^{-4}	215	–

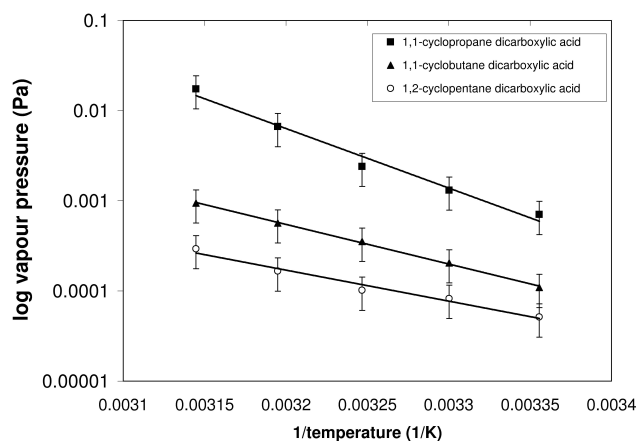
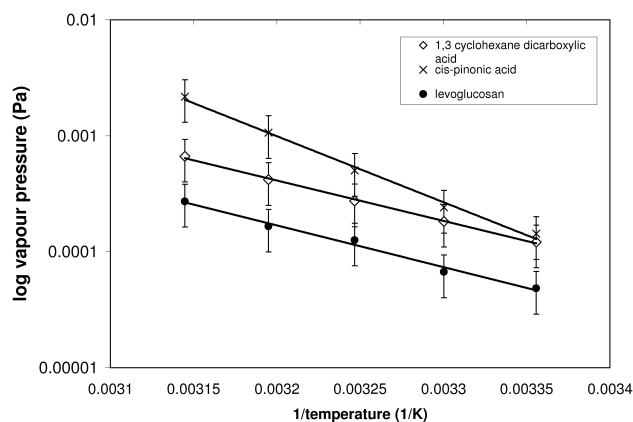
reported errors of $\pm 40\%$. The sub-cooled liquid vapour pressures, which are free of crystal structure effects, show a similar reduction (~ 1.6) from cyclic to straight. The differences between the C_5 acids as solids are similar to those as sub-cooled liquids, which indicates the crystal structure effects for these solids are negligible.

4.1.2 C_6 diacids

The C_6 diacids; 1,1 cyclobutane, adipic, 2-methyl glutaric and 3-methyl glutaric, show the solid state vapour pressure for the branched being approximately 1.5 times more volatile than the cyclic, but the straight chain results are lower by two orders of magnitude. This suggests a large difference

Table 2. Solid state vapour pressure data (Pa) at different temperatures.

Temperature (K)	298	303	308	313	318
1,1-cyclopropane diacid	7.04×10^{-4}	1.31×10^{-3}	2.41×10^{-3}	6.65×10^{-3}	1.74×10^{-2}
1,1-cyclobutane diacid	1.09×10^{-4}	2.05×10^{-4}	3.55×10^{-4}	5.67×10^{-4}	9.45×10^{-4}
1,2-cyclopentane diacid	5.13×10^{-5}	8.26×10^{-5}	1.02×10^{-4}	1.66×10^{-4}	2.93×10^{-4}
1,3-cyclohexane diacid	1.21×10^{-4}	1.83×10^{-4}	2.74×10^{-4}	4.19×10^{-4}	6.66×10^{-4}
<i>cis</i> -pinonic acid	1.43×10^{-4}	2.42×10^{-4}	5.03×10^{-4}	1.06×10^{-3}	2.18×10^{-3}
levoglucosan	4.83×10^{-5}	6.70×10^{-5}	1.26×10^{-4}	1.66×10^{-4}	2.72×10^{-4}

**Fig. 1.** Log vapour pressure (Pa) vs. 1/Temperature (1/K) for the data in table 2. Symbols; 1,1-cyclopropane dicarboxylic acid, 1,1-cyclobutane dicarboxylic acid, \circ 1,2-cyclopentane dicarboxylic acid.**Fig. 2.** Log vapour pressure (Pa) vs. 1/Temperature (1/K) for the data in Table 2. \times *cis*-pinonic acid, \diamond 1,3-cyclohexane dicarboxylic acid, \bullet levoglucosan.

between them in crystal structure. This is a manifestation of the well known odd-even effect of straight chain dicarboxylic acids. 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 (Thalladi et al., 2000). The sub-cooled liquid vapour pressures, compared to the C_6 cyclic compounds show a ~ 3 fold reduction for the straight chain and a 1.5 factor increase for the branched.

4.1.3 C_7 and C_8 diacids

The C_7 and C_8 diacid solid state vapour pressures show a similar pattern to the C_6 and C_5 . Solid state vapour pressures of the cyclic diacids are similar compared to straight chain diacids when the carbon chain length is odd numbered (C_5 and C_7), and two orders of magnitude higher when even numbered. This shows that none of the cyclic diacids have the very stable crystal structure of the even numbered straight chain diacids; succinic, adipic and suberic etc. The sub-cooled liquid vapour pressures all show the straight chain molecules with a lower pressure than the cyclic isomer by

a factor of 1.3 for C_7 and 20 for C_8 . The branched C_7 diacids do not have the literature data for T_m and ΔH_{fus} to do a sub-cooled liquid correction so only the solid state are available. 3-methyl adipic acid and 2,2-dimethyl glutaric acid have roughly the same vapour pressure, which is 3 times higher than the C_7 straight chain and cyclic diacid. 3,3-dimethyl glutaric acids is much more volatile with a vapour pressure 15 times that of the other two branched C_7 diacids.

4.1.4 C_5 - C_8 cyclic diacids

The sub-cooled liquid vapour pressure shows a similar trend to the solid state vapour pressures but are even closer to each other, within error the C_5 , C_6 and C_8 sub-cooled liquid are the same. The solid state vapour pressure falls from C_5 to C_7 and rises by C_8 . The slightly lower solid state vapour pressure for 1,2-cyclopentane dicarboxylic acid compared to the other cyclics may be explained simply by that compound having a more stable crystal structure, but that does not explain the difference in sub-cooled liquid vapour pressures which are independent of crystal structure effects. The enthalpy of sublimation, ΔH_{sub} , decreases rapidly as the ring size increases, from 126 kJ mol $^{-1}$ for C_5

Table 3. Sub-cooled liquid vapour pressures, melting points, enthalpies and entropies of fusion from DSC measurements and correction of solid vapour pressures in Table 1. Estimated maximum error on $P_{298 \text{ sub-cooled}} \pm 75\%$. Also shown are sub-cooled liquid vapour pressures derived from literature $P_{298 \text{ solid}}$, ΔH_{fus} and T_m (1) ^a Booth et al. (2010), (2) ⁺ Bilde et al. (2003) with ΔH_{fus} and T_m from Roux et al. (2005).

Name	$P_{298 \text{ sub-cooled}}$ liquid (Pa)	Ratio of sub-cooled liquid to solid P_{298}	T_m (K)	ΔH_{fus} (kJ mol ⁻¹)	ΔS_{fus} (J mol ⁻¹ K ⁻¹)
1,1-cyclopropane diacid	3.10×10^{-3}	5.2	413.0	17.4	42.1
1,1-cyclobutane diacid	6.47×10^{-3}	5.7	433.2	16.8	38.7
1,2-cyclopentane diacid	3.47×10^{-4}	7.0	428.6	19.1	44.5
1,3-cyclohexane diacid	4.60×10^{-4}	3.9	439.0	12.9	29.4
<i>cis</i> -pinonic acid	7.78×10^{-4}	6.0	377.8	23.8	63.0
Levoglucosan (1st transition)	1.35×10^{-4}	2.9	385.7	13.2	34.2
levoglucosan (2nd transition)	1.93×10^{-4}	1.3	455.3	3.2	7.0
glutaric ^a acid	1.96×10^{-3}	4.6	369.0	22.0	59.7
adpic ^a acid	2.14×10^{-4}	35.7	423.0	35.9	84.8
pimelic ^b acid	2.63×10^{-4}	5.1	368.2	23.7	64.3
suberic ^b acid	2.23×10^{-5}	18.6	413.2	30.7	74.3
2-methyl succinic ^a	5.58×10^{-4}	8.5	383.0	10.0	26.1
2-methyl glutaric ^a	9.63×10^{-4}	2.2	349.0	30.3	86.7

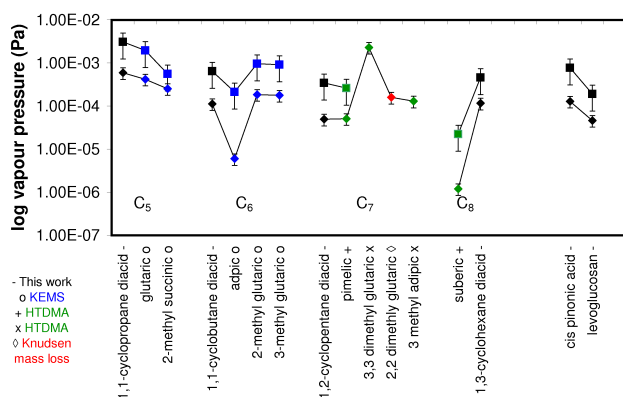


Fig. 3. Solid state (◆) and sub-cooled liquid (■) P_{298} (Pa). The estimated maximum error is $P_{298 \text{ solid}} \pm 40\%$ and $P_{298 \text{ liquid}} \pm 75\%$. – This work, ^o Booth et al. (2010) ⁺ Bilde et al. (2003) ^x Mønster et al. (2004) [◇] Riberio da Silva et al. (2001) extrapolated to 298 K.

to 66 and 67 KJ mol⁻¹ for C₇ and C₈ respectively. The C₅ straight chain diacid has a similar ΔH_{sub} to the cyclic, 123 vs. 126 KJ mol⁻¹, but the pattern for straight chain diacids shows an increasing ΔH_{sub} as chain length increases from 123 KJ mol⁻¹ for C₅ to 184 KJ mol⁻¹ for C₈. This makes for a substantial difference of 117 KJ mol⁻¹ between the cyclic and straight chain C₈ diacids. The widening gap with increasing carbon number between the ΔH_{sub} for straight chain and cyclic acids may be of consequence for thermal desorption measurements of mixtures of cyclic and branched acids as compounds with similar sub-cooled liquid vapour pressure and O to C ratio could have very different results after thermal processing and undesired distillation could occur.

The solid state *cis*-pinonic acid results here are slightly higher than those of Bilde and Pandis (2001) who, due to measurement problems, give an estimated range of $0.5\text{--}1 \times 10^{-4}$ Pa. The top end of this range however would agree well with our results using the error estimates in Booth et al. (2009, 2010) of $\pm 40\%$. Levoglucosan exhibits a solid phase transition at 385.7 K and a melting transition with a small enthalpy of fusion at 456 K (Oja and Suuberg, 1999), we have used the correction in Eq. (1) to adjust for both these transitions and arrive at a final sub-cooled liquid vapour pressure. Oja and Suuberg (1999) have measured levoglucosan below and above this transition getting vapour pressures of 1×10^{-5} and 1×10^{-4} Pa, respectively. The first is about a quarter of the value we measure, whereas the vapour pressure after the transition agrees with our value of 1.35×10^{-4} Pa within error. Epshtein (1964) has measured levoglucosan from 468 to 528 K, extrapolation of their values down to 298 K gives a vapour pressure of 1×10^{-3} Pa which is about 5 times higher than our final sub-cooled liquid vapour pressure of 1.93×10^{-4} Pa, although it should be noted that this extrapolation is for a two parameter Antoine equation fit 200 K above the desired temperature.

4.2 Vapour pressure estimates

Vapour pressure estimates were made using 3 methods; Nannoolal et al. (2004) T_b with Moller et al. (2008) vapour pressures, Nannoolal et al. (2004) T_b with Nannoolal et al. (2008) vapour pressures and Stein and Brown (1994) T_b with Myrdal and Yalkowsky (1997) vapour pressures. It has recently been suggested that the Moller et al. (2008) method becomes increasingly inaccurate as the number of functional groups

increases (Compernelle et al., 2010), however the majority of compounds in this study only have two groups. Table 4 shows the two different boiling points used, the Stein and Brown (1994) boiling points are higher by 2–7 K for the cyclic compounds (excepting levoglucosan) but are lower by similar amounts for the straight chain and methyl substituted diacids. Although compared to the differences in T_b values in Barley and McFiggans (2010), the differences here are quite small and the differences from the true T_b are unknown. Systematic errors in T_b can feed through to similar errors in vapour pressure. In this case it could lead to cancelling errors if the calculations were being used on an ensemble of condensing compounds containing both cyclic and straight chain diacids which have an opposing T_b bias. Other boiling point methods are available (ACD/labs) and have been shown to work well for certain classes of compounds, notably amines (Ge et al., 2010). However for these diacids, the ACD/labs T_b does not show a significant overall improvement compared to the Nannoolal et al. (2004) or Stein and Brown (1994) T_b (Ge, 2010), and as the mechanics of the estimation method are not disclosed, further improvement would be difficult.

Table 5 shows the estimated sub-cooled liquid vapour pressures using the 3 estimation methods. For the diacids the Moller/Nannoolal method performs best, on average overestimating vapour pressure by a factor of 2.7. The Nannoolal et al. (2008) method lacks the extra terms of the Moller et al. (2008) method for aliphatic carboxylic acids and its performance (with T_b by Nannoolal) reflects this with an average factor of 12.2 times our sub-cooled vapour pressure values. The Myrdal and Yalkowsky/Stein and Brown overestimated vapour pressures by an average factor of 74. *Cis*-pinonic acid, with a ketone group, causes more problems than the diacids. For this compound the Moller method is an order of magnitude too high, Nannoolal a factor of 70 and Myrdal and Yalkowsky a factor of 200.

Levoglucosan has no acids groups, but aliphatic alcohols, like carboxylic acids groups are known to cause problems for vapour pressure estimates (Booth et al., 2010; Moller et al., 2008). The Moller et al. (2008) method, despite extra terms for aliphatic OH groups, is the most inaccurate of the vapour pressure methods for this compound. The estimated vapour pressure was out by 3 orders of magnitude, compared to 2 orders of magnitude for the other two methods. The most likely cause for this is the interaction parameter between OH and ether groups being too high. This is similar to the raising of vapour pressure for compounds with OH + COOH groups compared to just COOH groups, as seen by Chattopadhyay and Ziemer (2005) and Booth et al. (2010). The vapour pressure method comparisons of Compernelle et al. (2010) also note problems with the Moller et al. (2008) method for poly-functional compounds, although it should be noted that all the methods perform badly with this compound.

Table 6 shows the estimated enthalpies of vapourisation ($\Delta H_{\text{vap}} = \Delta H_{\text{sub}} - \Delta H_{\text{fus}}$) compared with those from KEMS/DSC measurements. Barley and McFiggans (2010)

Table 4. Estimated boiling points for cyclic, straight chain and branched diacids using the Nannoolal et al. (2004) and Stein and Brown (1994) methods.

Name	Nannoolal T_b (K)	Stein and Brown T_b (K)
1,1-cyclopropane diacid	558.4	563.6
1,1-cyclobutane diacid	573.2	579.7
1,2-cyclopentane diacid	595.5	597.9
1,3-cyclohexane diacid	609.6	611.6
<i>cis</i> -pinonic acid	562.9	569.0
Levoglucosan	563.5	586.9
glutaric acid	573.8	569.0
adipic acid	587.9	583.5
pimelic acid	601.5	597.0
suberic acid	614.6	609.7
2-methyl succinic acid	563.6	559.8
2-methyl glutaric acid	578.1	574.8
3-methyl glutaric acid	578.1	574.8

in their study of vapour pressure methods noted that most of the error for the methods they looked at came from the estimation of the boiling point, and slope of the vapour pressure curve (enthalpy of vapourisation) estimates were generally much easier to get right. The Moller/Nannoolal and Nannoolal/Nannoolal methods here both use the same boiling point, but for most of the compounds there is an order of magnitude difference in the predicted vapour pressure at 298 K which can only come from the difference in predicted ΔH_{vap} between them. This should not be a complete surprise however as the changes to the Nannoolal et al. (2008) method that the Moller et al. (2008) is based on come from extra terms for carboxylic acids, which will obviously have a big impact for the diacids. The different methods show consistent bias in ΔH_{vap} for the diacids measured in this study. The Moller et al. (2008) method, excepting levoglucosan, always estimates a higher value for ΔH_{vap} than Nannoolal et al. (2008) which predicts higher ΔH_{vap} values than Myrdal and Yalkowsky (1997). The ΔH_{vap} estimates seem very good for the C₅ diacids (typically within 20 KJ mol⁻¹ or less) but as the number of carbon atoms in the molecule increases the behaviour of the straight chain and cyclic diacids diverge. ΔH_{vap} increases with carbon number for straight chain diacids and ΔH_{vap} decreases with increasing carbon number for cyclic diacids. The estimation methods however, do not significantly change their estimates, for example there is only a range of 23 KJ mol⁻¹ between the highest and lowest estimate for ΔH_{vap} using the Nannoolal method, but the experimental methods vary by 106 KJ mol⁻¹. In spite of this the estimation methods can sometimes give good P_{298} values, as opposing errors in ΔH_{vap} and T_b can cancel out.

Table 5. Estimated sub-cooled liquid vapour pressures. The ratio of estimated to measured sub-cooled liquid vapour pressure in brackets.

	KEMS P_{298} liquid (Pa)	Moller/Nannoolal P_{298} liquid (Pa)	Nannoolal/Nannoolal P_{298} liquid (Pa)	Myrdal and Yalkowsky/Stein and Brown P_{298} liquid (Pa)
1,1-cyclopropane diacid	3.1×10^{-3}	5.5×10^{-3} (1.8)	4.5×10^{-2} (14.4)	1.2×10^{-1} (37.0)
1,1-cyclobutane diacid	6.5×10^{-3}	2.5×10^{-3} (3.8)	1.4×10^{-2} (21.2)	5.3×10^{-2} (81.6)
1,2-cyclopentane diacid	3.5×10^{-4}	4.9×10^{-4} (1.4)	2.8×10^{-3} (8.0)	2.1×10^{-2} (60.8)
1,3-cyclohexane diacid	4.6×10^{-4}	1.7×10^{-4} (0.4)	7.5×10^{-4} (1.6)	1.1×10^{-2} (23.4)
<i>cis</i> -pinonic acid	7.8×10^{-4}	9.7×10^{-3} (12.5)	6.1×10^{-2} (78.2)	1.7×10^{-1} (223.7)
Levogluconan	1.9×10^{-4}	1.0 (5233)	4.1×10^{-3} (217.8)	3.2×10^{-2} (164.9)
glutaric acid	2.0×10^{-3}	1.3×10^{-3} (0.7)	1.3×10^{-2} (6.6)	6.5×10^{-2} (33.3)
adipic acid	2.1×10^{-4}	5.2×10^{-4} (2.4)	3.7×10^{-3} (17.1)	2.9×10^{-2} (133.5)
pimelic acid	2.6×10^{-4}	1.8×10^{-4} (0.7)	1.0×10^{-3} (4.0)	1.3×10^{-2} (48.7)
suberic acid	2.2×10^{-5}	5.9×10^{-5} (2.7)	3.0×10^{-4} (13.3)	5.8×10^{-3} (262.2)
2-methyl succinic acid	5.6×10^{-4}	3.4×10^{-3} (6.0)	2.9×10^{-2} (52.7)	1.3×10^{-1} (223.4)
2-methyl glutaric acid	9.6×10^{-4}	1.3×10^{-3} (1.4)	8.2×10^{-3} (8.5)	5.4×10^{-2} (55.7)
3-methyl glutaric acid	9.2×10^{-4}	1.3×10^{-3} (1.4)	8.2×10^{-3} (8.0)	5.4×10^{-2} (60.8)

Table 6. Estimated enthalpies of vapourisation compared with experimental values. KEMS ΔH_{vap} calculated using values from Tables 1 and 3 and $\Delta H_{\text{vap}} = \Delta H_{\text{sub}} - \Delta H_{\text{fus}}$.

	KEMS ΔH_{vap} (KJ mol ⁻¹)	Moller/Nannoolal ΔH_{vap} (KJ mol ⁻¹)	Nannoolal/Nannoolal ΔH_{vap} (KJ mol ⁻¹)	Myrdal and Yalkowsky/Stein and Brown ΔH_{vap} (KJ mol ⁻¹)
1,1-cyclopropane diacid	109	103	89	82
1,1-cyclobutane diacid	67	108	94	84
1,2-cyclopentane diacid	47	117	101	87
1,3-cyclohexane diacid	54	124	107	89
<i>cis</i> -pinonic acid	85	108	87	79
Levogluconan	52	77	89	86
glutaric acid	101	102	95	85
adipic acid	83	110	100	88
pimelic acid	123	119	106	90
suberic acid	153	129	112	93
2-methyl succinic	90	98	91	82
2-methyl glutaric	52	106	97	85
3-methyl glutaric	58	106	97	85

5 Conclusions

Solid state vapour pressures of aliphatic cyclic diacids tend to be very close to that of odd numbered straight chain diacids, but approximately 2 orders of magnitude higher when compared with even numbered straight chain diacids. The sub-cooled liquid vapour pressures are higher for the cyclic compounds than for comparable straight chain diacids, typically 1.5–3 times higher. The Moller et al. (2008) estimation method with Nannoolal et al. (2004) boiling points provides the best estimates of the cyclic diacids although it significantly over estimates the vapour pressure of levogluconan. It also overestimates *cis*-pinonic acid by a factor of 10, but this

is still a better result than the other two methods. As with the results of Booth et al. (2010) the main failing of the vapour pressure estimation methods is down to a poor representation of OH groups and their interactions with other groups.

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.

Edited by: J. B. Burkholder

References

- Barley, M. H. and McFiggans, G.: The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol, *Atmos. Chem. Phys.*, 10, 749–767, doi:10.5194/acp-10-749-2010, 2010.
- Bilde, M. and Pandis, S. N.: Evaporation rates and vapor pressures of individual aerosol species formed in the atmospheric oxidation of α - and β -pinene, *Environ. Sci. Technol.*, 35, 3344–3349, 2001.
- Bilde, M., Svenningsson, B., Monster, J. and Rosenorn, T.: Even – Odd Alternation of Evaporation Rates and Vapor Pressures of C3-C9 Dicarboxylic Acid Aerosols, *Environ. Sci. Technol.*, 37, 1371–1378, 2003.
- Booth, A. M., Markus, T., McFiggans, G., Percival, C. J., McGillen, M. R., and Topping, D. O.: Design and construction of a simple Knudsen Effusion Mass Spectrometer (KEMS) system for vapour pressure measurements of low volatility organics, *Atmos. Meas. Tech.*, 2, 355–361, doi:10.5194/amt-2-355-2009, 2009.
- Booth, A. M., Barley, M. H., Topping, D. O., McFiggans, G., Garforth, A., and Percival, C. J.: Solid state and sub-cooled liquid vapour pressures of substituted dicarboxylic acids using Knudsen Effusion Mass Spectrometry (KEMS) and Differential Scanning Calorimetry, *Atmos. Chem. Phys.*, 10, 4879–4892, doi:10.5194/acp-10-4879-2010, 2010.
- Boy, M., Petäjä, T., Dal Maso, M., Rannik, Ü., Rinne, J., Aalto, P., Laaksonen, A., Vaattovaara, P., Joutsensaari, J., Hoffmann, T., Warnke, J., Apostolaki, M., Stephanou, E. G., Tsapakis, M., Kouvarakis, A., Pio, C., Carvalho, A., Römpf, A., Moortgat, G., Spirig, C., Guenther, A., Greenberg, J., Ciccioli, P., and Kulmala, M.: Overview of the field measurement campaign in Hyytiälä, August 2001 in the framework of the EU project OSOA, *Atmos. Chem. Phys.*, 4, 657–678, doi:10.5194/acp-4-657-2004, 2004.
- Cappa, D. C., Lovejoy, E. R., and Ravishankara, A. R.: Determination of Evaporation Rates and Vapor Pressures of Very Low Volatility Compounds: A Study of the C₄-C₁₀ and C₁₂ Dicarboxylic Acids, *J. Phys. Chem.*, 111, 3099–3109, 2007.
- Chattopadhyay, S. and Ziemann, P. J.: Vapor pressures of substituted and unsubstituted monocarboxylic and dicarboxylic acids measured using an improved thermal desorption particle beam mass spectrometry method, *Aerosol Sci. Technol.*, 39, 1085–1100, 2005.
- Comperolle, S., Ceulemans, K., and Müller, J.-F.: Technical Note: Vapor pressure estimation methods applied to secondary organic aerosol constituents from α -pinene oxidation: an intercomparison study, *Atmos. Chem. Phys.*, 10, 6271–6282, doi:10.5194/acp-10-6271-2010, 2010.
- Epshtein, Ya. V., Duryina, L. I., and Pashinkin, A. S.: Vapor Pressure of Levoglucosan, *Zh. Prikl. Khim. (Leningrad)*, 37 2543, 1964.
- Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Schjoerring, J. K., Neftel, A., Burkhardt, J., Daemmgen, U., Neiryneck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J. P., Coyle, M., Fuzzi, S., Gerosa, G., Granier, C., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T. N., Ro-Poulsen, H., Cellier, P., Cape, J. N., Isaksen, I. S. A., Horva' th, L., Loreto, F., Niinemets, Ü., Palmer, P. I., Rinne, J., Laj, P., Maione, M., Misztal, P., Monks, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M. W., Vesala, T., Skiba, U., Brüeggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M. C., de Leeuw, G., Flossman, A., Chaumerliac, N., and Erisman, J. W.: Atmospheric composition change: Ecosystems-Atmosphere interactions, *Atmos. Environ.*, 43, 5193–5267, 2009.
- Frosch, M., Zardini, A. A., Platt, S. M., Müller, L., Reinnig, M.-C., Hoffmann, T., and Bilde, M.: Thermodynamic properties and cloud droplet activation of a series of oxo-acids, *Atmos. Chem. Phys.*, 10, 5873–5890, doi:10.5194/acp-10-5873-2010, 2010.
- Fu, P., Kawamura, K., Chen, J., and Barrie, L. A.: Isoprene, Monoterpene and Sesquiterpene Oxidation Products in the High Arctic Aerosols during Lawte Winrer to Early Summer, *Environ. Sci. Technol.*, 43, 4022–4028, 2009.
- Gao, S., Keywood, M., Ng, N. L., Surratt, J., Varutbangkul, V., Bahreini, R., Flagan, R. C., and Seinfeld, J. H.: Low-Molecular Weight and Oligomeric Components in Secondary Organic Aerosol from the Ozonolysis of Cycloalkenes and α -Pinene, *J. Phys. Chem. A.*, 108, 10147–10164, 2004.
- Goldstein, A. H. and Galbally, I. E.: Known and Unexplored Organic Constituents in the Earth's Atmosphere, *Environ. Sci. Tech.*, 41, 1514–1521, 2007.
- Grant, D. J. W., Mendizadeh, M., Chow, A. H.-L., and Fairbrother, J. E.: Non-linear van Hoff Solubility Temperature Plots and their Pharmaceutical Interpretation, *Int. J. Pharm.*, 18, 25–38, 1984.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys.*, 6, 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.
- Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric Amines – Part II. Thermodynamic properties and gas/particle partitioning, *Atmos. Environ.*, doi:10.1016/j.atmosenv.2010.10.013Ge, *Atmos. Chem. Phys. Discuss.*, 10, C10429–C10429, 2010.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.
- Henze, D. K. and Seinfeld, J. H.: Global secondary organic aerosol from isoprene oxidation, *Geophys. Res. Lett.*, 33, L09812, doi:10.1029/2006GL025976, 2006
- Hilpert, K.: Potential of mass spectrometry for the analysis of inorganic high temperature vapors, *Fresen. J. Anal. Chem.*, 370, 471–478, 2001.
- Joback, K. G. and Reid, R. C.: Estimation of pure-component properties from group contributions, *Chem. Eng. Commun.*, 57, 233–243, 1987.
- Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, *Atmos. Environ.* 30, 1709–1722, 1996.
- Kawamura, K., Imai, Y., and Barrie, L. A.: Photochemical Production and Loss of Organic Acids in High Arctic Aerosols During Long-Range Transport and Polar Sunrise Ozone Depletion

- Events, *Atmos. Environ.*, 39, 599–614, 2005.
- Koponen, I., Riipinen, I., Hienola, A., Kulmala, M., and Bilde, M.: Thermodynamic properties of Malonic, Succinic and Glutaric acids: Evaporation rates and saturation vapor pressures Nucleation and Atmospheric Aerosols, *Environ. Sci. Technol.*, 8, 920–923, 2007.
- Mauger, J. W., Paruta, A. N., and Gerraughty, R. J.: Solubilities of Sulfadiazine, Sulfomidine, and Sulfadimethoxine in Several Normal Alcohols, *J. Pharm. Sci.*, 61, 94–97, 1972.
- Mønster, J., Rosenørn, T., Svenningsson, B., and Bilde, M.: Evaporation of methyl- and dimethyl-substituted malonic, succinic, glutaric and adipic acid particles at ambient temperatures, *J. Aerosol. Sci.*, 35, 1453–1465, 2004.
- Moller, B., Rarey, J., and Ramjugernath, D.: Estimation of the vapour pressure of non-electrolyte organic compounds via group contributions and group interactions, *J. Mol. Liq.*, 143, 52–63, 2008.
- Myrdal, P. B. and Yalkowsky, S. H.: Estimating pure component vapour pressures of complex organic molecules, *Ind. Eng. Chem. Res.*, 36, 2494–2499, 1997.
- Oja, V. and Suuberg, E. M.: Vapor Pressures and Enthalpies of Sublimation of D-Glucose, D-Xylose, Cellobiose, and Levoglucosan, *J. Chem. Eng. Dat.*, 44, 26–29, 1999.
- Nannoolal, Y., Rarey, J., Ramjugernath, D., and Cordes, W.: Estimation of pure component properties Part 1. Estimation of the normal boiling point of non-electrolyte organic compounds via group contributions and group interactions, *Fluid Phase Equilib.*, 226, 45–63, 2004.
- Nannoolal, Y., Rarey, J., and Ramjugernath, D.: Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group contributions and group interactions, *Fluid Phase Equilib.*, 269, 117–133, 2008.
- Pankow, J. F.: An absorption-model of gas-particle partitioning of organic-compounds in the atmosphere, *Atmos. Environ.*, 28, 185–188, 1994.
- Pope, F.D., Tong H., Dennis-Smith, B. J., Griffiths, P. T., Clegg, S. L., Reid, J. P., and Cox, R. A.: Studies of Single Aerosol Particles Containing Malonic Acid, Glutaric Acid, and Their Mixtures with Sodium Chloride. II. Liquid-State Vapor Pressures of the Acids, *J. Phys. Chem. A.*, 37, 10156–10165, 2010.
- Prausnitz, J. M., Lichtenhaler, R. N., and de Azevedo, E. G.: *Molecular Thermodynamics of Fluid-phase Equilibria*, Prentice-Hall Inc, New Jersey, 419, 1986.
- Prausnitz, J. M., Lichtenhaler, R. N., and de Azevedo, E. G.: *Molecular Thermodynamics of Fluid-phase Equilibria*, Prentice-Hall Inc, New Jersey, 419, 1986.
- Riberio da Silva, M. A. V., Monte, M., and Ribeiro, J.: Vapour pressures and the enthalpies and entropies of sublimation of five dicarboxylic acids, *J. Chem. Thermodynamics*, 31, 1093–1107, 1999.
- Riberio da Silva, M. A. V., Monte, M., and Ribeiro, J.: Thermodynamic study on the sublimation of succinic acid and of methyl- and dimethyl-substituted succinic and glutaric acids, *J. Chem. Thermodynamics*, 33, 23–31, 2001.
- Riipinen, I., Koponen, I., Frank, G., Hyvärinen, A.-P., Vanhanen, J., Lihavaninen, H., Lehtinen, K., Bilde, M., and Kulmala, M.: Adipic and Malonic Acid Aqueous Solutions: Surface Tensions and Saturation Vapor Pressures, *J. Phys. Chem.*, 111, 12995–13002, 2007.
- Roux, M. V., Temprado, M., and Chickos, J. S.: Vaporization, fusion and sublimation enthalpies of the dicarboxylic acids from C₄ to C₁₄ and C₁₆, *Journal of Chemical Thermodynamics*, 37, 941–953, 2005.
- Salo, K., Jonsson, A. M., Andersson, P. U., and Hallquist, M.: Aerosol volatility and enthalpy of sublimation of Carboxylic acids, *J. Phys. Chem. A*, 114, 4586–4594, 2010.
- Sempere, R. and Kawamura, K.: Comparative distributions of dicarboxylic-acids and related polar compounds in snow rain and aerosols from urban atmosphere, *Atmos. Environ.*, 28, 449–459, 1994.
- Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and Cass G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, *Atmos. Environ.*, 33, 173–182, 1999.
- Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M. and Miller, H. L. (Eds.): *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Changes*, Cambridge University Press, Cambridge, 2007.
- Stein, S. E. and Brown, R. L.: Estimation of normal boiling points from group contributions, *J. Chem. Inf. Comp. Sci.*, 34, 581–587, 1994.
- Thalladi, V. R., Nüsse, M., and Boese, R.: The Melting Point Alternation in α,ω -Alkanedicarboxylic Acids, *J. Am. Chem. Soc.*, 122, 9227–9236, 2000.
- Tsonopoulos, C.: *Properties of Dilute Aqueous Solutions of Organic Solutes*, Ph.D. Dissertation, University of California, CA, USA, 1970.
- Yalkowsky, S. H.: Solubility and Partitioning. 5. Dependence of Solubility on Melting-Point, *J. Pharm. Sci.*, 70, 971–973, 1981.
- Zardini, A. A., Krieger, U. K., and Marcolli, C.: White light Mie resonance spectroscopy used to measure very low vapor pressures of substances in aqueous solution aerosol particles, *Optics Express*, 14, 2006.
- Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., Decarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, 34, L13801, doi:10.1029/2007GL029979, 2007.