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

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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 ~800 Tg C yr^{-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 remainder of emitted biogenic VOC's are oxygenated and are less reactive than isoprenes. Alcohol (e.g. methanol) and keto (e.g. acetaldehyde) groups are often emitted in large quantities (Fowler et al., 2009; Seco et al., 2007) and are linked to developmental and stress (damage) factors. Terpene compounds, such as isoprene have received considerable interest as sources of secondary organic aerosol (SOA). 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). Near-explicit (e.g., Jenkin et al., 1997) and reduced reaction mechanisms (e.g., Taraborrelli et al., 2008) have been developed to understand and quantify the chemical processes which would give rise to SOA from these sources. These have led to projects such as the Master Chemical Mechanism (MCM) which incorporate kinetics to model the formation and degradation of various organics in the atmosphere via OH, O_3 and NO_3 (e.g., Jenkin and Hayman, 1999; Saunders et al., 2003) including α-, and β-pinene and isoprene. Various terpenoid reactions have been studied using smog and aerosol chamber experiments (e.g., Sect. 4.1 of Hallquist et al., 2009; Fowler et al., 2009), including; isoprene (e.g., Rollins et al., 2009) and α and β-pinene (e.g., Bonn et al., 2002; Alfarra et al., 2006; Pathak et al., 2007) limonene (Pan et al., 2009) and β-caryophyllene (Asa-Awuku et al., 2009). And 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 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 Zieman, 2005), Electrodynamic Balance (EDB) (Pope et al., 2010; Soonsin et al., 2010), Optical tweezers (Pope et al., 2010), Knudsen 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 Zieman 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 Zieman 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., 2003; Kawamura et al., 2005) as likely products of VOC oxidation. *Cis*-pinonic acid in particular is thought to be a biogenic oxidation product. These dicarboxylic acids are solids at room temperature and pressure; however, current gas/particle partitioning models use the sub-cooled 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 use 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, especially *cis*-pinonic 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.

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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):

$$\ln \frac{P_\mathrm{l}}{P_\mathrm{s}} = \frac{\Delta H_\mathrm{fus}}{RT_\mathrm{m}} \left(\frac{T_\mathrm{m}}{T} - 1 \right) - \frac{\Delta c_\mathrm{p,sl}}{R} \left(\frac{T_\mathrm{m}}{T} - 1 \right) + \frac{\Delta c_\mathrm{p,sl}}{R} \ln \frac{T_\mathrm{m}}{T} \tag{1}$$

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 ($\mathrm{J\,mol^{-1}}$), $\Delta c_\mathrm{p;sl}$ denotes the change in heat capacity between the liquid and solid state at the melting point ($\mathrm{J\,mol^{-1}\,K^{-1}}$), 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 (Booth et al., 2010).

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 over a basis 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 pressure at different temperatures as a function of the normal boiling point T_b (which is also calculated) and some other properties such as group contribution parameter or vapourisation entropy. The equation describes a line with the boiling point at one end and in this case, a slope down to the P_{298} at the other. 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 Nanoolal 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

Samples of 1,1-cyclopropane dicarboxylic acid (>97%), *cis*-pinonic acid (>98%), 1,1-cyclobutane dicarboxylic acid (>99%), 1,2-cyclopentpane 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-Pffeifer quadrupole mass spectrometer.

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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). The cell has a chamfered effusing orifice with a size ≤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);

$$\ln P = \frac{\Delta H_{\mathrm{sub}}}{RT} + \frac{\Delta S_{\mathrm{sub}}}{R} \tag{2}$$

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.

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 using a heating rate of 10 C $\min^{-1}$ up to 200 °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. $\Delta c_{p,sl}$ is frequently estimated using one of 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). $\Delta c_{p,sl}=\Delta S_{fus}$ is used in this work. Booth et al. (2010) compared this assumption with literature values of $\Delta c_{p,sl}$ 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 $\Delta c_{p,sl}=0.5\Delta S_{fus}$ assumption leads to differences of 15–70%, and $\Delta c_{p,sl}=0$ gives differences between 35 and 260% for those compounds vs. literature $\Delta c_{p,sl}$.

4 Results and discussions

4.1 Experimental vapour pressures

Table 1 shows the $P_{298\ solid}$, ΔH_{sub} and ΔS_{sub} obtained by fitting (2) to the vapour pressure data in Table 2 measured using KEMS. The data are shown in Figs. 1 and 2. Table 3 shows literature results for some related compounds, included for comparison with our results. The Table 3 compounds include straight chain and branched diacids with the same O/C ratios as those measured in this study. Where possible we have used literature Knudsen mass loss data from Riberio da Silva et al. (2001) due to the good agreement between KEMS and Knudsen mass loss, the remaining literature measurements are using TDMA. Table 4 shows the thermochemical data obtained from DSC and the sub-cooled liquid vapour pressure determined from them and the KEMS results. Table 5 shows sub-cooled liquid vapour pressures calculated in this work from available literature data and the vapour pressures in Table 3. The difference between the solid state and sub-cooled liquid, which are dependant on T_m and ΔH_{fus} are illustrated in Fig. 3.

4.1.1 C_5 diacids

The aliphatic C_5 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. The sub-cooled liquid vapour pressures, which are free of crystal structure effects, show a similar reduction (~1.6) from cyclic to straight indicating only a small difference in the crystal structure effects between them, which is close in size to the reported errors of ±40%.

4.1.2 C_6 diacids

The C_6 diacids; 1,1 cyclobutane, adipic, 2-methyl glutaric and 3-methyl glutaric, show the same solid state vapour pressure for the cyclic and branched, but the straight chain results are lower by two orders of magnitude. This suggests a large difference between them in crystal structure. This is a manifestation of the well know 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 (Booth et al., 2010). 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.

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 due to similar T_m and ΔH_{fus} values. The vapour pressure falls from C_3 to C_5 and levels off or rises by C_6. The lower solid state vapour pressure for 1,2 cyclopentane dicarboxylic acid 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.

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 $0.5–1\times10^{-4}$ 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 ±40%.

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 and the number of function groups increases (Compernolle et al., 2010), however the majority of compounds in this study only have two groups. Table 6 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.

Table 7 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 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 Ziemen (2005) and Booth et al. (2010). The vapour pressure method comparisons of Compernolle et al. (2010) also note problems with the Moller et al. (2008) method for polyfunctional compounds.

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 levoglucosan. 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.

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Table 1. Solid state vapour pressure, enthalpies and entropies of sublimation measured in this work. Estimated maximum error on $P_{298\text{solid}}$ ±40%.

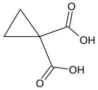
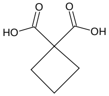
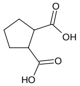
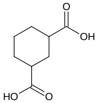
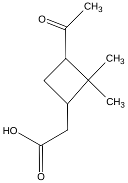
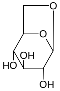
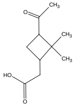
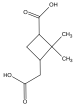
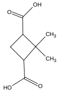
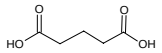
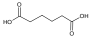
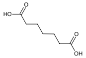
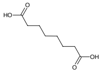
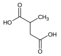
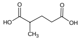
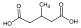
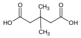
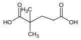
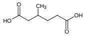
Structure	Name	$P_{298\ \text{solid}}$ (Pa) solid state	ΔH_{sub} (kJ mol^{-1})	ΔS_{sub} (J mol^{-1} K^{-1})
	1,1-cyclopropane dicarboxylic acid	5.95×10^{-4}	126	362
	1,1-cyclobutane dicarboxylic acid	1.13×10^{-4}	84	207
	1,2-cyclopentane diacarboyxlic acid	5.97×10^{-5}	66	138
	1,3-cyclohexane dicarboxylic acid	1.17×10^{-4}	67	148
	*cis*-pinonic acid	1.29×10^{-4}	109	291
	levoglucosan	4.65×10^{-5}	68	148

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

Temperature (K)	298	303	308	313	318
1,1-cyclopropane dicarboxylic acid	7.04×10^{-4}	1.31×10^{-3}	2.41×10^{-3}	6.65×10^{-3}	1.74×10^{-2}
1,1-cyclobutane dicarboxylic acid	1.09×10^{-4}	2.05×10^{-4}	3.55×10^{-4}	5.67×10^{-4}	9.45×10^{-4}
1,2-cyclopentane dicaboxylic acid	5.13×10^{-5}	8.26×10^{-5}	1.02×10^{-4}	1.66×10^{-4}	2.93×10^{-4}
1,3-cyclohexane dicarboxylic acid	1.21×10^{-4}	1.83×10^{-4}	2.74×10^{-4}	4.19×10^{-4}	6.66×10^{-4}
cis-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}

Table 3. Literature solid state vapour pressures (P_{298}) and calculated ΔH_{sub}, ΔS_{sub} (where available) for straight chain, branched and cyclic diacids.

Structure	Name	$P_{298\ solid}$ (Pa)	ΔH_{sub} ($kJ\,mol^{-1}$)	ΔS_{sub} ($J\,mol^{-1}\,K^{-1}$)
	*cis*-pinonic acid[a]	7.00×10^{-5}	–	–
	trans-norpinic acid[a]	1.41×10^{-4}	42	–
	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[f]	1.60×10^{-4}	–	–
	3-methyl adipic acid[e]	1.30×10^{-4}	215	–

[a] Bilde and Pandis (2001); [b] Booth et al. (2009); [c] Booth et al. (2010); [d] Bilde et al. (2003); [e] Mønster et al. (2004); [f] Riberio da Silva et al. (2001); extrapolated to 298 K.

Table 4. Sub-cooled liquid vapour pressures, melting points, enthalpies and entropies of fusion measured in this work. Estimated maximum error on $P_{298\ \text{sub-cooled}}$ ±75%.

Name	P_{298} sub-cooled liquid (Pa)	T_m (K)	ΔH_{fus} (kJ mol^{-1})	ΔS_{fus} (J mol^{-1} K^{-1})
1,1-cyclopropane dicarboxylic acid	3.10×10^{-3}	413.0	17.4	42.1
1,1-cyclobutane dicarboxylic acid	6.47×10^{-3}	433.2	16.8	38.7
1,2-cyclopentane diacarboyxlic acid	3.47×10^{-4}	428.6	19.1	44.5
1,3-cyclohexane dicarboxylic acid	4.60×10^{-4}	439.0	12.9	29.4
cis-pinonic acid	7.78×10^{-4}	377.8	23.8	63.0
levoglucosan	1.35×10^{-4}	385.7	13.2	34.2

Table 5. Sub-cooled liquid vapour pressures derived from literature $P_{298\ \mathrm{solid}}$, ΔH_{fus} and T_m.

Name	P_{298} sub-cooled liquid (Pa)	T_m (K)	ΔH_{fus} (kJ mol^{-1})	ΔS_{fus} (J mol^{-1} K^{-1})
glutaric[a]	1.96×10^{-3}	369.0	22.0	59.7
adpic[a]	2.14×10^{-4}	423.0	35.9	84.8
pimelic[b]	2.63×10^{-4}	368.2	23.7	64.3
suberic[b]	2.23×10^{-5}	413.2	30.7	74.3
azleaic[b]	5.09×10^{-5}	372.4	29.7	79.8
2-methyl succinic[a]	5.58×10^{-4}	383.0	10.0	26.1
2-methyl glutaric[a]	9.63×10^{-4}	349.0	30.3	86.7
3-methyl glutaric[a]	9.19×10^{-4}	356.0	27.4	76.8

(1) [a]Booth et al. (2010), (2) [b]Bilde et al. (2003) with ΔH_{fus} and T_m from Roux et al. (2005).

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Table 6. Estimated boiling points for cyclic, straight chain and branched diacids using the Nannoolal et al. (2004) and Stein and Brown (1994) methods.

	Nannoolal T_b	Stein and Brown T_b
1,1-cyclopropane dicarboxylic acid	558.4	563.6
1,1-cyclobutane dicarboxylic acid	573.2	579.7
1,2-cyclopentane dicarboxylic acid	595.5	597.9
1,3-cyclohexane dicarboxylic acid	609.6	611.6
cis-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
azealic acid	627.4	621.6
2-methyl succinic acid	563.6	559.8
2-methyl glutaric acid	578.1	574.8
3-methyl glutaric acid	578.1	574.8

Table 7. Estimated sub-cooled liquid vapour pressures.

	KEMS $P_{298\ \mathrm{liquid}}$ (Pa)	Moller/ Nannoolal $P_{298\ \mathrm{liquid}}$ (Pa)	Nannoolal/ Nannoolal $P_{298\ \mathrm{liquid}}$ (Pa)	Myrdal and Yalkowsky/ Stein and Brown $P_{298\ \mathrm{liquid}}$ (Pa)
1,1-cyclopropane dicarboxylic acid	3.1×10^{-3}	5.5×10^{-3}	4.5×10^{-2}	1.2×10^{-1}
1,1-cyclobutane dicarboxylic acid	6.5×10^{-3}	2.5×10^{-3}	1.4×10^{-2}	5.3×10^{-2}
1,2-cyclopentane dicarboxylic acid	3.5×10^{-4}	4.9×10^{-4}	2.8×10^{-3}	2.1×10^{-2}
1,3-cyclohexane dicarboxylic acid	4.6×10^{-4}	1.7×10^{-4}	7.5×10^{-4}	1.1×10^{-2}
cis-pinonic acid	7.8×10^{-4}	9.7×10^{-3}	6.1×10^{-2}	1.7×10^{-1}
levoglucosan	1.4×10^{-4}	1.0	4.1×10^{-3}	3.2×10^{-2}
glutaric acid	2.0×10^{-3}	1.3×10^{-3}	1.3×10^{-2}	6.5×10^{-2}
adipic acid	2.1×10^{-4}	5.2×10^{-4}	3.7×10^{-3}	2.9×10^{-2}
pimelic acid	2.6×10^{-4}	1.8×10^{-4}	1.0×10^{-3}	1.3×10^{-2}
suberic acid	2.2×10^{-5}	5.9×10^{-5}	3.0×10^{-4}	5.8×10^{-3}
azealic acid	5.1×10^{-5}	1.7×10^{-5}	8.5×10^{-5}	2.7×10^{-3}
2-methyl succinic acid	5.6×10^{-4}	3.4×10^{-3}	2.9×10^{-2}	1.3×10^{-1}
2-methyl glutaric acid	9.6×10^{-4}	1.3×10^{-3}	8.2×10^{-3}	5.4×10^{-2}
3-methyl glutaric acid	9.2×10^{-4}	1.3×10^{-3}	8.2×10^{-3}	5.4×10^{-2}

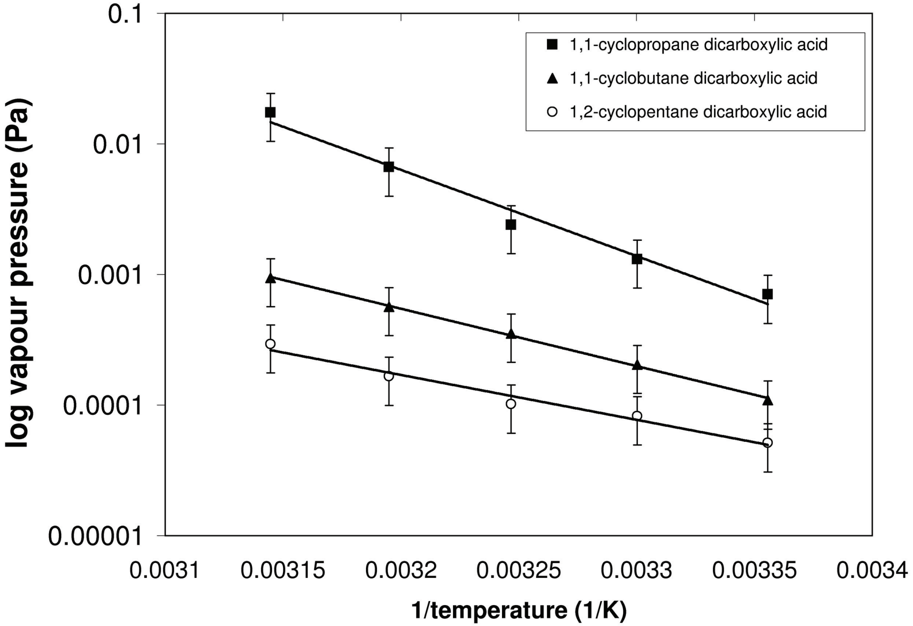

Fig. 1. Log vapour pressure (Pa) vs. 1/Temperature (1/K) for the data in Table 2.

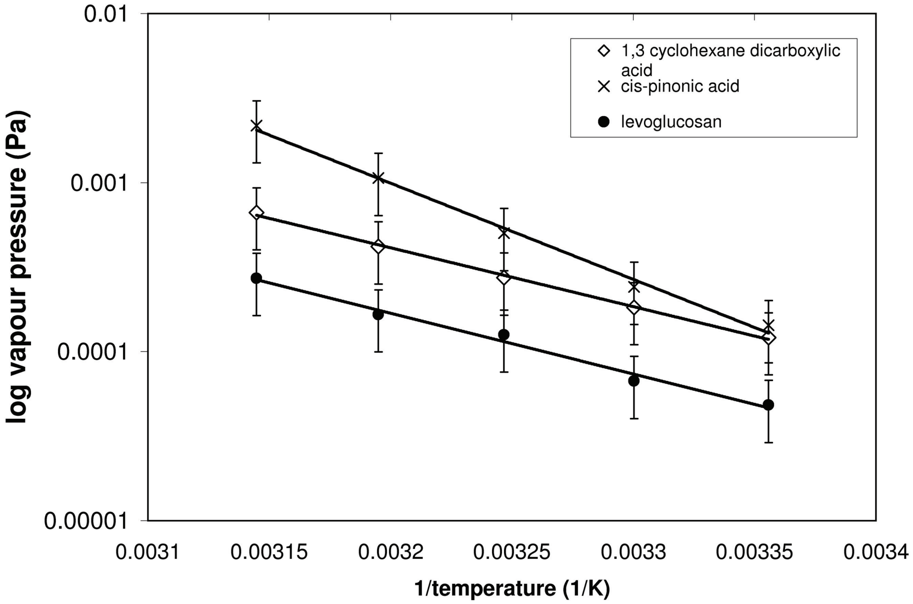

Fig. 2. Log vapour pressure (Pa) vs. 1/Temperature (1/K) for the data in Table 2.

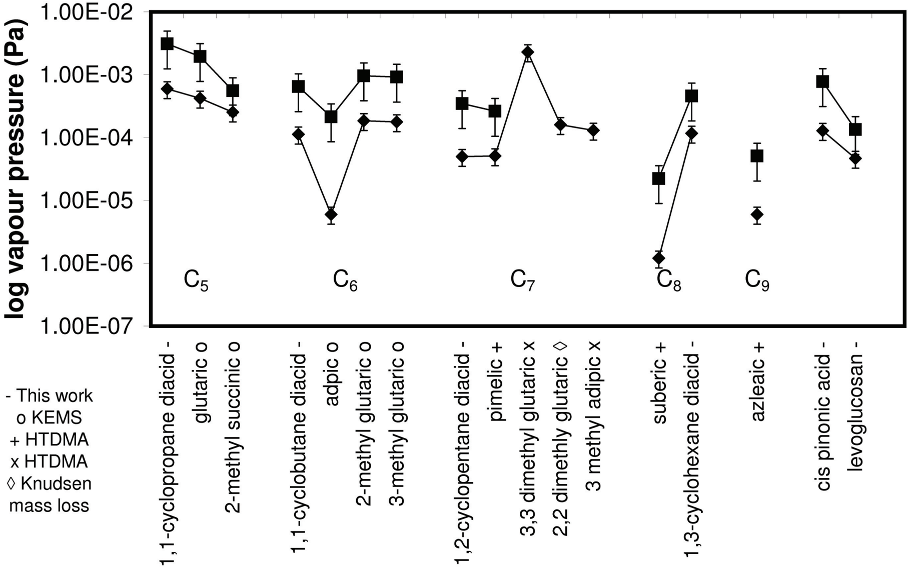

Fig. 3. Solid state (♦) and sub-cooled liquid (■) P_{298} (Pa). The estimated maximum error is $P_{298\ \mathrm{solid}}$±40% and $P_{298\ \mathrm{liquid}}$±75%. $^{-}$ This work, $^{\circ}$ Booth et al. (2010) $^{+}$ Bilde et al. (2003) ^{X} Mønster et al. (2004) $^{\diamond}$ Riberio da Silva et al. (2001) extrapolated to 298 K.