Atmos. Chem. Phys. Discuss., 10, C10753–C10756, 2010
www.atmos-chem-phys-discuss.net/10/C10753/2010/
© Author(s) 2010. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Solid state and sub-cooled liquid vapour pressures of cyclic aliphatic dicarboxylic acids" *by* A. M. Booth et al.

Anonymous Referee #2

Received and published: 6 December 2010

Review of "Solid state and sub-cooled liquid vapour pressures of cyclic aliphatic dicarboxylic acids by Booth et al. 2010

This manuscript presents solid state vapour pressures of a series of molecules of atmospheric relevance (cyclic aliphatic dicarboxylic acids levoglucosan) as a function of temperature. The measurements have been done using Knudsen Effusion Mass Spectrometry. Melting points and enthalpies of fusion were measured using Differential Scanning Calorimetry. For comparison, a number of estimation methods were used to calculate vapour pressures.

Prediction of organic aerosol yields and mass loadings is currently limited by lack of thermodynamic data, in particular vapour pressures and enthalpies of fusion. The data provided in this manuscript are therefore timely and relevant. The measurements seem

to be of good quality. The manuscript itself is however not satisfactory and should be improved, in particular the presentation of data, the comparison with literature data and the discussion. See detailed comments below.

Introduction: The paragraph on isoprene emission and the Master chemical Mechanism appears out of context. Some things are repeated many times (For example that cis-pinonic acid is a biogenic oxidation product (page 23019 line 18-19, page 23020 Line 13 and line 25)). It could be mentioned in the introduction why both solid state and sub-cooled liquid vapour pressures are relevant.

Section 2.2: The authors could consider showing the simple phase diagram they refer to in the text. The last paragraph is difficult to follow, I suggest rephrasing it.

Experimental: The KEMS technique relies on calibration using a reference compound. The authors have chosen malonic acid. Since there are deviations in the literature between reported vapour pressures of malonic acid the authors should provide the vapour pressure (vs.temperature) they have used for malonic acid. Page 23024: The last paragraph is unclear – what is meant with "those compounds" (line 13)

Results and discussion: The dH values are almost not discussed at all in the different sections, this should be done. I suggest to merge Table 1 and 3. It would be much clearer for the reader to see the literature data together with the results in the current work. Likewise tables 4 and 5 could be combined. Also, the tables could be organized in the same way as the figures (C5 acids together, C6 diacids together etc).

How was the error of 40% on the solid state vapour pressures and 75 % on the sub-cooled liquid state vapour pressures obtained?

It says that dSfus was measured, but I assume it was calculated from measured values of dHfus and Tm?

Table4: The subcooled liquid vapour pressures were inferred from other measured properties and rely on a correct determination of p(solid). This should be made clear

ACPD

10, C10753–C10756, 2010

from the text/ heading of the table.

4.1.1: It says that the subcooled liquid vapour pressure are free of crystal structure effects and then in the next line the smaller difference in crystal structure effects is inferred , this two statement seems contradictory?

The odd-even effect and crystal stability: a more original reference for example to Thalladi et al.2000 should be given instead of Booth et al. 2010.

Given the large uncertainties (40%) it seems that the straight chain and the branched C5 acids have the same vapour pressures. A similar comment to the comparison of sub-cooled liquid vapour pressures where the uncertainty is 75%.

4.1.2: The subcooled liquid vapour pressures obtained in the current manuscript should be compared with subcooled liquids vapour pressures obtained from EDB and TDMA techniques (at least glutaric and adipic acids are available).

4.1.4: I do not understand the text in this section. It does not explain what the trends are. Also it says that the vapour pressures falls from C3 to C5- but C3 and C4 are not shown in the figures or tables?

The following could be addressed: Why is the vapour pressure of azelaic acid (C9) subcooled higher than the subcooled liquid vapour pressure of suberic acid (C8). Why is C9 not discussed in the text?

It seems that except for C5 the cyclic dicarboxylic acids have the same subcooled liquid vapour pressure within experimental uncertainties. This could be mentioned in the text.

Minor

Line 25 I suggest to insert “experimental”: “There are several experimental methods. . . “

Abstract, l 3: I suggest to rephrase to “Additionally the solid state pressures of the atmospherically . . ..” I suggest to give the temperature range of the measurements.

ACPD

10, C10753–C10756, 2010

CC BY

References

Pope et al. J. Phys. Chem. A 2010, 114, 10156,

Riipinen et al. J. Phys. Chem. A 2007, 111, 12995,

Thalladi, V. R.et al. J. Am. Chem. Soc. 2000, 122, 9227.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 23017, 2010.

ACPD

10, C10753–C10756, 2010