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Interactive comment on “Solid state and sub-cooled liquid vapour pressures of substituted dicarboxylic acids using Knudsen Effusion Mass Spectrometry (KEMS) and Differential Scanning Calorimetry” by A. M. Booth et al.

Anonymous Referee #3

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This manuscript provides solid state vapour pressures at ambient temperature of a series of substituted dicarboxylic acids measured using Knudsen Effusion Mass Spectrometry (KEMS). Some of the vapour pressures have already been reported in the literature using other measurement techniques but some of the vapour pressures (e.g. the aminosubstituted acids) are to my knowledge reported for the first time here. The solid state vapour pressures are converted to subcooled liquid vapour pressures using Prausnitz formula and transition properties (dH_{fus} and dcp) measured using a Differential Scanning Calorimeter. The obtained values are compared to available literature

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data.

Vapour pressures of secondary aerosol components as provided in this work are important for modeling of gas/particle partitioning in the atmosphere. It is important to obtain and compare vapour pressures based on different techniques and to increase the database on vapour pressures. The results provided by Booth et al. are therefore relevant and timely.

The authors also compare the inferred sub-cooled liquid vapour pressures to predicted values using three methods available at the E-AIM website. They demonstrate that the three models give very different predictions of sub-cooled liquid vapour pressures. I find the intercomparison of the models informative. Finally, the authors use mole based partitioning theory to investigate the sensitivity of predicted total organic mass to predicted vapour pressures.

My main concern is related to the conclusion about which models perform the best and to the correct value of predicted secondary organic aerosol mass: The authors conclude quite firmly which model makes best predictions for which compound, but in Figures 3 and 4 the experimental uncertainties are not included. The experimental values from the KEMS method are used as the base case – but what would be predicted for OA formed at the uncertainty limits of the experimental value? Also there is currently some discrepancies between solid state vapour pressures of the dicarboxylic acids obtained from different techniques and one could expect similar discrepancies between the substituted dicarboxylic acids.

I suggest the text is checked throughout – sometimes the sentences do not seem properly finished or it is a bit unclear what is compared to what (see also examples below).

I find that the manuscript merits publication after addressing these issues as well as the comments below.

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General: The units should be given in each equation – it seems that some equations have the vapour pressure in Pa and some in atm.

It would be clearer if the subcooled vapour pressure was labeled for example p_{0L} to distinguish it from the solid state vapour pressure in the Table and figure headings.

I suggest the values of d_{cp} used is provided in Table 4.

Abstract: The temperature range of this work should be provided.

I suggest mentioning in the abstract that the molecules studied are of atmospheric relevance

Text

Page 5718, Line 19: It does not sound correct to say that the organic fraction "arise from partitioning" – it enters the aerosol phase by partitioning?

P. 5719, line 13: I suggest some field studies are referenced here.

Page 5720, Lines 16-18: This sentence seems misplaced here – the authors should consider moving it to the introduction.

Page 5721: The text is not easy to follow. It is not clear exactly what equations are involved in the Nannoolai 2008 method – this section should be improved.

Line 15: " a,b,c are adjustable parameters from a linear regression" it should be explained what this linear regression is – of what to which data?

In equation 3 the units should be given, also I do not think it is necessary to introduce the parameter Tr_b it makes it easier to compare with equation 6 if the notation T/T_b is kept.

P. 5722, Line 13: "...replaced with the following term" – it should be said in which method – Moller et al?

p. 5723: "ensuring the mole balance between the two phases" this is not clear what is

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meant here Equation 11: I think the index should be “i” and not 1.

P. 5724: I would suggest to write ...provides the “amount of “ of the total condensed OA in mass based units

p. 5724, Line 16: it should be made clear that this was using the same system.

Line 23-24: “... but it is expected that they are minimized by appropriate choice of similar reference and sample compounds...” are there any references supporting this statement?

P. 5726 the first two lines are unclear and should be rewritten

P. 5727: “...” They see an even greater increase in solid state vapour pressure for succinic substitutions”. Compared to whom and compared to which other molecules?

P. 5727: It is not clear how solubility or surface tension effects could explain the differences in the size of the keto and methyl substitution effects? I think this should be explained in more detail. How about the influence of the structure of the solid state?

Frosch et al. points out that the 3-oxoglutaric acid and the oxo-succinic acid may undergo decarboxylation and rearrangement in aqueous solution and thus the vapour pressures reported for these two molecules may thus not be the vapour pressure of the original molecules. The authors should make a note about this, also in Table 3.

Table 5: Zardini et al. 2006 have also reported the sub-cooled liquid vapour pressure of malonic acid (3.2×10^{-4} Pa).

P. 5731 Line 21: I would suggest to write: “... The methods underestimate the “observed” vapour pressure of dicarboxylic acids reported in this work...”.

Line 31: removed “the”.

References Mønster et al. 2004 and Mønster et al. 2006 (Corrigendum) are missing in the reference list

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Suggestions for additional references :

Zardini, A. A.; Krieger, U. K.; Marcolli, C. *Opt. Expr.* 2006, 14, 6951.

Chattopadhyay, S.; Ziemann, P. J. *Aerosol Sci. Technol.* 2005, 39, 1085.

Figures and Tables

Units should be provided in the figure caption.

Figure 2: the solid state vapour pressures appear as filled diamonds even if they should be open according to the Figure caption.

Figure 4: it should be explained in the caption exactly what is shown, what are the boxes - what do the dashed lines show? what are the crosses for estimation methods 5 and 6?

Table 7: It should be explained what J, N and S&B stand for

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