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Atmospheric
Chemistry
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Discussions

Interactive comment on "The vapor pressures and activities of dicarboxylic acids reconsidered: the impact of the physical state of the aerosol" *by* V. Soonsin et al.

Anonymous Referee #2

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The paper describes vapour pressure measurements of the shorter chain dicarboxylic acids from single particle measurements in an electrodynamic balance in solid, supercooled melt and as saturated solutions.

General comments

Although the dicarboxylic acids have received considerable attention, the paper is important in the light of recent interest in glassy aerosols. It will also provide useful data for constraining activity models. However strong statements about the physical state observed in previous measurements are not backed up by the experimental evidence and other reasons are far more likely to be the cause of discrepancies. These must

be changed before it can be accepted for publication and, whilst straightforward to address, constitute the grounds for the important major revisions I have requested. There are also a few additional considerations for determining the vapour pressures which I feel should be considered.

The physical state: The authors state that previous measurements may be compromised by amorphous and polycrystalline material. The work of Bilde, Riberio da Silva, Booth and Cappa all show the odd-even effect (the varying of certain solids state properties, e.g. VP, Tm delH(fus), with carbon chain parity), as this arises from the crystal structure its not clear how they would be anything other than crystalline solids. Also the Riberio da Silva malonic acid measurements cut across the onset temperature of one of the crystalline transition but still show a straight line (ln P vs. 1/T). The acid samples were recrystalised and dried in vacuo at 360K for several hours which would have removed any more volatile amorphous fractions (if they were present). The glutaric acid measurement is above one of the transition temperatures, but those of Bilde, Booth and Riipinen are (far) below it but the measurements still agree. This would suggest that either the polymorphic forms don't affect the vapour pressure, and/or the measurements made were of the entirely crystalline form.

Activity Model: The choice of activity model is an important factor in determining the vapour pressure using evaporation-type measurements. UNIFAC is known to be problematic for certain small molecules so use the authors use UNIFAC-Peng, but the Peng parameters are fitted to electrodynamic balance measurements so it seems somewhat circular as any systematic errors from EDB VP measurements may also affected the activity coefficients determinations. Koponen et al. explored the sensitivity of their evaporation based measurements and found that alternating between UNIFAC Dortmund and Van Laar activity models caused a difference in vapour pressures of two orders of magnitude for malonic acid, a sensitivity which decreases significantly as the chain length gets longer. This would suggest that the sensitivity of oxalic acid measurements to the choice of activity model even greater, and is far more likely to be the cause of most discrepancies between measurements. The authors should do a sensitivity comparison for oxalic and malonic acids with some other activity models, e.g. Van't Hoff, AIOMFAC, UNIFAC-Dortmund.

Solid state: The authors state that the ebd allows unambiguous identification of solids via the monitoring of the angular scattering pattern. What would happen if a solid particle was spherical, could this be distinguished?

Saturated solution: Why do the saturated solution vapour pressures show the odd-even dependence? I would have thought they'd be closer to the supercooled melt VP?

Differences between sub-cooled & solid: Other Workers, e.g. Booth & Koponen & Riipinen use the Prausnitz equation to correct between sub-cooled & solid. It would be interesting to compare the differences measured here with the calculated ones from thermochemical data. I think it will provide a useful check on the validity of using the Prausnitz eqn, and the thermochemical data used.

Kinetics: Water has been shown to bind much more strongly on defect sites of crystals (Laux et al;Davies and Cox). What would the implication be of the observed loss of water from your crystal be? i.e. can there be in effect two loss rates of water, one from a defect site and one from a non defect site? Also, do you need to assume an uptake coefficient or accomodation coefficient.

Minor comments.

Cappa et al., have also measured malonic acid (see ref) P298 solid 2.2x10-4 Pa.

There is a paper recently out that is probably worth comparing with, Pope et al., EDB measurements and optical tweezers.

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References

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