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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Vapor pressures of substituted polycarboxylic acids are much lower than previously reported" *by* A. J. Huisman et al.

Anonymous Referee #1

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Review of Husiman et al 2012

Vapour pressures are of great importance to our understanding of gas-to-particle partitioning and contributions to our understanding of these datasets is to be welcomed. As the paper is directly critical of other work in the field there are several points which must be added to the work to avoid drawing any misleading conclusions.

It is stated that (ln300) that the physical state in bulk vapour pressure measurements may not be fully controlled and they refer to Soonsin (2010). I don't think that statement is valid; Riberio da Silva (1999;2001) re-crystallise their samples to ensure the measurement state is well defined, Booth (2009;2010) performed DSC measurements of samples to verify they were in a solid crystalline state. Additionally the fact that an odd-even effect for the vapour pressure also confirms that bulk techniques measure

the crystalline solid phase. This should be added.

The authors mention that measurements generally agree where the sample state is positively identified (ln27). It should be mentioned that the level of agreement between bulk sample measurements is as good as that between single particle measurements (e.g. Soonsin (2010) Zardini (2006) and Pope(2010)). It should be mentioned that good agreement between bulk measurements are shown for; Riberio da Silva (1999;2001), Davies and Thomas (1960), Booth(2009;2010) and Tao and McMurry (1989) for diacids and branched diacids in Oja and Suuberg (1999) and Booth (2011) for levoglucosan. Colomina (1978) and Booth (2012) for anisic acid.

The paper makes comparisions with the methyl substituted diacid measurements of Monster (2004) and assigns these as liquid phase measurements. I believe these are solid phase measurements due to their result of a large leap in vp when adding an methyl group to an even carbon numbered acid and a small increase when adding to an odd acid, a result which arises from the crystal structre of diacids (this is discussed bottom of p 1462 of monster et al). Also, a corrigendum to this paper (Volume 37, Issue 9, September 2006, Pages 1164) states the methyl-malonic acid vp is 9.1e-4 Pa. This should be changed

Regarding the EDB measurements; Could the use of diethylene glycol as an anti-crystallisation agent (ln 173) have any effect on the vp measurement?

If the walls of the trap got contaminated with the evaporating species, would this cause a lowering of vapour pressure measured? This may explain these EDB results and those previous work (Soonsin 2011) such as that of oxalic acid where the EDB results are several orders of magnitude lower than the collective results of de Witt (1983), de Kruif (1975), Booth(2009), Bradley and Cotson (1953) and Noyes and Wobbe (1923). Or succinic acid where the solid measurements agree with Davis and Thomas (1960), Riberio da Silva (2001), Bilde (2003), Cappa (2007)and Salo (2010) but disagree after they leave a particle in the trap for a day and a half. This should be discussed in the

text.

There has been a lot of recent interest in glassy state aerosols. Could this cause any effects in the strongly saturated/subcooled samples measured in the trap?

The agreement (or lack thereof) between single particle and bulk measurements seems to range from very good to 5 orders of magnitude for the worst case. This is however not a unique situation for the ultra-low vapour pressures we are trying to measure. For example, reported P298 for the C7 to C12 diacids typically vary by 2 orders of magnitude and can reach more than 4 orders of magnitude for some measurements (e.g Salo (2010) and Cappa (2007) for Azelaic acid). I think when a discrepancy of this size occurs, more independent measurements are needed before we can side with certain values.

The authors mention that increased functionalisation of the carbon backbone is a counter intuitive result (ln41).We might naively think this is the case but there is a wealth of evidence and a suitable reason to suppose this is the case. The work of Chattopadhyah and Zieman (2005) suggested intra-molecular bonding as a physical mechanism to explain these results, they observed this phenomena for oxo-diacids as did Froesch (2010). It's quite hard to find a wide range aliphatic compounds where we can just add extra groups on in any position to probe this behaviour, the only relevant examples I can think of are butane-2-ol and DL-butane-2,3-diol (P298 2.4 and 32 Pa respectively (TRC Thermodynamic tables)) and b-keto esters and 1,3-dicarbonyl compounds (Nannoolal 2008). The idea of extra groups raising vapour pressure has been seen for a variety of aromatic compounds; e.g. Benzophenone, oxybenzophenone and dioxybenzophenone (Merck). The idea that this comes from intramolecular bonding is backed up by results showing an increased volatility when polar groups are adjacent e.g. OH groups adjacent to acid groups in hydroxbenzoic acids(Perlovich 2006), OH groups next to OH groups (Verevkin and Kozolva 2008) in catechols. They also state that and that Compernolle (2011) was unable to rationalise these measurements (ln59). Nannoolal (2008) acknowledges these effects but has to exclude them from his

method as it was too difficult to incorporate. To my knowledge Compernolle (2011) is the first attempt to include this phenomena. The dangers of overfitting to a small dataset are correctly identified by the authors, but in this case it could be avoided by using some of the other suggested examples of intramolecular bonding. It must be emphasised in the text that the idea of intramolecular bonding is not dependant on a single set of measurements.

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