Atmos. Chem. Phys. Discuss., 13, C2904–C2909, 2013
www.atmos-chem-phys-discuss.net/13/C2904/2013/

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.

A. J. Huisman et al.

huismana@union.edu

Received and published: 30 May 2013

Comments and Responses

Dr. Compernolle: I consider these new data very valuable, as it will allow improvement of partitioning models. Given the results of this work, we have now added the option to turn on or off the empirical correction term of the web-application of our EVAPORATION vapour pressure model, available at http://tropo.aeronomie.be/models/evaporation.htm.

Author response: The authors thank Dr. Compernolle for his interest in and careful reading of our manuscript. We will address each of his comments below.

Dr. Compernolle: *Comparison with other models and other data*

In this work, the experimental results are compared only with the EVAPORATION model. I suggest to compare also with other models, e.g. the model of Nannoolal et al. (2008) available at http://www.aim.env.uea.ac.uk/aim/ddbst/pcalc_main.php. de Wit et al. (1983) have obtained a solid-state vapor pressure for tartaric acid, so I think it is appropriate to compare also with this value. Chattopadhyay et al. (2005) and Frosch et al. (2010) have also reported data on diacids with an extra functional group. Although citric acid and tartaric acid were not among them, it might be worthwile to add the reference, and to discuss if the data are higher/lower than expected, compared to diacids without this functional group.

Author response: We thank Dr. Compernolle for his suggestions and for bringing the de Wit et al. (1983) study to our attention. We have included the data of de Wit et al. (1983) for sublimation meso-tartaric acid for comparison to our measurements of DL-tartaric acid. We have also updated Table 4 to include comparisons to the model of Nannoolal et at. (2008) and of Moller et al. (2008). We have also referenced the measurements of Chattopadhyay et al. (2005) as part of an expanded discussion of the impact of additional oxygen-bearing functional groups on vapor pressure (see reply to Referee #1).

Change to manuscript: Data for de Wit et al. (1983) solid state measurements of meso-tartaric acid will be included in Tab. 4, Fig. 2, and will be discussed in Sect. 4.7. Data from the Nannoolal et al. (2008) model and of Moller et al. (2008) will also be included in Tab. 4 and Fig. 2.

Dr. Compernolle: *Correlation log*$_{10}(p^0)$ - ΔH_v

The authors point out that in their case, and opposed to the results of Booth et al. (2010), more functionalised diacids have a lower vapor pressure compared to less functionalized ones, which is more in line with chemical intuition. One could also investigate the correlation between $\log_{10}(p^0)$ and enthalpy of vaporisation (Epstein, 2010), as done in Fig. 2 of Compernolle et al. (2011). Adding the 3 $\log_{10}(p^0)$ ΔH_v points of the present author's data, for 2-methyl malonic, 2-methyl glutaric and 2-hydroxy mal- onic acid, one can see that the points are somewhat below the correlation, but closer than the data of e.g. Booth et al. (2010) or Chattopadhyay et al (2005). As the correlation is empirical, this is no proof in itself for the correctness of the data, but it is an extra element in the discussion, which the authors could use.

Author response: Based on these data, we have updated our temperature extrapolations of vapor pressure to use a value of $\Delta H^{\ominus}_{\mathrm{vap}}$ which ranges from 75 kJ mol^{-1} to 250 kJ mol^{-1} (was 50 to 150 kJ mol^{-1}. As the plot demonstrates an empirical relationship (as noted by Dr. Compernolle) and we contribute only few points to the overall trend, we have chosen not to include it as an element of our discussion.

Change to manuscript: The extrapolations for CA and TA will be performed using the range $\Delta H^{\ominus}_{\mathrm{vap}}$ = 75 − 250 kJ mol^{-1} to be more consistent with the empirical relationship demonstrated in Fig. 2 of Compernolle et al. (2011). The text of Sect. 4.4 will be updated to reflect the origin of these values in Fig. 2 of Compernolle et al. (2011).

Dr. Compernolle: Title. This statement is quite strong, as it implies that previous data where simply incorrect. While I agree that intuitively the current data make more sense (more functionalized species have a lower vapour pressure), I feel that more data is needed, as well as a good understanding of why the previous data would be incorrect, before this statement can be made.

Author response: We agree that this is a strong statement. However, we believe the title is in agreement with our experiments and analysis. To be clear, we are not claiming that our measurements provide the definitive values for these vapor pressures. Rather, we claim that previous measurements are too high by several orders of magnitude, and that the vapor pressures of substituted polyacids is an area that needs more work to provide the best possible inputs to models.

Dr. Compernolle: Abstract, line 11-12: 'empirical correction terms in vapor pressure estimation models'. The plural suggests that such correction terms are introduced for multiple models, not only EVAPORATION. If so, which are these other models? Otherwise, use 'empirical correction term in a recent vapor pressure estimation model'.

Author response: We were referring only to the EVAPORATION model and have adopted the phrase suggested by Dr. Compernolle.

Change to manuscript: The abstract now uses the singular and includes the phrase suggested by Dr. Compernolle (line 10).

Dr. Compernolle: p. 1136, line 16 '...are not able to rationalize these effects.' This is true, and we also noted that there could be problems with the measurements, and that new measurements, using the methodology of Soonsin et al. (2010) could resolve this issue. (see e.g. our section 2.5.3, and section 6) So I would suggest adding a sentence like: 'They noted that measurements using the methodology of Soonsin et al. (2010) were needed for these compounds.'

Author response: The authors hope that our brevity on this topic was not misinterpreted. We will add the statement suggested by Dr. Compernolle.

Change to manuscript: The statement suggested by Dr. Compernolle will be included in the revised manuscript's introduction, on line 21 of p. 1136 of the discussion paper.

Dr. Compernolle: p. 1144, line 5. The vapour pressure of 2-methyl malonic acid is presented as 1.1x10^{-4} Pa, yet in Table 4 I read 1.1x10^{-3} Pa. Given the context, I assume that the 1.1x10^{-4} Pa value is a typo.

Authors' response: This is indeed a typo and will be corrected in the final manuscript. The correct value of (1.1±0.3)x10^{-3} Pa will be reported in the revised manuscript.

Change to manuscript: Changed the reported vapor pressure (p. 1144, line 5 of discussion paper) to the correct value of (1.1±0.3)x10^{-3} Pa. The correct value was used in all other locations, including tables and figures. This error does not impact the conclusions of this study, and significantly improves the agreement of this measurement with the measurement of Monster et al. (2004). This is improved agreement is reflected in Sect. 4.1.

References

- Chattopadhyay, S. Ziemann, P. J. Vapor Pressures of Substituted and Unsubstituted Monocarboxylic and Dicarboxylic Acids Measured Using an Improved Thermal Desorption Particle Beam Mass Spectrometry Method, Aerosol Sci. Technol., 39, 1085-1100, 2005
- de Wit, H. G. M.; Bouwstra, J. A.; Blok, J. G. de Kruif, C. G. Vapor pressures and lattice energies of oxalic acid, mesotartaric acid, phloroglucinol, myoinositol, and their hydrates J. Chem. Phys., AIP, 1983, 78, 1470-1475
- Epstein, S. A.; Riipinen, I. Donahue, N. M. A Semiempirical Correlation between En- thalpy of Vaporization and Saturation Concentration for Organic Aerosol, Environ. Sci. Technol., 44, 743-748, 2010

- Frosch, M.; Zardini, A. A.; Platt, S. M.; Müller, L.; Reinnig, M.-C.; Hoffmann, T. Bilde, M. Thermodynamic properties and cloud droplet activation of a series of oxo-acids Atmos. Chem. Phys., 10, 5873-5890, 2010
- Moller, B., Rarey, J., and Ramjugernath, D.: Estimation of the vapour pressure of non-electrolyte organic compounds via group contributions and group interactions, J. Mol. Liq., 143, 52–63, 2008.
- Nannoolal, Y., Rarey, J., and Ramjugernath, D.: Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group contributions and group interactions, Fluid Phase Equilibr., 269, 117133, 2008.
- Soonsin, V., Zardini, A. A., Marcolli, C., Zuend, A., and Krieger, U. K.: The vapor pres- sures and activities of dicarboxylic acids reconsidered: the impact of the physical state of the aerosol, Atmos. Chem. Phys., 10, 11753–11767, doi:10.5194/acp-10-11753-2010, 2010.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 1133, 2013.