Atmos. Chem. Phys. Discuss., 13, C2929–C2937, 2013
www.atmos-chem-phys-discuss.net/13/C2929/2013/

Atmospheric Chemistry and Physics
Discussions
Open Access

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

Referee #2: This manuscript describes measurements of subcooled liquid vapor pressure of sub- stituted polycarboxylic acids by probing the evaporation of levitated droplets of super- saturated aqueous solutions of these compounds. The manuscript is well-written, clear and contains interesting results. However, I think there are few relatively minor issues that need to be addressed before the manuscript can be considered for publication in ACP:

Authors' response: The authors thank Referee #2 for their positive review and will address their suggestions and queries below. Changes and clarifications to the revised manuscript will be noted at each step.

Referee #2: Although the structures of the investigated compounds are given in multiple places elsewhere, I think giving them in a figure here too would increase the readability of the manuscript.

Authors' response: We agree and will include the structures in as part of Fig. 2 in the updated manuscript for clarity.

Manuscript revision: Figure 2 will be updated to include the structures of the molecules.

Referee #2: I have one issue related to the terminology that I would like to raise: Now the authors refer to saturation or equilibrium vapor pressures as just "vapor pressures". I find this terminology confusing, as the term "vapor pressure" could be mixed up with a partial (potentially non-equilibrium) vapor pressure of the species. I therefore would recommend the authors to use either equilibrium vapor pressure or saturation vapor pressure when they refer to thermodynamic equilibrium.

Authors' response: We thank the Referee for pointing out this area of potential confusion. We note that in common language use, the term "vapor pressure" is sometimes incorrectly used to denote the total pressure over a mixture or a non-equilibrium partial pressure. However, in thermodynamics the term "vapor pressure" is unambiguously defined (e.g., Dykyj et al, 2000). The term "saturation vapor pressure" is defined in the IUPAC gold book as "The pressure exerted by a pure substance (at a given temperature) in a system containing only the vapour and condensed phase (liquid or solid) of the substance." (IUPAC, 2006). Saturation vapor pressure is therefore typically used only in the context of pure, single component systems. The "vapor pressure" of a component is identical to (i) the saturation vapor pressure for a single component system or (ii) the partial pressure of a component in equilibrium with a mixed condensed phase. Hence, "vapor pressure" is only a correct term for a partial pressure (or total pressure in case of single component systems) in the presence of a vapor-liquid (VLE) or vapor-solid (VSE) equilibrium. The terms "vapor pressure" and "equilibrium vapor pressure" have identical meaning, the latter just emphasizes the existence of thermodynamic equilibrium.

Manuscript revision: On page 1134, line 24, we add the following statement: Note that throughout this article, the term 'vapor pressure' is used as defined by chemical thermodynamics to denote the partial pressure of a compound in equilibrium with a liquid or solid phase, which is sometimes emphasized by the equivalent term 'equilibrium vapor pressure'.

Referee #2: There is a continuous flow of N2 in the chamber. It is well known that a flow inluences the evaporation/condensational mass fluxes (see e.g. Smolik et al., Journal of Aerosol Science 32, 739-748, 2001). Have the authors thought about this and how large is the effect expected to be in their setup?

Authors' response: We considered the effect before, but did not discuss the result in the text. It turns out that under our experimental conditions the effect is negligible. We will extend the description in the revised manuscript as indicated below. A more detailed argumentation following Zhang and Davis (1987) is given here:

Eq. (1) may be rewritten as:

$$\frac{dr^2}{dt} = -2D_v p \frac{(xM_{org} + (1-x)M_W)}{x\rho RT} a \tag{1}$$

This equation is for a stagnant gas for which the Sherwood number, $Sh = 2$. For convective mass transfer the evaporation rate becomes:

$$\frac{dr^2}{dt} = -Sh \cdot D_v p \frac{(xM_{org} + (1-x)M_W)}{x\rho RT} b \tag{2}$$

with

$$Sh = 2 + \left\{ \frac{1}{(0.5Pe + 0.3026Pe^2)^3} + \frac{1}{1.008Pe} \right\}^{-1/3} .c \tag{3}$$

Here the Péclet number, Pe, is $Pe = 2r \cdot v_{gas}/D_v$, v_{gas} being the velocity of the gas in the flow. Equation eq:Sh for Sh was proposed by Zhang and Davis (1987) based on experimental data obtained for particles of similar size as ours, levitated in an EDB of comparable design. In our setup the flow (20-35 cm^3/s) is expanding from a 1/4" tubing to a cylindrical volume with a cross section of 12 cm^2, the levitated particle being balanced 15 mm below the end of the tubing. This leads to $Pe \lesssim 5 \cdot 10^{-4}$, hence $Sh/2 < 10^{-3}$, i.e. the effect on vapor pressure is negligible.

Manuscript revision:
We will add the following clarifying statements after line 9 on page 1138:

Strictly, eq. (1) is valid for stagnant conditions. However, the geometry of our EDB together with the flows used keeps the enhancement in evaporation rate due to the gas flow (Zhang and Davis, 1987) below 0.1%. On the other hand, the flow needs to be sufficiently large to avoid any significant contamination of the gas phase by the organic vapor evaporating from the particle. The partial pressure of the organic substance far from the particle, p_∞, has to be only a small fraction of the vapor pressure p. Our flows are sufficient to keep the ratio p_∞/p below 1%, cf. (Zhang and Davis, 1987).

Referee #2: The authors report very low saturation vapor pressures for the investigated compounds, which naturally means very slow evaporation rates / changes in the particle size. Although the authors are using relatively large samples and purified compounds, I was wondering have the authors thought about the maximum possible contamination (e.g. through gas phase ammonia or other kind of impurity) in their system and whether that could have any detectable effect on the results?

Authors' response: There are two potential sources for contaminations: first a contamination may be introduced during the initial injection or while preparing the solution used in the inkjet type single particle generator, the second through uptake from a contaminated gas phase during the evaporation phase. We are convinced that the first problem does not occur to a significant degree in our setup since a significant amount of a water soluble contamination would also shift the deliquescence relative humidity (DRH) and water activity of the solution droplet. However, we never observed such shifts when testing our setup versus water activity data and DRH of reference materials. Also we tested the stability of the single particle generator against solubilization of the inkjet-cartridge surfaces (Knopf, 2003). If a non-soluble contamination is present in a levitated droplet it is easily detected, even if extremely small, by measuring lightscattering intensity fluctuations (Krieger and Braun, 2001). In our experiments we are sure that no insoluble contaminations of any significance were present. The influence of the second type of contamination is more difficult to quantify. The nitrogen gas flow is generated from liquid nitrogen, hence the partial pressure of all volatile gases should be extremely low, the water bath to humidify the gas stream is not pure water, but a 2.5 wt-% aqueous solution of sulfuric acid, which should trap ammonia if present. The whole gas phase and the levitated particle is concealed in a vacuum cell at reduced pressure (600 torr). However, there could

be residual gases diffusing through the Teflon tubing or O-ring sealing into the cell which are then continuously taken up by the particle, distorting the evaporation rate. Two arguments should resolve all doubts that this might be occurring: We were able to measure water activity of concentrated sulfuric acid solution over the course of days down to temperatures of 160 K (Krieger et al., 2000). If ammonia had been present in significant amounts in the gasphase, it would have been taken up and form a solid ammonium sulfate inclusion which is easily detected, see above. The other argument that the experiments are not affected by contamination are for example the measurements of 2-Methylglutaric acid as shown in Fig. 5 (see also the examples in Soonsin et al., 2010). Our data are consistent with those of other sources, but even more important, there is consistency of the data over a large vapor pressure range, i.e. from $5 \cdot 10^{-4}$ Pa to $1 \cdot 10^{-6}$ Pa. A gas phase contamination would influence lower pressures (with lower evaporation rates) more noticeably than data taken at higher pressures. There is no indication for this behavior in Fig. 5.

Referee #2: In the supplementary material the authors investigate the possible effect of gas phase dimerization of the organic molecules. I would imagine it would be relatively straightforward to calculate the kinetic minimum time scale for dimerization (i.e. the collision timescale) for the given organic concentrations, and compare that to the timescale of diffusion. I would think that this way the authors' argumentation about the dimerization would be even more convincing.

Authors' response: We performed a calculation using the dimerization constants of Tsonopoulos and Prausnitz (1970) for mono-carboxylic acids. The dimerization constant for most mono-acids is approximately the same (cf. Eq. 7 of Tsonopoulos and Prausnitz, 1970); our calculation was performed using Eq. (7) of Tsonopoulos and Prausnitz (1970) and solving the quadratic equation as described in, e.g., Zuend et al. (2011). Even at the highest vapor pressures we measured of around 1×10^{-3} Pa, less

p_{acid} (Pa)	Dimerization ratio (-)
1.00	9.19×10^{-3}
1.00×10^{-2}	9.36×10^{-5}
1.00×10^{-4}	9.36×10^{-7}
1.00×10^{-6}	1.28×10^{-8}

Table 1. Calculated fraction of carboxylic acid dimerized at various partial pressures. The dimerization ratio is defined as the pressure of dimer divided by the pressure of dimer and monomer.

than 1 molecule in 10^5 is dimerized. The dimerization ratios at a few pressures is given at right to illustrate that even at vapor pressures much higher than our measurements, dimerization is not predicted to play a significant role in our measurements of vapor pressure.

Manuscript revision: We have modified and expanded the statement on discussion paper p. 1155, beginning at line 24, to reflect the results of this calculation: Assuming that di- and mono-carboxylic acids have similar dimerization properties (the dissociation constants for monocarboxylic acids in the gas phase are large, e.g. formic acid, $3.6 \times 10^2\, Pa$ at 296 K, Vander Auwera et. al. 2007), that the effect of chain length on enthalpy of dimerization is minimal (cf. Eq. (7) of Tsonopoulos and Prausnitz 1970) and solving the quadratic equation as described in e.g., Zuend et al. (2011), the fraction of molecules dimerized would be less than 1 per 1×10^8 for a sample with $p{,}^{L}(T^{\ominus}) \sim 1 \times 10^{-6}$ Pa . Even at the highest vapor pressures observed in this study of $\sim1\times10^{-3}$, less than 1 molecule in 1×10^5 is predicted to be dimerized. Thus dimerization is unlikely to play a major role in these experiments.

References:

- Dykyj, J., Svoboda, J., Wilhoit, R. C., Frenkel, M., and Hall, K. R.: Organic Compounds, C1 to C57. Part 1, in: Landolt-Börnstein - Group IV Physical Chemistry Numerical Data and Functional Relationships in Science and Technology, edited by: Hall, K. R., SpringerMaterials - The Landolt-Börnstein Database, 14-110, 2000.

- IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: http://goldbook.iupac.org (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. doi:10.1351/goldbook.

- Knopf, D. A.: Thermodynamic Properties and Nucleation Processes of Upper Tropospheric and Lower Stratospheric Aerosol Particles, Diss. ETH No. 15103, 2003.

- Krieger, U. K., Colbgerg, C. A, , Weers, U., Koop, T., and Peter, T.: Supercooling of single H2S04/H20 aerosols to 158 K: No evidence for the occurrence of the octahydrate, *Geophys. Res. Lett.* **27**, 2097-2100, 2000.

- Krieger, U. K. and Braun, C.: Light-scattering intensity fluctuations in single aerosol particles during deliquescence, *J. Quantitat. Spectr. Rad. Trans.* **70**, 545-554, 2001.

- Tsonopoulos, C. and Prausnitz, J.: Fugacity coefficients in vapor-phase mixtures of water and carboxylic acids, Chem. Eng. J., 1, 273–278, DOI: 10.1016/0300-9467(70)85014-6, 1970.

- Vander Auwera, J., Didriche, K., Perrin, A., and Keller, F.: Absolute line intensities for formic acid and dissociation constant of the dimer, J Chem Phys, 126, 124311, DOI:10.1063/1.2712439, 2007.
- Zhang, S. H. and Davis, E. J.: Mass transfer from a single micro-droplet to a gas flowing at low Reynolds number, *Chem. Eng. Comm.* **50**, 51-67, 1987.
- Zuend, A., Marcolli, C., Booth, A. M., Lienhard, D. M., Soonsin, V., Krieger, U. K., Topping, D. O., McFiggans, G., Peter, T., and Seinfeld, J. H.: New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups, Atmos. Chem. Phys., 11, 9155–9206, DOI: 10.5194/acp-11-9155-2011, 2011.

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