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Atmospheric
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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.

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Comments to A. Khlystov

The authors would like to sincerely thank A. Khlystov for his constructive comments. We have addressed his concerns point-by-point as shown in the following. Our comments are given in italic.

I would like to second the comment by Reviewer 2 that "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." We have demonstrated that solvent, if any is present in the particles, does not affect the vapor pressure and enthalpy of vaporization of adipic acid and azelaic acid aerosols (Saleh et al., 2010). In our study, the aerosols produced by homogeneous nucleation from a dry gas and by spray-drying aqueous solutions showed the same thermodynamic properties. Therefore, I find the author's statements about the solvent effects quite objectionable. The authors should either present the evidence of the solvent effect or remove such statements from the manuscript. With respect to the presence of amorphous material, it would be interesting to know whether the optical scattering data could distinguish crystalline and amorphous forms and/or differences in the amount of crystal structure defects. Such data would make the argument for the effects of solid structure on OA vapor pressure much more compelling. In our study, SEM measurements of the particles produced with or without solvent did not reveal any significant differences in particle morphology or presence of amorphous material. It is possible that significantly larger sizes of particles used in the EDB experiments favor formation of amorphous material and/or crystal structure defects. However, since the ambient OA is found mostly in sub-micrometer aerosol, could the authors comment on the relevance of such effects of particle structure on vapor pressure (if any) to ambient particles?

Unfortunately we have not measured the longer chain dicarboxylic acids that Saleh et al., (2010) measured. Thus a direct comparison with our data is not possible. However, since our data are approximately consistent with the Cappa et al., (2007) data we suspect that the same discrepancy as the one between the Saleh et al. data and the Cappa et al. data would arise if we had measured the longer chain acids. The explanation offered by Dr. Khlystov that our particles are significantly larger than atmospheric ones and may favor crystal wit high defect density material upon efflorescence as well as liquid inclusions cannot be dismissed easily. However, our supercooled melt data as well as the ones for the saturated solutions are not influenced by the size at *all and since the saturated solution data agree within error with the ones of the solids, we are confident that our data are of atmospheric relevance. Unfortunately the optical scattering data do not provide any direct information on amorphous fractions or liquid inclusions. The only way to retrieve this information is the evaporation rate measurements as explained in the text discussing Fig. 9. This yields an initial volume fraction of liquid (just after efflorescence) of about 34%. Again we agree with Dr. Khlystov that this fraction could be considerably smaller in particles of atmospheric sizes. However, to stress this again, it does not influence our derived vapor pressures.*

Further, if I am not mistaken, there is an error in Equation 1: x should be in the denominator and the right hand side should be negative. The authors should present the derivation of this equation or provide a reference containing one. It should be also noted that x is not the molar fraction of solute in a solution in equilibrium with the gas phase at the given RH. Rather, it is a steady-state molar fraction, which for the given mixture is very close to the equilibrium molar fraction. The authors should explain this to the reader.

We thank Dr. Khlystov and Dr. Bilde for pointing out this error to us. Unfortunately this error was not just a typing error but the equation in its wrong form was used for the evaluation of the evaporation rates of the aqueous succinic and aqueous glutaric acid. We have carefully reevaluated all data to avoid any further errors and updated all figures and tables accordingly. While this error influences the vapor pressures significantly it does not change any of the conclusions drawn. The corrected vapor pressures at 298.15 K for succinic and glutaric acid are:

$p^{\circ,\mathrm{L}}(succinic) = (1.7 \pm 0.5) \times 10^{-3}$ Pa,

$p^{\circ,\mathrm{L}}(glutaric) = (9.3 \pm 2.8) \times 10^{-4}$ Pa,

$p^{\mathrm{sat,L}}(succinic) = (1.5 \pm 0.8) \times 10^{-5}$ Pa,

$p^{\mathrm{sat,L}}(glutaric) = (5.6 \pm 1.8) \times 10^{-5}$ Pa.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 20515, 2010.