Atmos. Chem. Phys. Discuss., 11, C3480–C3485, 2011
www.atmos-chem-phys-discuss.net/11/C3480/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Hygroscopic behavior of atmospherically relevant water-soluble carboxylic salts and their influence on the water uptake of ammonium sulfate" *by* Z. J. Wu et al.

Anonymous Referee #2

Received and published: 17 May 2011

This manuscript describes hygroscopic growth measurements by H-TDMA. It focuses on the deliquescence and hygroscopic properties of organic salts and their mixtures with ammonium sulfate. It also compares the hygroscopicity parameters of three mixtures calculated based on the measured growth factor against the values predicted from the individual species by simple additive rule. The authors concluded that organic salts have significant effects on the deliquescence of ammonium sulfate and the modeled hygroscopicity parameter is lower than that derived from H-TDMA measurement. The paper is rather straight forward.

This manuscript provides some insight into the hygroscopic properties of organic salt

particles, which are sparingly investigated. The authors concisely presented the measurement results and simple calculation for hygroscopicity parameter. However, there is a major weakness that the manuscript is lack of comprehensive discussion to elucidate the atmospheric implication of the measurement. Moreover, there are several unclear issues that need to be clarified. Given the journal scope on the general implications for atmospheric science, a major revision is required to improve the paper. The authors are recommended to make appropriate modifications in consideration of the following points.

1. The authors compared in the text the measured DRH and hygroscopic properties of the organic salts with the previous findings. It may be more straightforward and clearer to include the previous data in the graphs.

2. (P.7699, section 3.1.1) The authors mentioned that they measured lower DRH than that detected by Peng and Chan (2001) due to different diameters. Although a reference paper is provided, the authors should further explain the issue so that the readers can easily follow.

3. Peng and Chan (2001) reported residual water in sodium acetate and sodium malonate at low RH conditions but this is not observed in the current study. The authors may want to explain the difference between two observations.

4. The author reported different deliquescence properties of sodium succinate from those observed by Peng and Chan (2001) and "the reason is unclear" (P7699, section 3.1.4). I would like to see the authors can make some effort on speculating a possible reason, rather than leaving the situation unclear. 5. Overall, the authors have made a straightforward report of their measurements and brief comparison between their results and the few literature findings. Given that there are other published works of similar nature and also most of the specific organic salts have been studied previously, they should consider a comprehensive discussion to provide more insight over the existing literature. More specific comments and suggestions are as follows.

6. Mass transfer effect has been shown to be the limitation of hygroscopic measurements by HTDMA (Chan and Chan 2005 and the references therein). How does the issue affect the current results? The author will need to consider this issue in the comparison of their measurements with the equilibrium measurements using EDB by Peng and Chan (2001) in section 3.1 as well.

7. Since the organic salts are formed from the neutralization of their acid forms, one interesting and important implication from this aspect is how the transformations alter the hygroscopic properties of particles. Unfortunately this issue is missing in the paper. The hygroscopic growths of many organic acids have been extensively studied (e.g. Peng et al. 2001, Prenni et al. 2001, Choi and Chan 2002, Braban et al. 2003, Chan and Chan 2003, Parson et al. 2004 and many others). The authors may want to compare the organic acids against their corresponding salts in order to show the significance of organic salt formation.

8. The statement "...lower DRH (73%+/-1) of Mix_mar indicates that ammonium sulfate in the mixture starts to take up some water before reaching its deliquescence point" (P7701, line26) needs to be clarified. It is less convincing without any evidence from suitable characterization for the component phase identity. On the other hand, early water-uptake in mixed particles of ammonium sulfate and organic acids has been characterized in some EDB/Raman studies (e.g. Ling and Chan 2008, Yeung and Chan 2010). The authors may find these papers useful to support the statement.

9. In section 3.2.2, the authors focus on hygroscopic growth of the three mixtures above 80% RH. Why limited to this high RH range? Would data below 80% RH that illustrate the thermodynamics of aerosol drops at high solute concentrations and high ionic strength be more interesting?

10. One intriguing finding is that the hygroscopic growth of mix_mar and mix_bio particles above 80% RH was found to be close to that of pure ammonium sulfate. The observation implies that the major fraction of organic salt in these particles (ammo-

nium oxalate) should contribute to the water uptake close to that of ammonium sulfate. I would like the authors to elaborate on this observation in the revised paper.

11. Further to the point 8, more discussion on the use of a modified Kohler theory are expected (as they mentioned in P.7702, line 15-16). However, I'm not able to find such discussion in section 3.2.3. The information available in that section basically only focuses on the comparison of the hygroscopicity parameters calculated by different methods.

12. The hygroscopic properties of three mixed particles that simulate the ambient aerosols of different sources (replace carboxylic acids by carboxylic salts) are examined. I would be further interested to know if any differences in term of the hygroscopic properties between the simulate aerosols and the "real ones" (with organic acids). On the other hand, the hygroscopic growth of ambient aerosols from different sources has been extensively studied (e.g. Mcfiggans et al. 2006, Swietlicki et al. 2008). The authors may want to compare their results with the literature findings.

13. I'm not very sure whether the calculation works in section 3.2.3 is relevant to the rest of the paper. The single hygroscopicity parameter is used to correlate the hygroscopic growth of aerosols with their CCN activity (Petters and Kreidenweis 2007), which is obviously not the objective of this paper. The authors will want to clarify the purpose of the calculation in this section.

14. Furthermore, I suggest the authors to compare their measurement with the predictions from other well-established thermodynamic model approach (e.g. E-AIM, ADDEM, simple ZSR calculation) over the range of RH. This is a more complete comparison and is also useful to evaluating the model predictions for hygroscopic growth at high solute concentrations.

References:

Peng, C. G. and Chan, C. K.: The water cycles of water-soluble organic salts of atmo-

spheric importance, Atmos. Environ., 35, 1183–1192, 2001.

Chan, M.N. and Chan, C.K.: Mass Transfer Effects in Hygroscopic Measurements of Aerosol Particles", Atmos. Chem. Phys., 5, 2703-2712, 2005.

Peng, C. G., Chan M. N. and Chan, C. K.: The hygroscopic properties of dicarboxylic and multifunctional acids measurements and UNIFAC predictions. Environ. Sci. Technol., 35, 4495-4501, 2001.

Choi, M. Y. and Chan, C. K.: Continuous measurements of the water activities of aqueous droplets of water-soluble organic compounds. J. Phys. Chem. A, 106, 4566-4572, 2002.

Braban, C. F., Carroll, M. F., Styler, S. A. and Abbatt, J. P. D.: Phase transitions of malonic and oxalic acid aerosols. J. Phys. Chem. A, 107, 6594-6602, 2003.

Chan, M. N. and Chan, C. K.: Hygroscopic properties of two model humic-like substances and their mixtures with inorganics of atmospheric importance, Environ. Sci. Technol., 37, 5109–5115, 2003.

Parson M. T., Mak J., Lipetz S. R., and Bertram A. K.: Deliquescence of malonic, succinic, glutaric, and adipic acid particles. J. Geophys. Res., 109, D06212, doi:10.1029/2003JD004075, 2004.

Ling, T. Y., and Chan, C. K.: Partial crystallization and deliquescence of particles containing ammonium sulfate and dicarboxylic acids. J. Geophys. Res.,113, D14205, doi:10.1029/2008JD009779, 2008.

Yeung, M. C. and Chan, C. K.: Water content and phase transitions in particles of inorganic and organic species and their mixtures using micro-Raman spectroscopy. Aerosol Sci. Technol., 44, 269–280, 2010.

McFiggans, G., Artaxo, P., Baltensperger, U., Coe, H., Facchini, M. C. and co-authors: The effect of physical and chemical aerosol properties on warm cloud droplet activa-

tion. Atmos. Chem. Phys. 6, 2593–2649, 2006.

Swietlicki, E., Hansson, H. C., Hameri, K., Svenningsson, B., Massling, A. and co-authors: Hygroscopic properties of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in various environments - A review. Tellus B, 60, 432–469, 2008.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, 2007.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 7693, 2011.