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Atmospheric
Chemistry
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Discussions

Interactive comment on "A combined particle trap/HTDMA hygroscopicity study of mixed inorganic/organic aerosol particles" *by* A. A. Zardini et al.

A. A. Zardini et al.

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We thank the reviewer for the constructive comments and suggestions. Please find below the answers to every specific point (numbered as in the reviewer's original comment) where page and line number refer to the on-line version of the paper.

1. We agree with the reviewer on this point, therefore we added the following text (Page 5251, line 30). "So far, this interpretation is based on indirect evidence. There are no direct experimental observations of the postulated complex dynamics such as swelling and collapsing of particle veins. Measurement techniques with high spatial resolution - in the order of nanometers - are needed to confirm the presence and the postulated development of vein systems in AS/AA particles as a function of RH."

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2. Concerning glutaric acid: The E-AIM model [http://www.aim.env.uea.ac.uk/aim/aim.php. - accessed June 12, 2008] predicts a hygroscopic growth which is either based on Peng et al. (2001) UNIFAC parametrization or on a fitted activity equation. The difference between the two is negligible. Not surprisingly, the model predictions are consistent with the Peng et al. data. As shown in Fig. 4, our data are in very good agreement with the Peng et al. data and hence the E-AIM does not provide any additional information. The E-AIM output for the 1:1 AS/GA mixture yields the same hygroscopic growth of the ZSR approach shown in Fig. 7. Again, that is not surprising since the two approaches are based on the same parametrization. Concerning the other organics: Any other organic compound which is added by the user in the E-AIM model simply uses the Raoult's law if no additional parametrization is available and hence does not go beyond the ZSR approximation used when discussing the other organic/inorganic mixtures. Therefore we decided not to include a comparison between E-AIM predictions and our measurements.

3. J. Kelly correctly points out that the time resolution of our light scattering intensity fluctuations measurement is about two orders of magnitude slower than the measurement of the pattern distortion parameter introduced in Braun and Krieger (2001). Both techniques can be used to study deliquescence and also to detect efflorescence, with the intensity fluctuation measurement limited to a temporal resolution of about 10 seconds. However, the present study is not focusing on the kinetics of the efflorescence process, but on the hygroscopicity of mixed organic/inorganic particles in equilibrium with the gas phase. Here, time resolution is not as important as sensitivity. Because of the dynamic range of the detector (photomultiplier in the case of the temporal fluctuations measurement, an 8 bit CCD image sensor in the case of the distortion parameter) our temporal intensity fluctuation measurement is more sensitive (by a factor of 2 to 3, depending on the size of the particle) for slight changes in the scattering phase function compared to the distortion parameter. As can be seen in Fig. 9 of the present paper, these changes are occurring on a time scale of several 100 to 1000 seconds so that a higher temporal resolution does not mean any advantage.

4. The discussion on temperature effects and DRH of glutaric acid was not very clear. We rewrite the paragraph (page 5246, line 4) as copied below. Concerning the presence of impurities, we know that insoluble impurities can act as seeds for heterogeneous nucleation while soluble impurities reduce the DRH. We were therefore thinking of the influence of soluble impurities in the glutaric acid solution. The purity of marketed glutaric acid is indeed variable, so that impurities might have an influence on the DRH. In addition, we had not thought about possible polymorphic forms of solid glutaric acid. However, another even more probable explanation might be polymorphism: Chak Chan in his comment referred to a very recent paper by Ling and Chan pointing out that glutaric acid can be present in an alpha (stable above 336 K) and a beta form (stable below 336 K). For AS/GA particles levitated in their EDB, they observed first the formation of the alpha form (metastable at RT) followed by the transformation into the beta form (stable at RT) over a timescale of hours when the particle is held at 60% RH. If for faster hygroscopicity cycles and pure GA particles this phase transformation does not occur, the alpha form might deliquesce directly. This would happen at a lower RH than the deliquescence of the beta form because the stability of the alpha form is lower and the solubility higher. Therefore the whole paragraph reads now as:

"Pure glutaric acid exhibits hysteresis with distinct deliquescence and efflorescence as shown in Fig. 4. In this study we find DRH approx 90% at 291 K. The DRH of glutaric acid has been determined by several groups: Brooks et al. (2002): DRH = 87.5%; Wise et al. (2003): DRH = 88.9%; Marcolli et al. (2004) DRH = 88.2% (all bulk measurements at 298 K). Pant et al. (2004) found DRH approx 89% at 293 K by using a reflected-light microscope technique. Parsons et al. (2004) used also a microscope technique to study the temperature dependence of DRH for several dicarboxylic acids. Unlike ammonium sulfate, the solubility of glutaric acid is strongly temperature dependent. Their parametrization of glutaric acid DRH with temperature agrees within error with all the bulk measurements reported and also with the value for glutaric acid corresponding to our experimental temperature. HTDMA data from Cruz and Pandis (2000) strongly underestimate the amount of water uptake at deliquescence

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(DRH approx 85%). In addition, a size decrease at RH approx 50% possibly caused by structural rearrangements inside the particle or shrinking due to evaporation was observed. The DRH determined with EDB at 298 K by Peng et al. (2001) is 83% $<$ DRH $<$ 85%, about 3 to 5% lower than what has been observed in the bulk. Possible reasons for this lower value might be the presence of soluble impurities in the glutaric acid used for their experiment or the polymorphism of glutaric acid: this substance exists in an alpha and a beta form, stable at temperatures above and below 336 K (Ling and Chan, 2008), respectively. During hygroscopicity cycles of AS/GA particles levitated in the EDB, Ling and Chan observed first the formation of the alpha form (metastable at room temperature) followed by the transformation into the beta form (stable at room temperature) over a timescale of hours when the particle was held at 60% RH. If for faster hygroscopicity cycles and pureGA particles this phase transformation does not occur, the alpha form might deliquesce directly. Deliquescence of the alpha form will occur at a lower RH than for the beta form because the stability of the alpha form is lower and its solubility higher. In our EDB experiments, RH was changed at a rate of typically 10%/h, giving the particle enough time to transform into the beta form before DRH was reached.

5. We extended Table 1 by including solubilities, vapor pressures, and the reference papers from where the data were taken (Saxena 1996, Bilde 2003, Lide 2004).

6. We added the following references (Page 5238, lines 11-12): Limbeck et al., 2001; Mochida et al., 2003; Narukawa et al., 2003; Decesari et al., 2006.

7. We add the following numbers to our description of the experimental setup (p.5239, line5): "...which can be associated with the particle morphology: low values (ca. 0.03 microV up to 0.09 microV) for spherical homogeneous particles and high values (greater than 0.2 microV, up to 10 microV) for particles with a distinct crystalline shape. Mixed phase particles or solid particles with an almost spherical shape lead to values in between (see Videen, 1997, and Krieger and Braun, 2001, for details).

8. The paper is now cited, see also answer to Comment S1661.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 5235, 2008.