

## ***Interactive comment on “Water activity and activation diameters from hygroscopicity data – Part II: Application to organic species” by K. A. Koehler et al.***

**K. A. Koehler et al.**

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We would like to thank Referee #1 for the supportive comments and address the numbered issues below.

1. What is the uncertainty that arises from the fact that the hygroscopic growth curves are referenced to particles at low RH that have not effloresced and still contain some residual water? As pointed out on page 10885, molecules such as malonic acid effloresce at low relative humidities but the growth measurements (Figure 1) illustrate that insufficient drying occurred to make the particles effloresce under the experimental conditions.

In Part I (Kreidenweis et al., 2005), there is an extensive discussion about uncertainty that would result from incorrect growth factors, as is the result of water remaining on the “dry” particles. The volume of water left on the particles is expected to be quite small, giving an error in the growth factor likely less than 0.02. Referring to Figure 7 in Part I, this produces about a 2% error in the predicted critical dry diameters. Perhaps a brief reference back to this discussion would be useful for readers; we will add this to the revision.

2. On this topic, it is important that the residence times in the experiment and the manner by which the drying was performed should be given in the paper. What were the sheath/sample flows in the DMA? If extra drying between DMA1 and DMA2 is occurring, why was not an extra mixing volume added to the experiment prior to DMA1 to increase the residence time at low RH to allow the drying to proceed fully?

The residence time in the HTDMA is less than 5 s. The sheath: sample ratio in the DMA was 10:1 lpm. We have added these to the paper. While we believe that the change in size between DMA1 and DMA2 is due to the evaporation of the organic particles, we cannot completely rule out the possibility of further drying, so we leave that as a possibility in the text. The particles are indeed sent to a dilution chamber with a residence time of about 30 s prior to being sampled by the HTDMA (this has been added to the text). We believe this is sufficient time to remove the water, however, there has been the suggestion in the literature that metastable states of these organics can be formed upon evaporation, therefore it is unknown how long would be sufficient for complete drying.

3. One of the novel aspects of this work is that evaporation of the organics is accounted for in the data analysis. It would be valuable to provide a back-of-the-envelope calculation to confirm that it is indeed organic evaporation that is proceeding between DMA1 and DMA2. This can be readily done by assuming an organic vapour pressure, residence time, particle number density, etc. This calculation could confirm in an order of magnitude sense whether or not it is indeed particle evaporation that is proceeding, or

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whether some other factor like structural rearrangement leading to a change in mobility diameter is occurring instead. The reason I bring this up is that I am surprised that molecules that have such low vapor pressures (e.g.  $10e-5$  torr or lower, see Table 1) are evaporating on the timescales of seconds.

By assuming that the pressure of the organic away from the drop surface remains zero (back of the envelope, maximum evaporation) we find that in 5 s a solid malonic acid particle initially 100 nm in diameter will have shrunk by only 0.01 nm. In this calculation the vapor pressure (as listed in Table 1) is not taken as a function of temperature, instead the value at 303 K is used, and the temperature of the drop is not taken into account, instead it is assumed to be constant at 303 K. Both assumptions will maximize the calculated evaporation rate. It is so small because the reported vapor pressure over the solid is quite low. This leads to two possible hypotheses: first, particle evaporation is not the cause of particle shrinking and restructuring may be the more accurate explanation; or second, the vapor pressure estimates for these organics are incorrect. In the first instance, an irregular dry particle having a shape factor of about 1.2 which then takes up water and becomes spherical (shape factor of 1) would exhibit a change in mobility diameter equivalent to that observed and attributed to evaporation. While some studies have found significant shrinking due to restructuring can occur (Jimenez et al., 2003), we do not believe we are observing restructuring, because the particles do not deliquesce, suggesting the particles are retaining water and therefore should be nearly spherical, highly concentrated solution droplets. A shape factor of 1.2 is much larger than even for a cube (shape factor = 1.08) and corresponds to a highly irregular particle. It is difficult to observe this because the particles are so volatile under an electron beam. With regard to the second hypothesis, the vapor pressure must be too low by about a factor of 100 to account for the observed evaporation. The vapor pressure predictions in Makar (2001) also suggest that the vapor pressures listed in Table 1 are at least in an order of magnitude sense correct. However, these vapor pressures are for the crystalline organic. Malonic acid crystals, left in an open container, do not evaporate. Again, because we never see deliquescence, but instead observe contin-

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uous water uptake, we can assume that the particles are not crystals, but extremely supersaturated solution droplets. In this case, it stands to reason that the vapor pressure of the organic in these solutions could be different than that for the solid, and specifically could be significantly higher. Whether this enhancement can be a factor of 100 is unknown, but many other groups doing similar experiments have all observed evaporation or similar anomalous behavior for particles composed of these species.

4. In Table 1, there are a number of small errors: What is meaning of “z” in column 7? What is the meaning of the caption of the top of column 9? The stoichiometric coefficient “2” is missing from chemical formula for the dihydrate of oxalic acid (column 2).

In Table 1, “z” is defined directly below the table with the references. The referee is indeed correct about the missing “2” in the chemical formula for oxalic acid dihydrate and the caption of column 9 should read “pKa and associated nu for a 1 molar solution”. We will ensure these corrections are made for the final version.

5. In Table 2, there seem to be too many significant figures in the values for alpha and beta.

The number of significant figures can be reduced to two without significantly changing the predicted critical dry diameters; we will therefore make this change in the final version.

6. In Table 3, it would be useful to state what the parameter “k” refers to.

There is a rather extensive discussion on “k” in Sections 5 and 6. We could refer the reader to Equation 12 for the exact definition of “k” in Table 3.

## References

Jimenez, J.L., R. Bahreini, D.R. Cocker, H. Zhuang, V. Varutbangkul, R.C. Flagan, J.H. Seinfeld, C.D. O’Dowd, and T. Hoffmann, New particle formation from photooxidation of diodomethane (CH<sub>2</sub>I<sub>2</sub>), *Journal of Geophysical Research-Atmospheres*, 108 (D10),

2003.

Kreidenweis, S.M., K. Koehler, P.J. DeMott, A.J. Prenni, C. Carrico, and B. Ervens, Water activity and activation diameters from hygroscopicity data - Part I: Theory and application to inorganic salts, *Atmospheric Chemistry and Physics*, 5, 1357-1370, 2005.

Makar, P.A., The estimation of organic gas vapour pressure, *Atmospheric Environment*, 35 (5), 961-974, 2001.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 5, 10881, 2005.

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5, S4372–S4376, 2005

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