Atmos. Chem. Phys. Discuss., 12, C3802–C3808, 2012
www.atmos-chem-phys-discuss.net/12/C3802/2012/

Atmospheric
Chemistry
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Discussions

Interactive comment on "Glass formation and unusual hygroscopic growth of iodic acid solution droplets with relevance for iodine oxide particles in the coastal marine boundary layer" *by* B. J. Murray et al.

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Received and published: 19 June 2012

The referees' comments are italicised and our response is in plain text.

The referees' primary comment concerned our interpretation of the EBD measurements. The referee has made a number of plots using our data in which the assumption is explicitly made that 'the data have to approach an aw of 0 at a mass fraction of 1'. Hence, in the referees' plots the HIO_3 mass fraction approaches 1.0 as aw approaches 0. For a material such as sodium chloride or ammonium sulphate which crystallise to an anhydrous crystal at low RH, this assumption is justified and appropriate. However, for this particular system, we do not think this assumption can be justified. On drying, many solutions can form metastable amorphous solid or semi-solid states, rather than crystallise. Such states are no longer in equilibrium with the surroundings and can retain water. For such systems, the composition of the aerosol particle may be extremely inhomogeneous and the water activity will no longer be equal to the RH of the surrounding gas phase. For example, Peng et al.(Peng et al., 2001) showed that at 5% RH, citric acid, malic acid and tartaric retained between 5 and 10% water by mass, i.e. the mass fraction does not tend to 1.0. Cohen et al.(Cohen et al., 1987) report that CaCl2 retains 40 wt% water when at 10% RH, which is equivalent to 4 moles of water for every mole of CaCl2. Similarly they found MnSO4 to retain 30% water. Cohen et al. suggest that these materials may have formed a glass or a gel at low RH. Tong et al. (Tong et al., 2011) have shown that the kinetics of water loss at low RH are slow in sucrose solutions and cautioned against assuming that aerosol are at equilibrium. Indeed, there has been an ongoing debate for many years about the reliability of using the 'dry' state as a reference point for mass and diameter growth factor measurements. A much more reliable choice is to use a reference point corresponding to the saturation concentration of the solute, equivalent to the deliquescence point for inorganic salts. Given that the fast EDB measurements presented here confirm that a 'dry' iodic acid particle still contains a considerable mass fraction of water that is released only slowly over time, using the 'dry' state as the reference point is inappropriate. Instead we decided to reference our data at a point where the aerosol is unambiguously in equilibrium and where data from the two measurement techniques overlap. As a consequence we have used a RH of 84% as the reference point. At this RH Kumar et al. (Kumar et al., 2010) have shown that water activity measurements agreed with deliquescence measurements. Consequently, we feel that the data should be reported in the way already presented in the original manuscript.

The referee has highlighted an important issue which we have now addressed more directly in the manuscript. We have modified the discussion on the old page 7891 which now reads as follows: 'For solutions such as aqueous NaCl, which crystallise to an anhydrous salt on drying, it is appropriate to determine the mass fraction from growth factor data making the assumption that on approaching 0% RH, the mass fraction of solute is 1.0. This assumption is not appropriate for many materials. For example Peng et al.(Peng et al., 2001) showed that at 5% RH, citric acid, malic acid and tartaric acid retained between 5 and 10% water, i.e. the mass fraction does not tend to 1.0. Cohen et al.(Cohen et al., 1987) report that CaCl2 retains about 40 wt% water when at 10% RH, which is equivalent to 4 moles of water for every mole of CaCl2. Similarly they found MnSO4 to retain about 30% water. Cohen et al. (1987) suggest that these materials may have formed a glass or a gel at low RH. More recently, it has been shown that the kinetics of water loss in sucrose solutions are slow at low humidity and it should therefore not be assumed that aqueous droplets are at equilibrium at low RH Tong, 2011 1030;Zobrist, 2011 1046. Indeed, there has been an ongoing debate for many years about the reliability of using the 'dry' state as a reference point for mass and diameter growth factor measurements. A much more reliable choice is to use a reference point corresponding to the saturation concentration of the solute, equivalent to the deliquescence point. Since we know that iodic acid droplets form an ultra-viscous liquid or glass at low RH and most likely retains water (reinforced by the fast measurements of water release: Figure 7), we chose to reference our data sets at a point close to the deliquescence RH for HIO3. At this RH, the solution droplets are unambiguously in equilibrium (i.e. water activity = RH) and water activity measurements are in excellent agreement with deliquescence measurements Kumar, 2010 43. The resulting solute concentration is shown in Figure 9. Where the Kumar et al.Kumar, 2010 43 and present EDB data sets overlap they are in agreement within experimental uncertainty. In addition, the general trend at lower RH is also consistent with the previous bulk measurements.'

In addition we have added a line to the abstract: 'Water retention in amorphous material at low RH is important for understanding the hygroscopic growth of aerosol particles.'

The referee also had a number of other comments which we address below:

1. The title seem to imply that the fact that aqueous HIO3 becomes glassy under very dry conditions has relevance for the marine boundary layer. My feeling is that these very dry conditions are not too important.

The fact that iodic acid forms a glass is critically important for understanding growth factors and appreciating that water is retained even at low RH. Expressed another way, although the dry conditions are not relevant for the marine boundary layer, laboratory measurements under such conditions are crucial for interpreting measurements in the marine boundary layer.

2. Abstract: reconsider the mass growth factor, see comments above.

This has been addressed above.

3. page 7883, line 14: consider adding a reference to previous work: Chan C. K., Flagan, R. C. and Seinfeld, J. H., J. Am. Ceram. Soc., 81 [3] 646-48 (1998)

Reference added

4. page 7884, line 9: again the technique as been developed earlier: Koop T. et al., J. Phys. Chem. A 1998, 102, 8924-8931.

Reference added

5. page 7885, line 24: does 'fixed position' mean 'null point of the electrodynamic field'?

Yes. Inserted 'null point' in brackets to clarify

6. page 7885, line 25: This is a considerable flow. How is the drag force accounted for? Please explain.

The volume of the chamber is large (1 L)relative to the flow rate (0.2 L/min), hence the velocity of the air flow over the droplet is very slow making the drag force insignificant.

7. the two last paragraphs of the section Raman study: these are very interesting experiments. It is important to tell the reader the timing of the RH changes shown in Fig. 6. Since this is clearly a kinetic effect, it is necessary to know what kind of RH versus time profile was applied to interpret the data. Do the authors think they are able to estimate at which viscosity the semi-solid is able to show the flow that they observe?

We have added details in the figure caption describing the rough timescales involved. We did not employ a smooth ramp in temperature which makes estimates of viscosity difficult.

8. page 7890, first sentence: This growth can be calculated already from the data of Kulmar et al. (2010), see comment above. The authors should clearly state that no single particle measurements are needed to come to this conclusion.

We do not understand how the growth of a supersaturated solution can be calculated from the water activity data for a under saturated bulk solution. This requires careful measurement since the amount of water retained in the droplet at low RH can only be determined experimentally.

9. page 7892, line 3: My feeling is the kappa value will change after refreferencing the EDB data.

This is addressed above, the Kappa value does not need to be changed.

10. Fig. 5: a scale bar is missing

An indication of scale is now given in the caption.

11. Fig. 6: again a scale bar is missing; also the RH versus time should be given, see my comment above.

An indication of scale is now given in the caption. We have added a description of the approximate RH vs time profile in the caption.

12. Fig. 7(a): it would be very interesting to estimate the concentration of the droplet at

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about 1.8 s where the pronounced kink is. This is the concentration when most likely a 'glassy' crust develops, slowing down the subsequent evaporation of water from the more dilute core of the particle.

Unfortunately we can only determine the concentration in moles Liter-1 and without density we cannot convert this into an accurate weight or mole fraction.

13. Figs. 8 and 9: see the comments at the beginning.

Addressed above.

References

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 7879, 2012.