

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.

Anonymous Referee #1

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The paper extends the previous work by some of the authors (Kumar et al., 2010) about the hygroscopic properties of iodic acid solutions by performing single particle experiments. They use Raman microscopy on particles on hydrophobic cover slips and two different electrodynamic balances to study levitated particles. They observe that the particles do not crystallize at dry conditions, but exist in a semi-solid or glassy state below 15 % RH. They also show that the hygroscopic growth factor of iodic acid solution droplets is very small and suggest that the small growth observed for nucleation mode particles in the coastal marine boundary layer is indicative of these particles being

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composed of iodic acid.

The topic is well suited for publication in ACP and it present significant advances in our knowledge about iodine oxide particles. However, I do have a number of questions/comments, one which seems to require revisions:

In my opinion the authors do not take full advantage of their EDB measurements. I will illustrate this with three figures showing that the bulk data of Kulmar et al. (2010) and the EDB data are not completely consistent at present. However, I believe the data can be used to derive a water activity-concentration parameterization improving the one given in Kulmar et al. (2010) considerably. It is not clear to me how the authors derived Fig. 9 from the data shown in Fig. 8a. If I take some of the data of Fig. 8 and the data and parameterization and of Kulmar et al. (2010) I come up with my Figure 1. It is obvious from Fig. 8a of the paper that due to some noise in the data at low humidity the mass growth factor is sometimes smaller than 1 and hence the concentration in mass fraction is above 100 %. This is missing in Fig. 9 of the paper. Also the data have to approach an aw of 0 at a mass fraction of 1. My guess is that there might be an error in referencing the data to the bulk concentration properly.

The same problem becomes visible if you plot the data and parametrization of Kulmar et al. (2010) into Fig. 8a, as I did in my Figure 2. Since the bulk data of Kulmar et al. (2010) are considered to be very reliable, there seem to be a problem with the adjustment of the EDB data to the bulk reference. In addition it becomes obvious from this figure that the parametrization of Kulmar et al. (2010) should not be used for extrapolations. However, I am very convinced that the EDB data after proper referencing can be used to derive a very significant improvement to the Kulmar et al. (2010) parameterization to lower humidities. The author should provide one for the benefit of the community.

Combining both data sets very carefully will also provide a better estimate of the mass growth factor. It seems to me that the 20 % mass growth the author report are not

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consistent with the bulk measurements of Kulmar et al. (2010). Rather from my Fig. 2 I read 1.35 at 90 % RH.

I provide a third figure to show that if mole fraction of water is plotted versus water activity there seem to be indications (once the referencing problem has been accounted for) that the nonideality of aqueous HIO₃ solutions is especially pronounced for dilute solutions and becomes more ideal for the more concentrated solution. Again a parameterization could be given by the authors.

Minor comments:

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.
2. Abstract: reconsider the mass growth factor, see comments 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)
4. page 7884, line 9: again the technique as been developed earlier: Koop T. et al., J. Phys. Chem. A 1998, 102, 8924-8931.
5. page 7885, line 24: does 'fixed position' mean 'null point of the electrodynamic field'?
6. page 7885, line 25: This is a considerable flow. How is the drag force accounted for? Please explain.
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?

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May be they are able to (gu)es(s)time a viscosity?

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.
9. page 7892, line 3: My feeling is the kappa value will change after rereferencing the EDB data.
10. Fig. 5: a scale bar is missing
11. Fig. 6: again a scale bar is missing; also the RH versus time should be given, see my comment above.
12. Fig. 7(a): it would be very interesting to estimate the concentration of the droplet at 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.
13. Figs. 8 and 9: see the comments at the beginning.

Reference: Kumar R. et al., ACP 10, 12251-12260, 2010.

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

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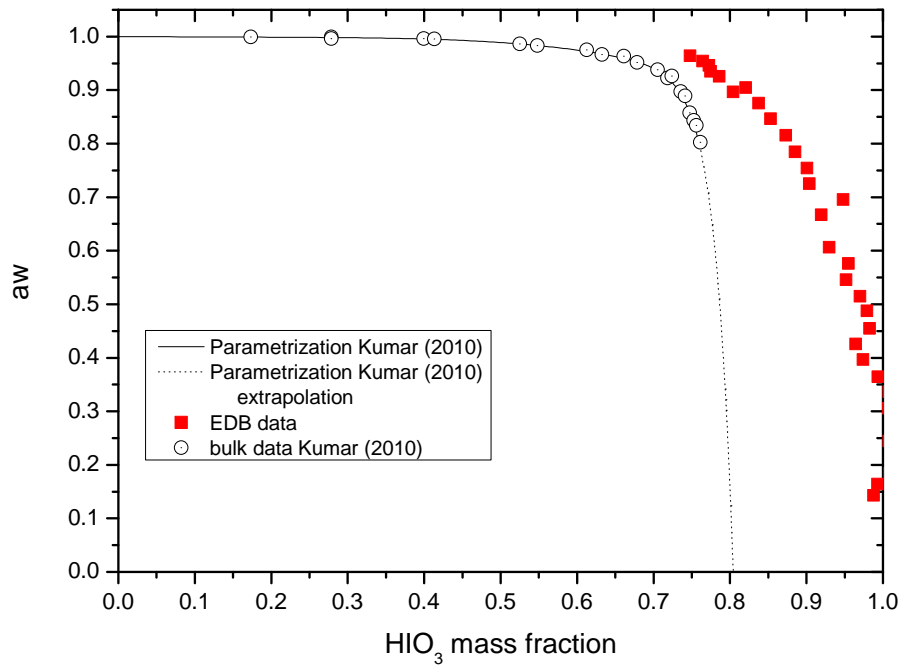


Fig. 1. a_w versus mass fraction of HIO_3 , see text for details

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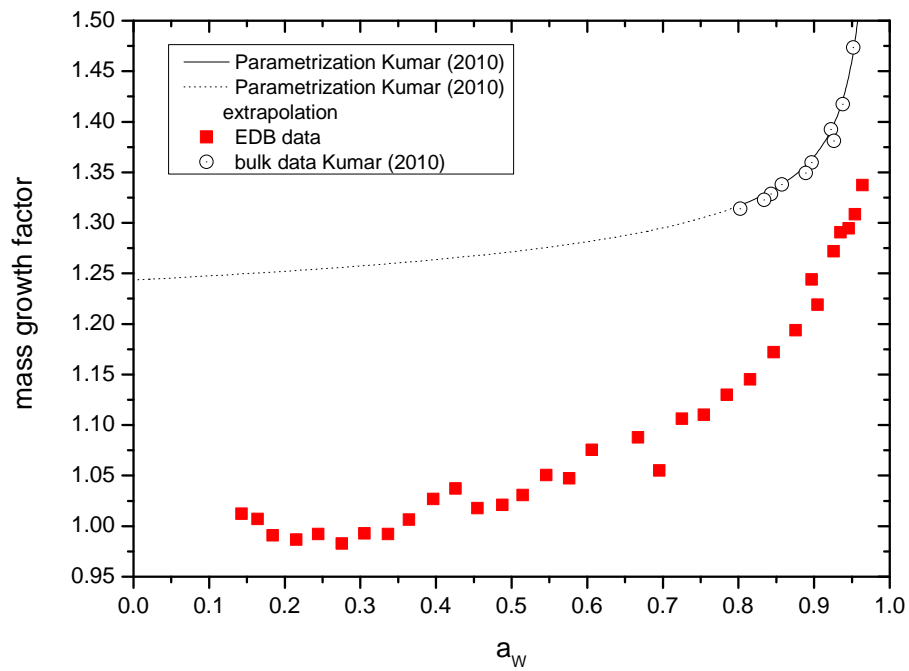


Fig. 2. mass growth factor of HIO_3 versus water activity

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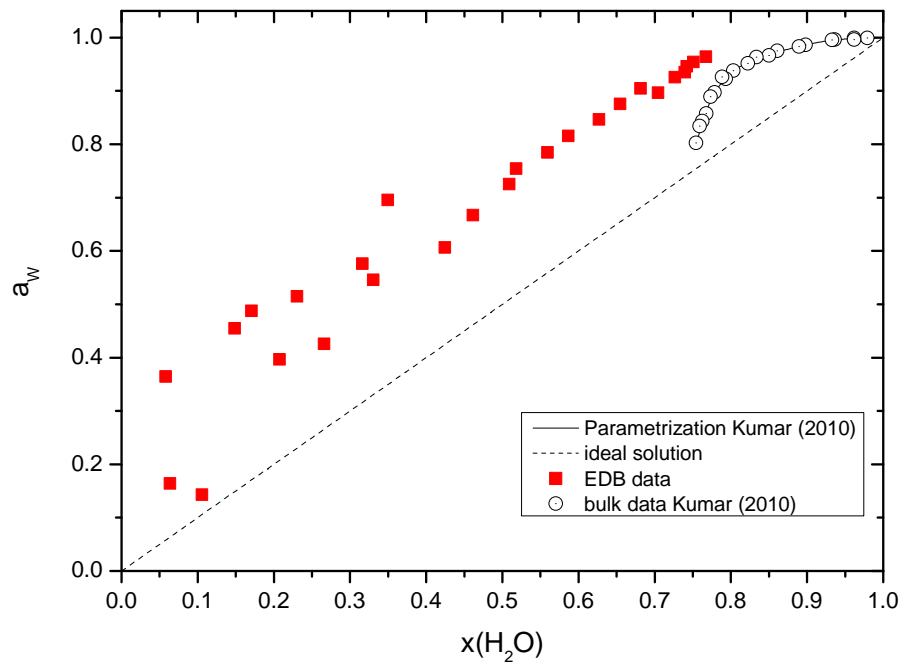


Fig. 3. water activity versus mole fraction of H2O

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