

Review revised manuscript # acp-2021-486 by Shuang Han et al.: «Hygroscopicity of organic compounds as a function of organic functionality, water solubility, molecular weight and oxidation level»

I am sorry but I am still convinced that this manuscript needs major revision or be rejected and not be published in ACP.

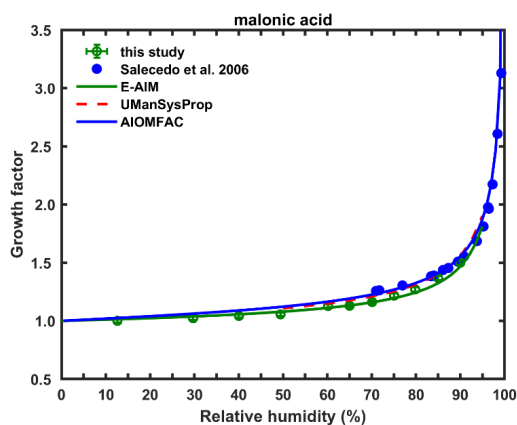
The main concern in my initial review was that with the approach used by the authors, they only measure hygroscopic growth under subsaturated conditions for all compounds, which crystallize in a binary aqueous mixture. That holds for example for all dicarboxylic acids besides malonic acid. I argued that an organic atmospheric aerosol particle typically contains a multitude, thousands of compounds, which each single compound only being present in a small fraction. In such multi-compound mixtures, the organics do not crystallize as have been proven by Marcolli et al. (2004). What is needed to constrain or to compare to thermodynamic models are the data in the liquid, supersaturated (often called sub-cooled) state. If you are interested in a comparison of thermodynamic models in the subsaturated state, bulk experiments yield much more accurate data than HTDMA experiments.

The authors reply to these concerns that crystallization does occur in binary mixtures, which is true, but irrelevant, if you want to constrain or compare to thermodynamic models as written above. The authors further argue that bouncing experiments with SOA particles show that particles are solid or semisolid at intermediate RH. This is correct, but these particles are not crystalline solids, but in an amorphous state. So, you cannot argue that solid means crystalline. An amorphous solid may be slow in taking up water (as your sucrose example) but will not show deliquescence. If you wait long enough, it will reach thermodynamic equilibrium even at low humidity.

They write in their reply: *In our study, we dried the aerosols to relatively quite low RH, ensuring the crystallization of the organic compounds that likely crystallize under real conditions. Thus, the measured hygroscopic growth at elevated RHs could represent their hygroscopic behavior under ambient conditions, forming a realistic dataset.*

I strongly disagree with this statement as explained above.

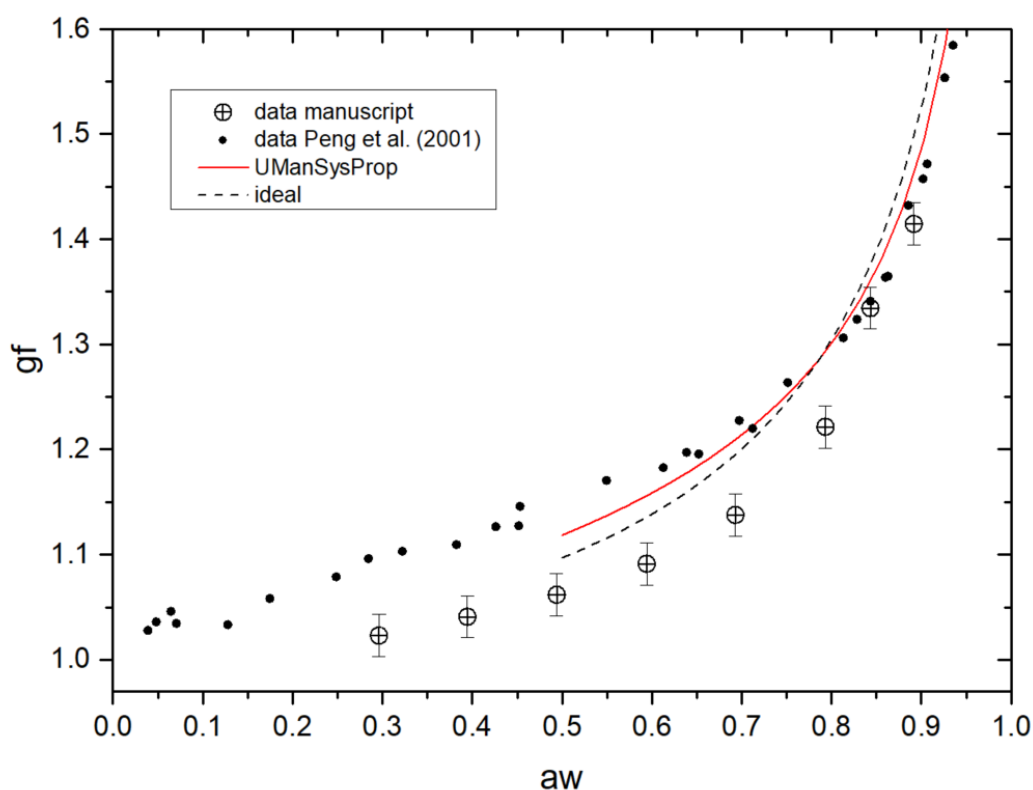
Second, the authors fail to compare their data with data available in the literature using different techniques. I tried in my initial review to illustrate this with the data by Salecedo et al. (2006). The authors did a comparison with their data now and provided this figure:



However, they do not include it in the revised manuscript. Why?

This is exactly what is needed: comparison to previous data (which is available for almost all compounds discussed in the manuscript!) and a critical discussion of such a comparison. In the example for malonic acid shown above, it is not trivial to judge whether the E-AIM fits the complete dataset better of AIOMFAC or UManSysProp. Nor is it clear whether the different data agree within experimental error. Presently, such a discussion is missing in the manuscript.

To show another example: In the figure below I plot the data of malic acid of the manuscript together with the data from Peng et al. (2001) and two UManSysProp simulations (I used the density from UManSysProp from Girolami (1994) for the conversion of the Peng et al. data to size growth):



You may argue that all data agree at high humidity (> 85 %), but it is obvious that there is an increasing deviation between both data sets at lower humidity. (This is definitely larger than any error in the density estimation may cause.) The UManSysProp simulation assuming AIOMFAC activities comes closer to the Peng et al. data while assuming ideality in UManSysProp is closer to the data of the manuscript. It is not clear which data are the correct ones. Are the authors growth factors at low RH limited by kinetic uptake limitations (as in sucrose) also for malic acid?

What is however obvious to me is that a comparison of all data in the manuscript with literature data is essential as well as a discussion of discrepancies of these datasets.

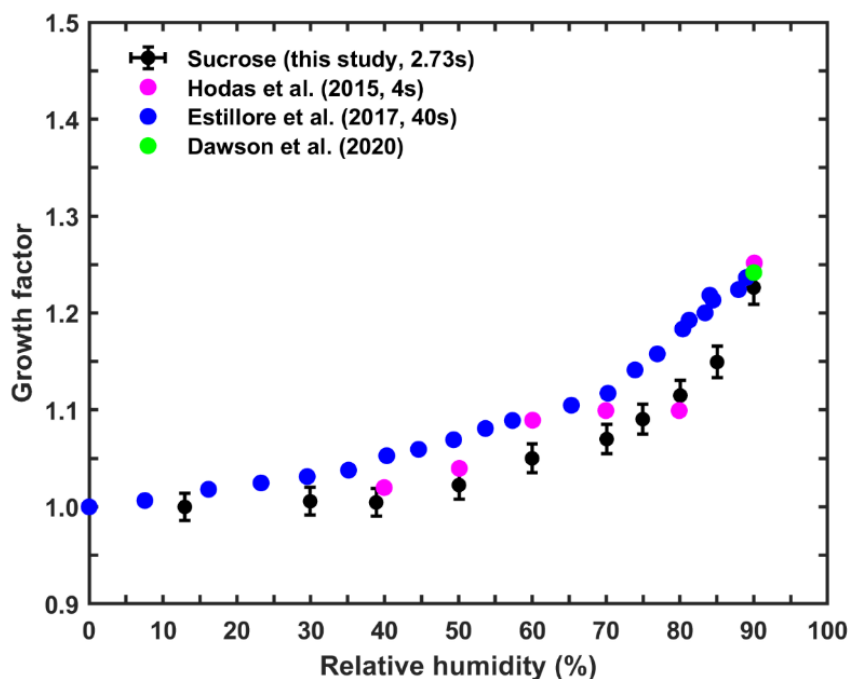
Third, I feel the authors did not describe the UManSysProp on-line model well enough. As far as I understand, it is based on AIOMFAC for calculating the water activity (or did the authors assumed it to be ideal?). Hence it is clear that the curves shown in Fig. 1a of the manuscript for the dicarboxylic acid describe the liquid state hygroscopicity and cannot compared to the data if the experiments are

done with crystalline particles. Again, a comparison would be possible only if the supersaturated liquid particle were studied experimentally.

There are several options for selections with the UManSysProp web-model, for example the method to estimate supersaturated density. The authors do not write which method they used nor why they selected a particular one.

I feel, given the considerable discrepancies between the data presented and other datasets, it is not appropriate to judge which thermodynamic model represents the data better as done by the authors for the dicarboxylic acids.

Fourth, I appreciate the authors address the issue of kinetic limitations to water uptake in their text now, but they do not show how significant the effect could be. In the reply to my question, they provided a nice figure, which I copy here and which in my eyes show the problem unambiguously. It nicely shows that at low RH with high viscosity of the sucrose the authors do not reach water equilibrium while at high RH with water acting as a plasticizer they do. This figure may also explain the differences in the malic acid figure above?



However, the author ones more do not include this figure in the revised manuscript. Why? This figure needs to be discussed together with the added text!

Overall, I conclude that the manuscript requires at least a major revision with a comparison of all data to the data available in the literature, so that a reader sees the discrepancies and are not left with the impression that there are no other data available and also clearly see the limitations of the technique the authors have been using.