

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-486

Anonymous Referee #2

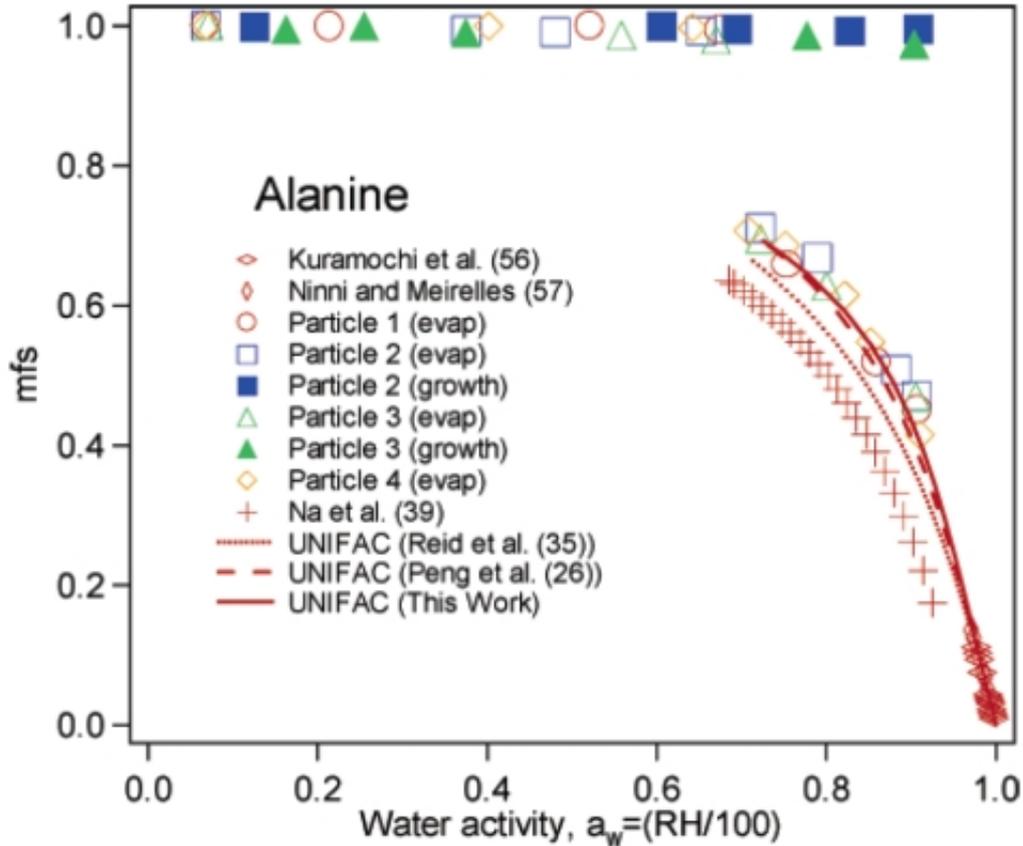
Referee comment on "Hygroscopicity of organic compounds as a function of organic functionality, water solubility, molecular weight, and oxidation level" by Shuang Han et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-486-RC2>, 2021

The authors present hygroscopicity data for 23 organic compounds measured with an HTDMA instrument. They compare these data with two thermodynamic models (AIOMFAC and E-AIM) and conclude that the models do not represent the hygroscopicity well.

Unfortunately, the study is conceptually flawed. The experimental design allows studying the hygroscopic growth starting from dry conditions to elevated relative humidities. This way, as the authors illustrate in Fig. S2 for an inorganic salt (ammonium sulfate), they can only probe the properties of the aqueous system at relative humidities, beyond those corresponding to the solubility limit of each binary system. However, what is relevant for the atmospheric application, where an aerosol particle consist of a multitude of organic compounds, is the water activity (or hygroscopicity) of the liquid state, because the organics will not crystallize under realistic atmospheric conditions (e.g. Marcolli et al., 2004).

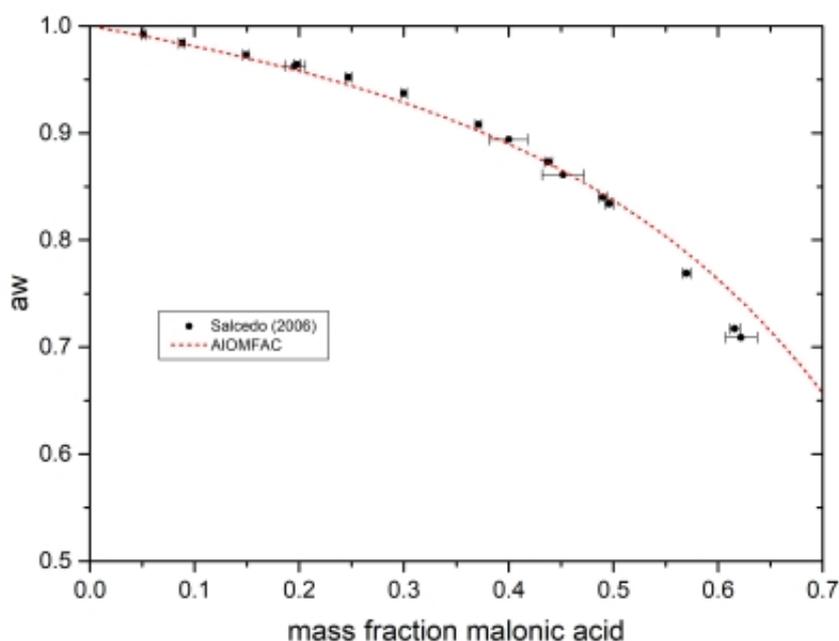
The HTDMA instrument as used by the authors probe only the thermodynamics of the 23 binary systems in the water activity range, which is accessible to bulk methods, the technique used here is simply not appropriate to determine thermodynamic data with high accuracy.

This is best illustrated by comparing the data presented in this work for the amino acid alanine with previous data by Chan et al. (2005):



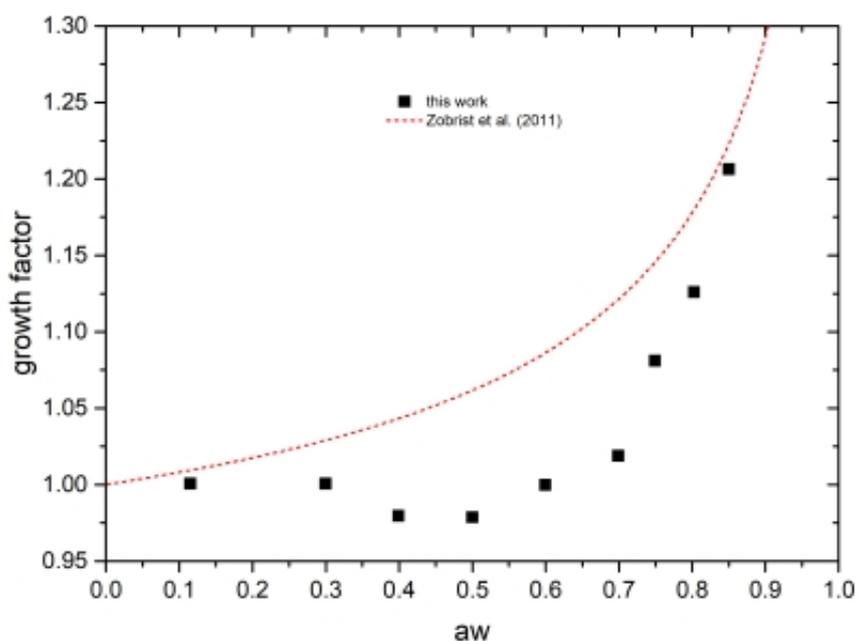
The authors observe no growth up to a relative humidity of 90 % which seems to be the highest they can reach in their setup. That is consistent with the data of Chan et al. upon humidification. But the data of interest are the ones when starting at high humidity and drying which the metastable, subcooled binary liquid being probed. These can be compared to the thermodynamic data as done by Chan et al. (2005) for different UNIFAC parameterizations.

In addition to this conceptual flaw, the experimental data raise questions as well. In Fig. 1(a) the authors observe considerable deviations between their data for malonic acid and the AIOMFAC model in the range of 60% to 80 % RH. However if I compare AIOMFAC with existing experimental bulk data the agreement is very satisfactory in the same range of humidities:



As the bulk data are clearly the reference, the authors need to explain the difference to those, before concluding that the thermodynamic models are failing for the binary aqueous components. One possible reason could be that the authors are using ideal mixing to convert from size growth to mass concentration?

And a last comment. Sucrose has been used as a proxy for viscous or even glassy aerosol particles during the last years in a large number of studies. Its hygroscopicity is very well established. However, the authors do not at all compare their data with data available in the literature. Besides this problem, it is obvious that they are not aware of the kinetic limitations to water uptake by viscous aerosol. Most likely, the short residence time in the HTDMA limits the water uptake for aqueous sucrose at intermediate and low humidities. This can be seen by comparing the data of this work with standard parameterizations for hygroscopicity of sucrose (e.g. Zobrist et al, 2011):



The gap between measurement and parameterization at RH smaller about 0.8 is probably due to kinetic water uptake limitations.

Overall, I feel this work does not contribute much new science, needs more thorough comparison to existing literature. It also uses a method not really suited for determining water activity of binary systems if the interest is in comparing to thermodynamic models.

References:

Chan et al., Environ. Sci. Technol. 2005, 39, 1555-1562.

Marcolli et al., J. Phys. Chem. A 2004, 108, 2216-2224

Salecedo, J. Phys. Chem. A 2006, 110, 12158-12165

