

Response to comments by anonymous referee #2:

The manuscript by Lei et al. reported the HTDMA data for levoglucosan and D-glucose particles for the size range of 6 ~ 100 nm. Both of these compounds are atmospherically important chemical species. The data for 100 nm particles agreed well with literature. In the case of levoglucosan particles, measurement of hygroscopicity for particles smaller than 15 nm was challenging due to evaporation. The issue was not observed for D-glucose. In the case of D-glucose particles, a significant size-dependence in hygroscopic growth was observed only for the high RH (RH > 80%) region. The data of the study will serve as a reference for future studies on hygroscopicity of atmospheric nanoparticles. The topic is obviously a part of the scope of the research community. The following points should be considered prior to the acceptance of the manuscript.

Response: We are grateful to referee #2 for the comments and the constructive suggestions. We address in the following the comments and suggestions by referee #2 and provide improvements based on these clarify the questioned issues in the revised manuscript in red. We repeat the specific points raised by the reviewer in italic font in blue, followed by our response. The lines mentioned are with respect to the Atmospheric Chemistry and Physics Discussions (ACPD) version.

Major comments:

(1) The authors state that the UNIFAC model does not provide highly accurate results for organic compounds which contains many polar functional groups (e.g., the description starts from L354). However, the discussion is not well supported by references. Thus, it is difficult for a reader to evaluate the level of uncertainty. As D-glucose is an important chemical compound in various research areas, a numerous number of studies should have been conducted for investigating its interaction with water. It would be great if the authors could provide further detailed discussion using these references to support their argument.

Response: Thanks for the comments. According to the previous studies (Fredenslund et al., 1975; Hansen et al., 1991; Fredenslund and Sørensen, 1994; Mochida and Kawamura, 2004; Lei et al., 2014, 2018), the UNIFAC model was not recommended to predict the hygroscopic behavior of organics whose polar functional groups are separated by less than three or four carbon. For example, Mochida and Kawamura (2004) reported a large disagreement between the UNIFAC model prediction and hygroscopic measurements of levoglucosan and D-glucose containing OH groups

in series, indicating the UNIFAC model without consideration intramolecular interaction. We have removed the following sentence as it is discussed in line 361-364 “Note that, E-AIM (standard UNIFAC) model prediction is optimized for organic compounds with lesser polar groups in series, i.e., intramolecular interaction, such as hydrogen bond between polar 356 groups, may result in model prediction inaccuracy.”

The hygroscopic properties of D-glucose aerosol particles are investigated by many groups (Mochida and Kawamura, 2004; Chan and Chan, 2005; Suda and Petters, 2013; Estillore et al., 2017; Mikhailov and Vlasenko, 2020). We have added more discussion as follows:

Line 357-366, we added references and revised: “Figure 9a and Fig. S3 show that the measured growth factors of 100-nm D-glucose nanoparticles are lower than predicted growth factors from E-AIM (standard UNIFAC) model, especially at RH below 85 %. Also, E-AIM (standard UNIFAC) model could predict well the measured hygroscopic growth factor of 6-nm D-glucose aerosol nanoparticles at RH above 40 % shown in Fig. 9a and Fig. S3. The possible reason for discrepancies between E-AIM (standard UNIFAC) model and measurements is inaccurate thermodynamic parameters (e.g., water activity, surface tension) estimated by the E-AIM (standard UNIFAC) model without consideration intramolecular interaction (Fredenslund et al., 1975; Hansen et al., 1991; Fredenslund and Sørensen, 1994; Mochida and Kawamura, 2004). D-glucose contains five OH groups in series, hydrogen bond could potentially exist and affects the E-AIM (standard UNIFAC) model-measurement agreement for D-glucose aerosol nanoparticles system (Mochida and Kawamura, 2004; Lei et al., 2014, 2018).”

Line 325-328, we added references and revised: “Also, measured hygroscopic growth factors of 100-nm D-glucose are consistent with results from previous studies (Mochida and Kawamura, 2004; Chan and Chan, 2005; Suda and Petters, 2013; Estillore et al., 2017; Mikhailov and Vlasenko, 2020). For example, Mikhailov and Vlasenko, (2020) investigated the hygroscopic behavior of 100-nm D-glucose aerosol particles using a HHTDMA in hydration, dehydration, and restructuring modes of operation, respectively. A clear morphology effect on the hygroscopicity of D-glucose aerosol particles is observed in the RH range from 2 % to 96 % RH.”

(2) It is interesting that the authors only observed the size-dependence in growth factor of D-glucose for the range of RH > 80%. There seems to be no size dependences for the lower RH region. To the best of the reviewer’s knowledge, it is not a well-known phenomenon. Do the authors have any potential hypothesis for explaining it? I believe that it will be beneficial for future studies if the author could add some ideas that can explain the observation to the manuscript.

Response: Thanks for the comments. Our hypothesis is that the distinct behaviors between high RH and low RH region can be attributed to the distinct size effect on the hygroscopic growth and adsorption, i.e., the growth factor shows size dependence only in the regime of hygroscopic growth ($RH > 80\%$), and not in the regime of water adsorption ($RH < 80\%$). We have included this hypothesis in the revised manuscript.

Related additions and changes included in the revised manuscript:

Line 340-342, we added references and revised: “There is no evident difference in hygroscopic growth factors of D-glucose nanoparticles at RH below 80 % in size range from 6 to 100 nm. The reason that the growth factor shows size dependence only in the regime of hygroscopic growth ($RH > 80\%$), and not in the regime of water adsorption ($RH < 80\%$) has not been explained before. Our hypothesis is that the distinct behaviors between high RH and low RH region can be attributed to the distinct size effect on the hygroscopic growth and adsorption, i.e., the growth factor shows size dependence only in the regime of hygroscopic growth ($RH > 80\%$), and not in the regime of water adsorption ($RH < 80\%$).

Minor comments:

(1) abstract: The current abstract is a little bit long and redundant. It describes what the authors have done, but it does not tell the key conclusions of the manuscript well. I suggest the authors to revise it.

Response: Thank you for the comments. We have revised the whole abstract section, and now they read as:

Line 13-41: Abstract: The interaction between water vapor and aerosol nanoparticles is important in atmospheric processes. Hygroscopicity of sub-10 nm organic nanoparticles and their concentration-dependent thermodynamic properties (e.g., water activity) in the highly supersaturated concentration range are, however, scarcely available. Here we investigate the size dependence of hygroscopicity of organics (i.e., levoglucosan, D-glucose) in dry particle diameter down to 6 nm using a nano-hygroscopicity tandem differential mobility analyzer (nano-HTDMA). Our results show that there is only a weak size dependent hygroscopic growth of both levoglucosan and D-glucose nanoparticles with diameters down to 20 nm. In the diameter range smaller than 20 nm (down to 6 nm), we observed a strong size-dependent hygroscopic growth for D-glucose nanoparticles. The hygroscopic growth factors cannot be determined for levoglucosan below 20 nm due to its evaporation. In addition, we compare hygroscopicity measurements for levoglucosan

and D-glucose nanoparticles with the E-AIM (standard UNIFAC), the ideal solution theory, and DKA predictions, respectively. The ideal solution theory describes well the measured hygroscopic growth factors of levoglucosan with diameters down to 20 nm and D-glucose nanoparticles with diameters higher than 60 nm, respectively, while the E-AIM (standard UNIFAC) model can successfully predict the growth factors of D-glucose nanoparticles with diameters from 100 down to 6 nm at RH above 88-40 % (e.g., at RH above 88 % for 100 nm D-glucose, at RH above 40 % for 6 nm D-glucose). The use of the DKA method leads to a good agreement with measured hygroscopic growth factors of D-glucose aerosol nanoparticles with diameters from 100 down to 6 nm. Predicted water activity for these aqueous organic solutions (i.e., levoglucosan, D-glucose) from different parameterization methods agrees well with observations in the low solute concentration range ($< 20 \text{ mol kg}^{-1}$), and start to deviate from observations in the high solute concentration ($> 20 \text{ mol kg}^{-1}$).”

(2) Mochida and Kawamura (2004) are cited for three times for describing the atmospheric significance of levoglucosan and D-glucose. However, the paper by Mochida and Kawamura (2004) focused on hygroscopicity measurement of levoglucosan and other important marker compounds for biomass burning. Other references that directly supports the corresponding descriptions need to be provided.

Response: Thank you for your comments. There are several references supporting the descriptions. For example, Bhattarai et al. (2019) reported the chemical composition of the WSOC fraction of particles generated biomass burning. On the basis of chemical structure, neutral compounds mainly consist of sugar-like compounds such as levoglucosan and D-glucose, which are the most abundant oxygenated products of the pyrolysis of cellulose.

We have added these corresponding references into the revised manuscript:

Line 58-64, we added references and revised: “Also, levoglucosan is typically the most abundant species in wood burning aerosols, which contributes substantially (16.6–30.9% by mass) to the total organics in $\text{PM}_{2.5}$ (Mochida and Kawamura, 2004; Bhattarai et al., 2019). D-glucose, a hydrolysis product of cellulose and levoglucosan, is a major pyrolysis product of wood (Mochida and Kawamura, 2004; Bhattarai et al., 2019; Mikhailov and Vlasenko., 2020). Levoglucosan and D-glucose substances may be representative in reproducing the hygroscopic behavior of the real biomass burning aerosol particles (Bhandari and Bareyre. 2003; Mochida and Kawamura, 2004; Chan et al., 2005; Koehler et al., 2006; Peng et al., 2010; Mikhailov and Vlasenko., 2020).”

(3) I agree that levoglucosan and D-glucose are important chemical species for biomass burning particles. However, they would probably be one of the most polar chemical species among constituents of biomass burning particles. It is not clear to me if they can be considered as representative compounds for hygroscopicity.

Response: Thank you for your comments.

We have revised “Levoglucosan and D-glucose substances may be representative in reproducing the hygroscopic behavior of the real biomass burning aerosol particles.” **as** “Hygroscopicity of levoglucosan and D-glucose substances is thus important in reproducing the overall hygroscopic behavior of the real biomass burning aerosol particles.”

Related additions and changes included in the revised manuscript:

Line 61-64, we added references and revised: “Hygroscopicity of levoglucosan and D-glucose substances is thus important in reproducing the overall hygroscopic behavior of the real biomass burning aerosol particles. For example, a small difference in the hygroscopicity parameter (κ) between measured data of model mixtures including levoglucosan and ammonium sulfate in the laboratory using HTDMA and biomass burning aerosol particles in the field using CCN activity measurement due to the similar O: C ratios of levoglucosan and ammonium sulfate mass fractions used in model mixtures when experimental κ data from sub- and supersaturated water vapor conditions are compared (Bhandari and Bareyre, 2003; Mochida and Kawamura, 2004; Chan et al., 2005; Koehler et al., 2006; Peng et al., 2010; Pöhlker et al., 2016; Lei et al., 2018; Mikhailov and Vlasenko., 2020).”

(4) L123-125 Generally, the issue of multiple charge particles is not a significant concern for small (diameter < 30 nm) particles. Could the authors make the corresponding description to be more detailed?

Response: Thank you for your comments. Yes, reviewer is right, the influence of multiple charges on sub-10 nm particles is expected to be very small. However, the different concentrations are used to make sure that the sizes selected by the nano-DMA1 are always around the peak of the number size distribution of the nanoparticles generated by the electrospray. This is to ensure that we could have as many particles as possible to compensate for the strong loss of very small particles in the whole humidification system.

Related additions and changes included in the revised manuscript:

Line 123-125, we revised: “Note that the size selected by the nano-DMA1 should be the right part of peak diameter of the number size distribution of the generated nanoparticles, which minimizes

the influence of the multiple charged nanoparticles in hygroscopicity measurements. This is to ensure that we could have as many particles as possible to compensate for the strong loss of very small particles in the whole humidification system.”

(5) L169 The equation (2) looks like an equation for the ideal solution to me. Although the idea of ideal solution can occasionally be applied for the Köhler theory, the Köhler theory is not equivalent as the ideal solution. It would be better to change the name of the corresponding section.

Response: Thank you for your comments. Equation (2) is the Simplified Köhler Theory (SKT) for ideal and diluted solution. We have revised “Köhler” as “SKT” in the whole manuscript.

Line 26, 106, 166, 233, 234, 235, 314, and 399, we revised “Köhler” as “SKT”.

Line 692-695 and Line 758-762:

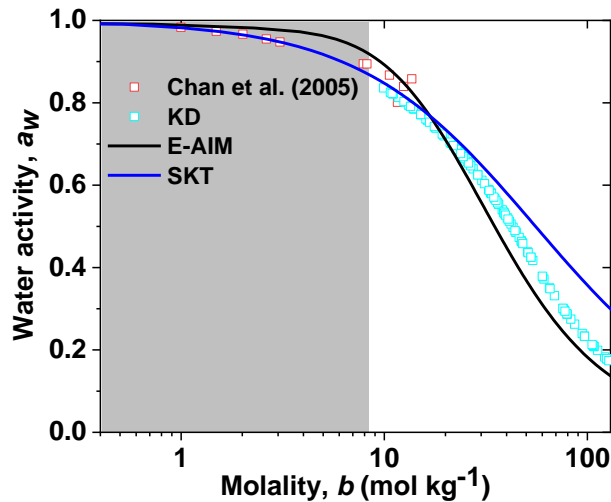


Figure 2. Concentration-dependent water activity (a_w) of levoglucosan solution. The KD-derived a_w (KD=Kreidenweis, cyan open square) is compared with observations (red open square), E-AIM (Extend-Aerosol Inorganic Model, black line), and a_w model (SKT, blue line). The light grey shaded areas mark the sub-saturated concentration with respect to bulk solution.

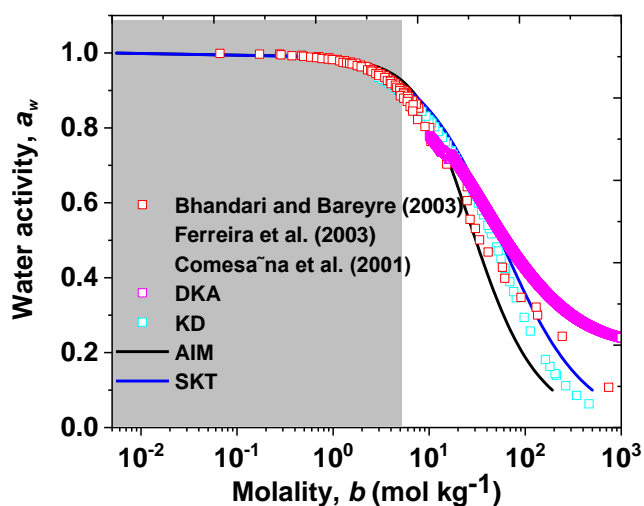


Figure 6. Concentration-dependent water activity (a_w) of D-glucose solution. The DKA-derived a_w (Differential Köhler Analysis, magenta open square) is compared with observations (red open square), E-AIM (Extend-Aerosol Inorganic Model, black line), a_w model (SKT, blue line), and parameterization model for a_w (KD=Kreidenweis, cyan open square). The light grey shaded areas mark the sub-saturated concentration with respect to bulk solution.

(6) L235 I wonder what the author's definition of 'diluted aqueous droplet' is. 20 mol kg-1 is highly concentrated. Please clarify.

Response: Thank you for your comments. We have removed the “diluted” and only mentioned the concentration. .

(7) L237 Please indicate the saturation concentration of levoglucosan in water before mentioning about supersaturation.

Response: Thank you for your comments. According to Zamora et al. (2011), the solubility of levoglucosan is 8.23 mol/kg at 20°C.

We have marked saturation concentration of levoglucosan in the following Fig. 2.

Related additions and changes included in the revised manuscript:

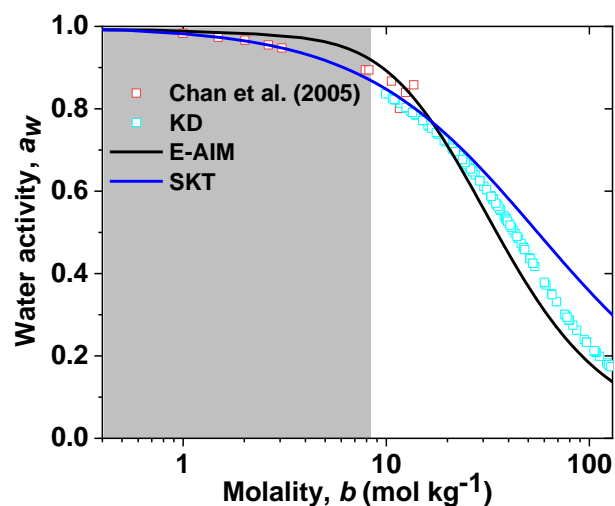


Figure 2. Concentration-dependent water activity (a_w) of levoglucosan solution. The KD-derived a_w (KD=Kreidenweis, cyan open square) is compared with observations (red open square), E-AIM (Extend-Aerosol Inorganic Model, black line), and a_w model (SKT, blue line). The light grey shaded areas mark the sub-saturated concentration with respect to bulk solution.

(8) L248 (and other places) No deliquescence/efflorescence were observed in the study. It may not be appropriate to call the operation modes of the HTDMA as ‘deliquescence/efflorescence modes’ under this condition. Hydration/dehydration might be a better expression.

Response: Many thanks. They are the same, and thus we have changed the notion of hydration and dehydration mode to deliquescence and efflorescence modes to avoid confusion.

(9) Reference: The reference list needs to be carefully checked. There are numerous issues. For instance, I do not believe that the names of the authors of the following paper accurately represented in the current version of the manuscript.

Response: Many thanks. We have carefully checked and revised all reference format, and now they read as:

Line 458-459: Chan, M. N. and Chan, C. K.: Mass transfer effects in hygroscopic measurements of aerosol particles, *Atmos. Chem. Phys.*, 60 5, 2703–2712, <https://doi.org/10.5194/acp-5-2703-2005>, 2005.

Reference

- Bhattacharai, H., Saikawa, E., Wan, X., Zhu, H., Ram, K., Gao, S., Kang, S., Zhang, Q., Zhang, Y., Wu, G., Wang, X., Kawamura, K., Fu, P., and Cong, Z.: Levoglucosan as a tracer of biomass burning: Recent progress and perspectives, *Atmos. Res.*, 220, 20–33, 2019.
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- Mochida, M. and Kawamura, K.: Hygroscopic properties of levoglucosan and related organic compounds characteristic to biomass burning aerosol particles, *J. Geophys. Res.*, 109, D21202, <https://doi.org/10.1029/2004JD004962>, 2004.
- Lei, T., Zuend, A., Cheng, Y., Su, H., Wang, W., and Ge, M.: Hygroscopicity of organic surrogate compounds from biomass burning and their effect on the efflorescence of ammonium sulfate in

mixed aerosol particles, *Atmos. Chem. Phys.*, 18, 1045–1064, <https://doi.org/10.5194/acp-18-1045-2018>, 2018

Pöhlker, M. L., Pöhlker, C., Ditas, F., Klimach, T., Hrabec de Angelis, I., Araújo, A., Brito, J., Carbone, S., Cheng, Y., Chi, X., Ditz, J., Gunthe, S. S., Kesselmeier, J., Könemann, T., Lavrič, J. V., Martin, S. T., Mikhailov, E., Moran-Zuloaga, D., Rose, D., Saturno, J., Su, H., Thalman, R., Walter, D., Wang, J., Wolff, S., Barbosa, H. M. J., Artaxo, P., Andreae, M. O., and Pöschl, U.: Long-term observations of cloud condensation nuclei in the Amazon 110 rain forest – Part 1: Aerosol size distribution, hygroscopicity, and new model parametrizations for CCN prediction, *Atmos. Chem. Phys.*, 16, 15709–15740, <https://doi.org/10.5194/acp-16-15709-2016>, 2016

Romakkaniemi, S., Hämeri, K., Väkevää, M., and Laaksonen, A.: Adsorption of Water on 8–15 nm NaCl and (NH₄)₂SO₄ Aerosols Measured Using an Ultrafine Tandem Differential Mobility Analyzer, *The Journal of Physical Chemistry A*, 105, 8183–8188, 2001.

Zamora, I., Tabazadeh, A., Golden, D., and Jacobson, M.: Hygroscopic growth of common organic aerosol solutes, including humic substances, as derived from water activity measurements, *Journal of Geophysical Research (Atmospheres)*, 116, 23207, [10.1029/2011JD016067](https://doi.org/10.1029/2011JD016067), 2011.