Response to Anonymous Referee #2 on “Influence of Organic Compound Functionality on Aerosol Hygroscopicity: Dicarboxylic Acids, Alkyl-Substituents, Sugars and Amino Acids”

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The authors would like to thank the referee for their generally positive comments on the quality of the manuscript. We respond to the specific comments made by the referee below and identify the changes we have to the manuscript.

<u>Referee Comment:</u> *Page 1 line 12 “The dual micro dispenser set up allows for sequential trapping of probe and sample droplets for accurate determination of droplet water activities from 0.45 to > 0.99.” This sentence is not entirely correct. The CK-EDB is based on kinetic measurements and it does have the advantage of fast measurements that reduce evaporation of volatile materials.*

<u>Response:</u> In prior publications we have provided considerable data that confirm the validity of the technique for a wide range of inorganic and organic systems. See particularly:

Rovelli, G., Miles, R. E. H., Reid, J. P., & Clegg, S. L. (2016). Hygroscopic Properties of Aminium Sulphate Aerosols. Atmospheric Chemistry and Physics Discussions. https://doi.org/10.5194/acp-2016-959

Rovelli, G., Miles, R. E. H., Reid, J. P., & Clegg, S. L. (2016). Accurate Measurements of Aerosol Hygroscopic Growth Over a Wide Range in Relative Humidity. The Journal of Physical Chemistry A, 120, 4376−4388. https://doi.org/10.1021/acs.jpca.6b04194

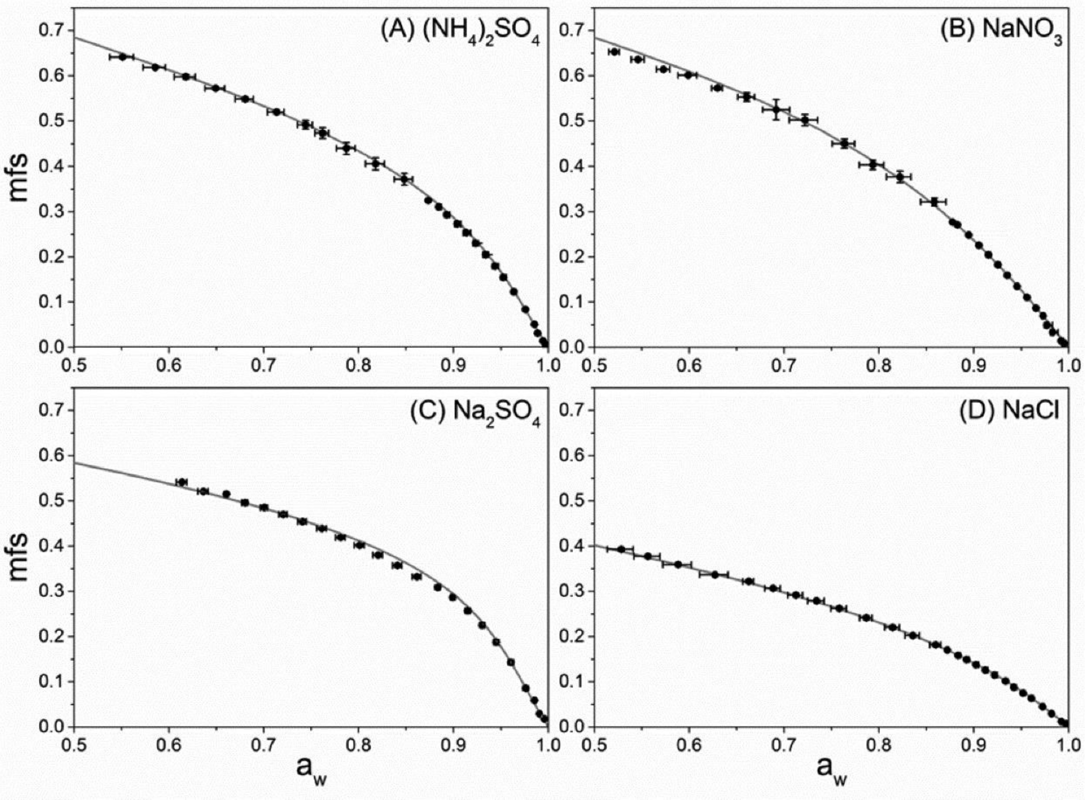
Davies, J. F., Haddrell, A. E., Rickards, A. M. J., & Reid, J. P. (2013). Simultaneous Analysis of the Equilibrium Hygroscopicity and Water Transport Kinetics of Liquid Aerosol. Analytical Chemistry, 85, 5819–5826. https://doi.org/dx.doi.org/10.1021/ac4005502

The referee is correct in suggesting that the measurements are in essence kinetic, however we still consider that our statement is accurate. Compared with the timescale of internal dynamics within the droplet (diffusional mixing, heat transport), the evaporative process may actually be considered to be sufficiently slow that the droplet adopts a uniform composition, a particular water activity and, consequently, the equilibrium vapour pressure for the solution composition at that moment in time. Indeed, based on the expression for the mass flux, equation (5), it is the water activity in the droplet that is the determining quantity and it is this that is measured.

<u>Referee Comment:</u> *However, the fast measurements would also potentially lead to non-equilibrium measurements, especially for some organics at low RH. The authors seem to admit a potential shortcoming of the technique on page 11, line 23, “For many compounds, measurements unimpeded by kinetic limitations have not been possible below 80 % RH, and consequently data presented below 80 % do not average to a consistent series of points”. More evidence to demonstrate that the measurements presented in this paper are equilibrium measurements would be needed.*

<u>Response:</u> We have responded in detail to this comment in our response to referee #1. In brief, we have clearly shown in our earlier publications that equilibrium hygroscopicity curves can be retrieved with high accuracy. We reproduce below Figure 5 from Rovelli et al. (2016) as an example, comparing hygroscopicity measurements of inorganic salts taken using the CK-EDB with equilibrium thermodynamic model predictions,

all of which are in very good agreement. For some organic components that lead to viscous droplets on drying, departure from equilibrium behaviour with varying water content is clearly apparent from the measurements. We show in our response to referee #1 (and discuss further below) that the hygroscopicity measurement remains extremely accurate unless the viscosity increases above 0.1 Pa s. We have included the data for such systems in this manuscript to be entirely transparent and to demonstrate when the approach does not work, as well as showing when it does.



Measured mfs vs *a*w plots for $(NH_4)_2SO_4$, $NaNO_3$, Na_2SO_4, and NaCl (panels A–D). Symbols: filled circles, experimental data; solid lines, calculation from the E-AIM model. Note: error bars are smaller than the data point when not shown.

<u>Referee Comment:</u> Page 1 line 15: This significance of this sentence is not clear. New data agree better with the UNIFAC predictions than the old data, from which UNIFAC parameters were derived, do. Are the UNIFAC parameters/predictions useful or not?

<u>Response:</u> The reproducibility of our measurement is much better than that of Peng et al. and, thus, our method is much better equipped to help refine the UNIFAC model parameters than the work of Peng et al.

<u>Referee Comment:</u> Page 1 line 22 - The authors should discuss the agreement between the measured hygroscopicities and UNIFAC predictions on sugars/alcohols.

<u>Response:</u> The level of agreement between the measurements and predictions for the sugars/alcohols is highly system dependent and no general statements can be made. Instead, we have added the phrase: “and show variable levels of agreement with predictions” to the end of line 22.

<u>Referee Comment:</u> Page 8, line 25: "In addition, the short timescale of the measurement ensures that evaporation of the semi-volatile components, such as these dicarboxylic acids, is avoided". Has this been verified or is this merely an assumption? Did they experimentally verify this with some other semi-volatile solutes? Can they really say that evaporation is avoided? In reality, there must be a range of vapor pressure

that evaporation is "negligible" but appreciable at larger values.

Response: As a first indicator, it is clear that the evaporation of water (with a gradient in vapour pressure of >100 Pa from the droplet surface to infinite distance at ~80 % RH) occurs in a timescale of ~ 10 s. Thus, components less than 1 Pa can be expected to take >1000 s to evaporate. More precisely, we can estimate the lower limit in vapour pressure that the CK-EDB is sensitive to in a 10 s period, equivalent to the hygroscopicity measurement timescale. The uncertainty in radius in a CK-EDB measurement is ± 100 nm. Then, assuming a droplet size change from 10.1 to 10 μm in the measurement period of 10 s due to volatilisation, we can infer the vapour pressure of the volatile component, p_i (Pa) would be 0.43 Pa, using the Maxwell equation:

$$\frac{dr^2}{dt} = -\frac{2M_i D_i}{RT\rho} p_i \qquad (1.0)$$

r is radius (m), t is time (s), M_i is molecular weight (kg mol^{-1}, taken here as 100 g mol^{-1}), D_i is the gas phase diffusion constant (~1×10^{-5} m^2 s^{-1}) , R is the ideal gas constant, T is the temperature (K) and ρ is the droplet solution density (kg mol^{-1}, taken here as 1.46 g cm^{-3}). This is considerably more volatile than any of the species that we investigate in this study; for example the vapour pressure of malonic acid (one of the most volatile species in this study) is 10^{-4} Pa. Thus, during the timescale of the measurement only water is lost from the droplet.

Referee Comment: Page 10, line 1 - "In summary, UNIFAC predictions agree well with measurements for simple unbranched dicarboxylic acids with the exception of pimelic acid," Is there any explanation why the UNIFAC cannot predict the hygroscopicity of pimelic acid? Can the authors provide suggestions to make improve the predictions of UNIFAC?

Response: We can only comment that pimelic acid was not included in the original compounds used to parametrise the UNIFAC groups for the dicarboxylic acids.

Referee Comment: Page 10, line 30 - "The model (equation 27 in Dutcher et al. 2013) is fitted to molality experimental data with respect to water activity for finding the parameter value, which results in a significant improvement in the MFS than UNIFAC." Why does the multilayer adsorption isotherm based model from Dutcher et al. (2013) give a better prediction beyond the use of an adjustable parameter?

Response: We agree that this was not clear. The sentences now read (P10 L30): "The model (equation 27 in Dutcher et al. 2013) is fitted to experimental data for solute molality as a function of water activity, in order to determine the adjustable model parameter. The model predicts solute activities and concentrations across all water activities, by combining short-range adsorption isotherm and long-range Debye-Huckel expressions. The isotherm model results in improvement in MFS predictions when compared to UNIFAC. However, the notable difference in accuracy between the two models is not overly surprising: the isotherm based model of Dutcher et al. 2013 has an adjustable parameter (Table S0.2), while UNIFAC is a fully predictive model."

Referee Comment: Page 10 line 20. From Figure 8a, it seems L-threonine, rather than L-valine, deviates from the other three compounds most.

Response: We agree with the reviewer and have amended the sentence Page 10 line 20 "On a MFS scale, the hygroscopic response of these compounds is similar except for L-threonine which is less hygroscopic, an observation that is not expected given the additional hydrophilicity of the hydroxyl substituent."

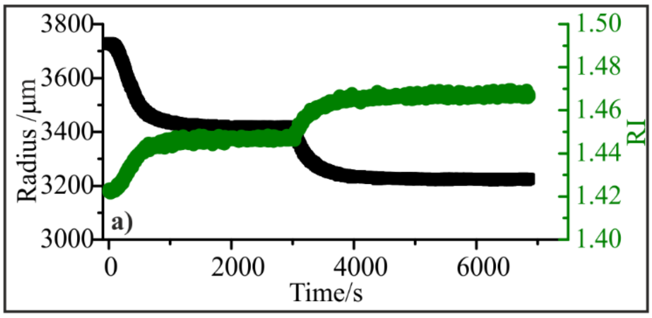
Referee Comment: Page 11 line 6: Is there any other possible explanation for the discrepancy between measured and literature (Chan et al., 2005) data on those amino acids? Can they rule out the possibility of mass transfer effects or evaporation of solute? They show that their data are consistent with Na et al. (1995), which are compromised by evaporation of solute since they made EDB measurements in vacuum. Furthermore, Chan et al. also made measurements of these amino acids to lower RH to determine the mfs of solid of unity. The assertion that Chan et al. were wrong, which is possible, need to be accompanied by the discussions on *how that would affect the mfs of the dried particles. Would the new data provided here yield unreasonable mfs of the dried particles?*

<u>Response:</u> Volatilisation is not a concern for the amino acid measurements on the timescale of our measurement: once solvated in water, amino acids become zwitterionic and behave more like inorganic salts. In addition, in our previous response we have shown that volatilisation is insufficient to give any appreciable change in composition during the measurement time frame for any component with a vapour pressure less than 1 Pa. At a MFS as low as 0.0075, the pH of an aqueous solution of glycine is high enough for nearly 100 % of the solution to contain zwitterionic amino acid species (Kuramochi et al. (1997)). To further confirm this, we show below measurements made using the aerosol optical tweezers technique for an aqueous glycine droplet, suspended at variable RH's for thousands of seconds. Even over such prolonged periods, once water was removed following a step in RH from 75 % to 55 %, there was minimal observed volatilisation. For example, over a period of 1000 s, the size decreases from 3227 to 3218 nm (between times of 5000 and 6000 s). Thus, over a 10 s measurement time in our CK-EDB measurements, volatilisation can be ignored. By contrast, the data taken by Chan et al. (2005) require much longer confinement of droplets in the EDB (10 – 20 hours) (Chan et al., 2005).

Further, our CK-EDB measurements reach a sufficiently high enough RH to *overlap* with all bulk data available from Kuramochi et al. (1997) and Ninni and Mereilles (2001), which both show very good agreement. Instead, we believe that the discrepancy between our data and that of Chan et al. arises because of the extrapolation required to reconcile their first aerosol phase measurement (at the highest water activity) with the bulk data.

Based on these two facts, our data are not compromised by volatilisation and overlap with bulk data where available. By contrast, neither of these two concerns can be ignored when considering the data of Chan et al. We must stress that there are challenges associated with these measurements, particularly in reaching a high enough water activity to overlap and compare with bulk data, a challenge which our technique is able to address.

Chan, M. N., Choi, M. Y., Ng, N. L., and Chan, C. K.: Hygroscopicity of Water-Soluble Organic Compounds in Atmospheric Aerosols, Environ. Sci. Technol., 39, 1555-1562, 2005.



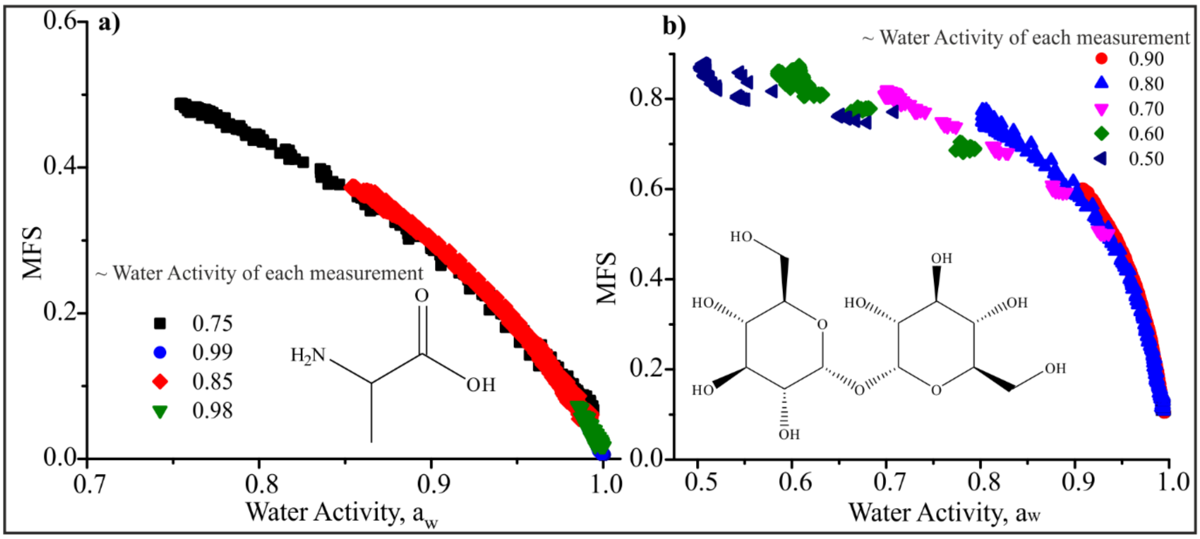
Glycine hygroscopicity experiment a) Radius vs time and RI vs time.

<u>*Referee Comment:*</u> *Page 11 line 23: It is unclear why kinetic limitations will not affect the hygroscopicity measurements of sugars and alcohols in this study by saying "as established by the RH of the gas phase the droplet is drying in". Elaborate please.*

<u>Response:</u> We have added the following discussion and Figures to the SI, "The kinetic modelling framework used in the analysis of the droplet evaporation events is valid only in the absence of a bulk-kinetic limitation on near surface composition, i.e. the particle must be assumed to be homogeneous in composition. Such a limitation was obvious for hygroscopicity measurements of trehalose, galactose and sorbitol at RH's lower than 80 %. To ensure the measurements are not compromised by bulk diffusion, we consider two important factors.

Firstly, the impact of viscosity on the hygroscopicity retrievals becomes very obvious when we consider the consistency and uncertainty in the raw hygroscopic growth curves determined from different droplets evaporating into differing RHs. Droplets drying into different RHs reach different compositions at different times, and will retain different amounts of water because of different drying rates. This leads to an artificially low MFS at a particular RH which then slowly returns to the equilibrium curve overtime. Thus, an inconsistency is apparent between retrieved hygroscopic growth curves (or MFS vs a_w) when drying into different RHs. An example of this is shown in Figure S39.1, where we report unbinned hygroscopicity data for alanine (a non-viscous amino acid) and trehalose (viscous at RHs lower than 80%). It is clear here that the different portions of the hygroscopic curves retrieved from measurements at different RHs are consistent for alanine but not for trehalose. A further easy way to identify this retention of water in a particle that is not fully equilibrated is simply to measure the much longer time-dependence in size once the initial evaporation of water has stopped. In droplets that have reached a bulk diffusion limitation, the existence of a kinetic limitation is apparent in a steadily decreasing size as water continues to leave over a timescale longer than 10 s.

Fig S39.1 a) Unbinned hygroscopicity data for the compound alanine. b) Unbinned hygroscopicity data for the compound trehalose. At 50 % RH trehalose has a viscosity of 3.8 x 10^5 Pa.s (Song et al. 2016).



Secondly, we can determine the expected conditions under which we might expect problems to arise in retrieving hygroscopic growth curves from an evaporation measurement. Considering again trehalose at 80 % RH, an aqueous-trehalose droplet has a viscosity of 0.5 Pa.s, increasing to 3.8 × 10^5 Pa.s at 50 % RH (Song et al. 2016). Therefore, as the RH of the gas phase for the evaporation measurement is lowered, we can expect the increasing viscosity/decreasing diffusivity to become increasingly important. By contrast, for aqueous-carboxylic acid droplets, the viscosity never gets above 1 Pa s even at the driest RHs considered here (Song et al. 2016).

With these known dependencies of viscosity on water activity, we can estimate the timescale for diffusional mixing within a droplet, assuming that this provides an estimate of the timescale for an evaporating droplet to form a homogeneous mixture. This timescale must be considerably shorter than the evaporation timescale for our hygroscopicity estimations to be valid. First, the Stokes-Einstein equation is used to estimate the diffusion constant of water at varying viscosity (varying RH).

$$D = \frac{k_B T}{6\pi r_{mol}\eta} \qquad (1.1)$$

D is the diffusion constant, k_B is the Boltzmann constant, T is temperature, r_{mol} is the molecular radius of water (taken as 1.375 Å) and η is the viscosity. It should be noted that equation (1.1) is likely to provide a significant underestimate of the diffusion constant due to the failure of the Stokes-Einstein equation. At a viscosity of 100 Pa s, the diffusion constant for water in sucrose is already more than one order of magnitude larger than estimated from the viscosity (Power et al. 2013). However, using diffusion constants estimated from (1.1) will provide an upper limit on the diffusional mixing timescale. The timescale for diffusional mixing, τ, is then estimated using the expression

$$\tau = \frac{a^2}{\pi^2 D} \qquad (1.2)$$

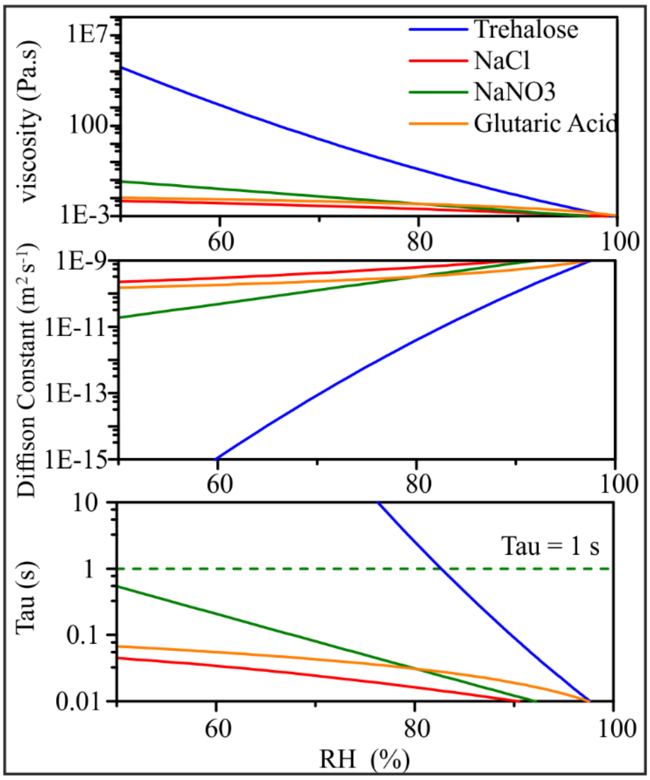
where a is the droplet radius (set as 10 microns in this calculation).

We compare the diffusional mixing timescales for aqueous droplets of trehalose, NaCl, $NaNO_3$ and glutaric acid in the newly added supplemental Figure S39.2 (and repeated below). Given that we have been able to report accurate hygroscopic growth curves for $NaNO_3$ down to 50 % RH (see Rovelli et al. 2016 and the response to referee 2), it is clear that a final viscosity at 50 % of ~ 0.1 Pa.s (Baldelli et al.) is insufficient to impede accurate measurement of the hygroscopicity. Indeed, this suggests that water transport in any aerosol droplet that maintains a viscosity lower than 0.1 Pa.s during drying should remain sufficiently fast to avoid a bulk diffusion limitation, permitting accurate hygrosocpicity measurements. As an example of the diacarboyxlic acids considered in this study, glutaric acid has a considerably lower viscosity at 50 % RH of ~ 0.01 Pa.s (Song et al. 2016), indicative of what we might expect for all such similar systems. By contrast, aqueous-trehalose droplets cross the 0.1 Pa.s viscosity threshold at a water activity of ~0.85 (Song et al. 2016), commensurate with the deviation and increased scatter in the hygroscopicity measurements reported above for this compound.

Again, we must reiterate that the true diffusion constants are generally found to be much larger than values estimated from the Stokes-Einstein equation. A droplet with a viscosity of 0.1 Pa s takes ~0.3 s to mix by diffusion based on our analysis here, but this is an upper limit on the timescale.

Based on the two considerations above and to indicate clearly the water activity ranges over which we consider the hygroscopicity measurements to be valid for trehalose (S30), galactose (S31) and sorbitol (S29), we have added a dashed line to indicate where the data appear to become kinetically limited. We have added the following words to the captions of these Figures: “Data taken at RHs lower than indicated by the dashed black line show increased error in hygroscopicity retrieval due to the imposition of a kinetic limitation on water transport.”

Fig S39.2 a) Viscosity of Trehalose, NaCl, NaNO3 and Glutaric Acid as a function of RH. b) Estimated diffusion constant as a function of RH. c) Timescale for diffusional mixing at the RH shown on x-axis. Dashed green line represents 1 second timescale for diffusional mixing.



A. Baldelli, R. M. Power, R. E. H. Miles, J. P. Reid and R. Vehring *Effect of crystallization kinetics on the properties of spray dried microparticles,* Aerosol Science and Technology, 2016, 50:7, 693-704, DOI:10.1080/02786826.2016.1177163

R. M. Power, S. H. Simpson, J. P. Reid and A. J. Hudson, *The transition from liquid to solid-like behaviour in ultrahigh viscosity aerosol particles,* Chemical Science, 2013, 4 , 2597, DOI: 10.1039/c3sc50682g
Y. Chul Song, A. E. Haddrell, B. R. Bzdek, J. P. Reid, T. Bannan, D. O. Topping,, C. Percival, and C. Cai *Measurements and Predictions of Binary Component Aerosol Particle Viscosity* J. Phys. Chem. A 2016, 120, 8123−8137, DOI: 10.1021/acs.jpca.6b07835"

Referee Comment: Page 11 line 26: Would the C4-polyol be described as "long chain"? Would sorbitol be classified as sugar?

Response: We have removed 'long chain' in the description of erythritol. Sorbitol and erythritol are best described as polyols (sugar alcohols) and they have now been correctly labelled in the amended text Page 11 line 26: "Equilibrium hygroscopicity curves for the two sugars galactose and xylose, and two sugar alcohols (polyols) erythritol and sorbitol, are shown in Fig. 10."

Referee Comment: Page 12 line 25: The authors discussed on the over-estimation of kappa parameter. However, it seems the UManSysProp model can over-estimate as well as under-estimate the kappa (Figure 12b).

Response: We agree with the referees comment and have expanded this sentence to indicate that the parameter can be underestimated. We have added on P12 line 25 "Further, UManSysProp predictions can also lead to an underestimation of κ for a limited number of compounds, including valine, histidine, and glutaric and methyl succinic acid."

Referee Comment: The authors seem to be sending very mixed messages on the reliability of simple parameterized models/equations for predicting hygroscopicity. On one hand, they criticized the limitation of UNIFAC in predicting hygroscopicity of branched acids. On the other hand, they promoted the use of κ values and O:C and N:C ratios based on Figure 11(b) and 12 (a), which do show discrepancies between model predictions and experimental results in κ. When plotted in the form of mfs hygroscopic data, some of these differences are not much smaller than those between the measurements of the branched DCAs and the UNIFAC predictions based on parameterization of simpler acids. Furthermore, the comparison of data and model Kappa parameters are evaluated at 95% but the comparison of UNIFAC related results are in mfs as a function of RH. How would the results look like if Kappa values are evaluated at lower RH? Finally, are these predictive tools considering these very general and smooth relationships really much less computationally expensive than current group contribution methods? κ was calculated by isotherms that require an adjustable parameters. Overall, the comments made by the authors on the use of UNIFAC, Kappa/isotherm models, and more elaborated models such as AIOMFAC and UManSysProp appear not to be unbiased. Elaboration is needed.

Response: The main purpose of this manuscript is to provide an evaluation of the current thermodynamic models for predicting the hygroscopic response of aerosols. Models such as AIOMFAC, UNIFAC, E-AIM and UManSysProp will always be the preferred choice when a full and accurate representation of the equilibrium response is required (e.g. over a wide range in RH as the referee suggests). However, simple parametrisations such as κ are finding very widespread use in providing an albeit limited characterisation of the hygroscopic response – a single parameter is easier to report and measure than a full hygroscopicity curve. We are not aware of anywhere in the paper where we make a value judgement on the relative merits of these two approaches: both methods have the strengths and uses in different domains and are used to provide the appropriate level of information required in any application. Given that the κ treatment is increasingly used, we felt it was of importance to try and connect the more detailed thermodynamic models with the much more simplistic approach. We hope we have achieved this in the revised manuscript.