Response to Referee #1 (Andreas Zuend) 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 Andreas Zuend (Referee #1) for his generally positive comments on the manuscript. We respond to the specific comments made by the referee below and identify the changes we have made to the manuscript.

On consideration of the comments, all predictions generated by AIOMFAC-web have been repeated with careful consideration of the functional groups used. Methyl malonic acid, 3-methyl adipic acid, dimethyl malonic acid, 2,3-dimethyl succinic acid and pimelic acid were found to differ marginally from the original predictions. All figures (Figure 2, 4, 5 and 7), supporting information and tabulated data have been updated to reflect these changes. Although the corrections lead to slight numerical changes, they do not alter the overall conclusions of the manuscript.

Response to general comments

<u>Referee Comment:</u> *Section 2. Methods and Materials. While the reader is referred to Rovelli et al. (2016) and Davis et al. (2013) for a detailed description of the CK-EDB method, a general description of the chemicals used, their purities and solution preparation is missing. Some of that information is provided in the SI 2 only. I suggest that a brief description is also given in the main text and that the reader should be informed about additional information on this in the SI.*

<u>Response:</u> As recommended by the referee, we have added a brief comment on P4 L21-23 to refer the reader to the detailed information in the SI: 'Purity and supplier for all compounds is presented in the supplementary information. Further, all measurements presented in this work are taken at 293.15 K. All solutions are prepared using HPLC grade water (VWR Chemicals).'

<u>Referee Comment:</u> *Temperature range and droplet temperatures. In the first paragraph of page 4 it is highlighted that the temperature in the EDB trapping region can be controlled well over a ~75 K range, however, throughout the main text information about the actual temperature used is missing (including tables and figures). As far as I can tell from the temperature information given in the SI, all experiments and model calculations were carried out at 293.15 K. Were hygroscopicity measurements at other temperatures considered (which would be useful, e.g. for improved, temperature-dependent thermodynamic model parameterisations given the temperatures were sufficiently different)?*

<u>Response:</u> We have now noted the temperature of all measurements (see previous response). We have conducted temperature dependent hygroscopicity experiments for a number of organic systems presented in this work and for a number of additional inorganic systems. However, these will be detailed in a subsequent publication due to the length of this manuscript and the length of discussion involved on the effect of temperature on hygroscopicity.

<u>Referee Comment:</u> *...a discussion on the EDB temperature range used and the actual droplet surface temperature during the evaporation experiments will require some discussion. From Rovelli et al. (2016) it seems clear that the time scale of the evaporation will lead to deviations between droplet and surrounding gas phase temperature. Moreover, given that the evaporation rate from a relatively concentrated solution droplet*

is different from the evaporation rate of the probe droplet, a discussion of such temperature related issues with respect to the retrieval of the sample droplet's water activity at a particular temperature seems appropriate.

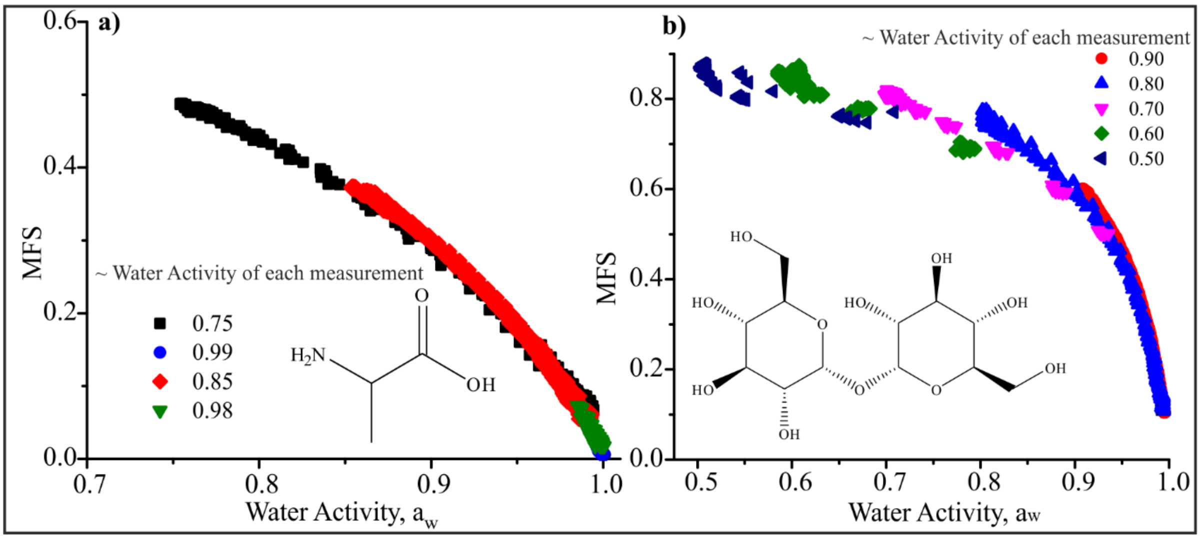
Response: We agree with the referee that accounting for the temperature suppression is important when retrieving the hygroscopic growth curve. We have provided an extensive discussion of this in our recent paper (Rovelli et al. 2016, as identified by the referee) where we provided considerable evidence to validate and benchmark the technique. Having previously provided this information in great detail, we feel that any further discussion provided here would be rather insubstantial and inferior to our previous discussion. Instead, we feel it is important that the reader be referred to the comprehensive account in our earlier report, with all procedures used in this manuscript carefully following our earlier recommendation. On P7 L11 we add the following comment: "It is imperative that the evaporative cooling be accounted for as this suppresses the apparent vapour pressure at any instant, particularly at early time when the mass flux is larger. Indeed, equation (5) explicitly accounts for the latent heat lost from the droplet. At very early times and when evaporating into low RH, the temperature suppression can be sufficient (>3 K) so as to reduce the accuracy of approximations made when deriving equation 5. Under these circumstances, when the temperature suppression is larger than this limit, we do not infer equilibrium water activities, but instead only retrieve the equilibrium hygroscopic growth when the temperature suppression is smaller than 3 K. This procedure has been discussed and verified in detail in our earlier work, and the reader is referred to Rovelli et al. (2016) for further details."

Referee Comment: *In contrast to the inorganic solutes used in Rovelli et al. (2016), the present study involves organic solutes, some of which may cause a significant increase in mixture viscosity with decreasing droplet water content during evaporation in the EDB. In this context, the time scale of 10 s for the evaporation from the droplets may become an issue for droplets > 10 µm radius, potentially impeding the droplet-gas mass transfer (e.g. Koop et al., 2011) and potentially violating assumptions about a homogeneous, concentration-gradient-free mixing of water and organic compound within sample droplets aside from a developing temperature gradient within a rapidly evaporating droplet. The authors discuss the viscosity concern in Section 3.3, where it is mentioned that for many compounds measurements unimpeded by kinetic limitations were not possible below 80 % RH. Because this consideration may not only apply to sugars and alcohols, but to many of the multifunctional organics of higher molar mass, a more general discussion of kinetic limitations and consequences for the CKEDB data processing should be provided in Section 2 where the method is described. If a relatively viscous binary aqueous droplet is exposed to low RH and evaporates water quickly, there may be insufficient time for homogeneous mixing in the droplet bulk compared to the near-surface volume of the droplet, which could lead to a concentration gradient and a higher solute concentration in the surface region of the droplet, affecting the local water activity there. Under such conditions, an organic solute may appear as more hygroscopic than it would be under actual gas-particle equilibrium conditions. Did the authors consider such effects in their method and the data processing? It is also not clear whether the authors considered a longer measurement time scale with slower evaporation settings for systems where substantial kinetic limitations may occur (and for which organic evaporation may not be a concern). Please discuss.*

Response: 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

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

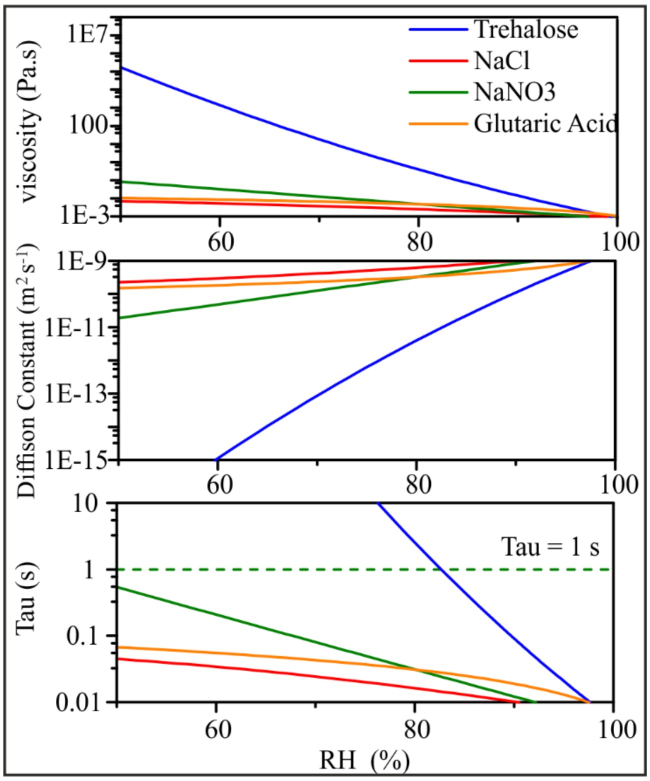
where a is the droplet radius (set as 10 microns in this calculation).

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: *UNIFAC models – three general comments and clarifications:*
1. The authors compare many of the measurements to predictions by "the" UNIFAC model, however, the information about the specific model version used and its parameterisation for some of the compounds is incomplete in the manuscript. While the original UNIFAC model theory by Fredenslund et al. (1975) is mentioned on page 2, several UNIFAC modifications 3 (changes to model equations, e.g. UNIFAC-Dortmund, UNIFAC-Lyngby, etc.) and several revisions of UNIFAC parameter tables applicable to certain UNIFAC versions have been published in the past 40 years. For example, the AIOMFAC model (Zuend et al., 2008; 2011), which includes a UNIFAC model based on the original theory of Fredenslund et al. (1975), relies mostly on the revised parameter set by Hansen et al. (1991). However, Zuend et al. (2011) discuss several modifications of the parameter database, including the use of improved interaction parameters determined by Marcolli and Peter (2005) for alcohols and multifunctional compounds containing hydroxyl groups, as well as modified interaction parameters by Peng et al. (2001) for a subset of interactions involving carboxylic acid groups. These modifications are detailed in Zuend et al. (2011) and are used in the online version of the AIOMFAC model (which was used for several comparisons with measurements in the present paper; see also www.aiomfac.caltech.edu/about.html). Similarly, the online UNIFAC versions in UManSysProp (http://umansysprop.seaes.manchester.ac.uk; Topping et al., 2016), which includes AIOMFAC and a UNIFAC version, and the E-AIM website's UNIFAC (www.aim.env.uea.ac.uk/aim/aim.php) contain modified parameter sets from Peng et al. (2001) and from other sources of UNIFAC parameter revisions (see also http://www.aim.env.uea.ac.uk/aim/phpmain/edit_help.php#section100 for details on UNIFAC in E-AIM). While some of these newer parameterisations lead to only slight changes to predicted water activities compared to the original UNIFAC by Fredenslund et al. (1975) with the Hansen et al. (1991) parameters, others are significant – and e.g. in the case of AIOMFAC, the description of alcohols and sugars is substantially modified by the introduction of specific subgroups and main groups in the model for these compounds (of relevance for the comparisons with CK-EDB data made in this study). Therefore, to provide sufficient detail for clarity and reproducibility, it is necessary to specify which models and parameterisations were actually applied (e.g. in the Methods section).

Response: All UNIFAC model predictions presented in this paper for dicarboxylic acids, sugars and alcohols were performed using AIOMFAC-web. This has been specified both in section 3.1. (Hygroscopic Response of Dicarboxylic Acids of Varying Complexity) and section 3.3. (Sugars and Alcohols) and in all relevant captions (Figure 2, 3, 5 and 10). We have added the following to ensure clarity:

P8 L11: 'All calculations for dicarboxylic acids were performed using the AIOMFAC-web model.'
P2 L33: 'AIOMFAC-web implements several improved parameters which are detailed by Zuend et al. (2011).'
P10 L13: With regard to amino acid modelling we have added the following: 'Hence UNIFAC (AIOMFAC-web) thermodynamic model predictions for amino acids were generated using E-AIM, using the UNIFAC model with Peng et al. parameterization (Peng et al., 2001) and Model III (Clegg et al., 1998).'

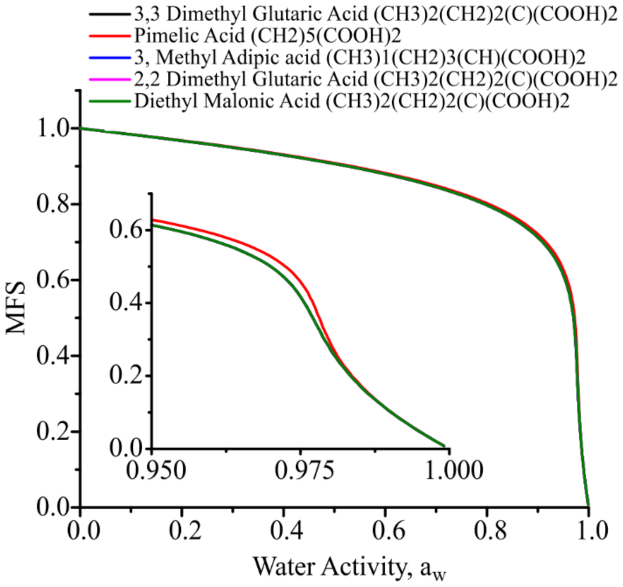
Referee Comment: *2. Contrary to the statements on page 2, lines 30 – 32 and on page 8, lines 20-21, UNIFAC (and AIOMFAC) actually account for the molecular structure and for certain differences between branched and straight-chain dicarboxylic molecules of the same molar mass – albeit in a limited way. For example, via the differing number in hydrogen atoms on CH_2, CH, and C subgroups, which leads to different values of the relative Van der Waals volume and surface area terms in the combinatorial part of the UNIFAC model for these alkyl subgroups (affecting predicted activity coefficients). For this reason, the UNIFAC subgroup assignments, as listed in Table S0 of the SI, are incomplete/incorrect in the case of the dicarboxylic acids. For example, CHn is not a UNIFAC/AIOMFAC subgroup and as such does not sufficiently characterise the compound; instead the appropriate subgroups need to be stated. For example, correct subgroup assignments show that the three distinct C7- dicarboxylic acids (see also Table 3 of Zuend et al. (2011): 3-methyl adipic acid, (CH3)(CH)(CH2)3(COOH)2, 3,3-dimethylglutaric acid, (CH3)2(C)(CH2)2(COOH)2, and pimelic acid, (CH2)5(COOH)2, have slightly different subgroup formulas in UNIFAC/AIOMFAC and consequently there should be distinct model curves in Fig. 5b and UNIFAC structure formulas in Table S0 of the SI. Although,* *this reviewer agrees that the differences between UNIFAC predictions for such similar dicarboxylic acids are likely small.*

Response: We have amended P2 L 31 to read: ‘In this approach, molecules are divided into characteristic molecular subgroups and the activity coefficients derived from group contributions with limited consideration for molecular structure.’ Further, we have removed the text on P8 L20-21 that reads: ‘…a consequence of representing all CH, CH2, and CH3 substituents by CHn (Zuend et al., 2008).’

We would like to apologise because these AIOMFAC-web predictions were labelled incorrectly in the previous version of Figure 5(b) and have been corrected in the new Figure 5(b). The caption now reads: “….where the AIOMFAC-web prediction for 3-methyl adipic acid, $[(CH_3)(CH)(CH_2)_3(COOH)_2]$, 3,3-dimethylglutaric acid, $[(CH_3)_2(C)(CH_2)_2(COOH)_2]$, 2,2-dimethylglutaric acid, $[(CH_3)_2(C)(CH_2)_2(COOH)_2]$ is represented by the blue dashed line. Note that the equilibrium curves for the first 4 compounds are in such close agreement and indistinguishable on this scale that only one curve is shown for clarity. The prediction for pimelic acid $[(CH_2)_5(COOH)_2]$ is shown as a black solid line.”

With respect to the AIOMFAC web prediction for 3-methyl adipic acid $[(CH_3)(CH)(CH_2)_3(COOH)_2]$, 3,3-dimethylglutaric acid $[(CH_3)_2(C)(CH_2)_2(COOH)_2]$, 2,2-dimethylglutaric acid $[(CH_3)_2(C)(CH_2)_2 (COOH)_2]$ and diethyl malonic acid $[(CH3)_2(CH2)_2(C)(COOH)_2]$, the predicted equilibrium activity curves (mfs vs water activity) are so similar that they are indistinguishable, as shown in the figure below. As a consequence, only one curve is used to represent all four compounds in Fig. 5.

We have now explicitly included all functional groups used in the prediction of the AIOMFAC–web curves in Table S0 of the SI as suggested by the referee.



Referee Comment: 3. The UNIFAC group-contribution method also offers another way to account for proximity effects by neighboring subgroups in organic molecules: specific subgroups can be assigned to larger sections of a molecular structure and that has been proposed for modified UNIFAC parameterisations in the case of amino acids. For example, Gupta and Heidemann (1990) introduced a specific “proline” UNIFAC subgroup (including a subset of determined interaction parameters for aqueous solutions of amino acids). Kuramochi et al. (1997) introduced a series of new functional groups and determined UNIFAC parameters for the description of most amino acids, including histidine, for a modified UNIFAC version based on “Larsen’s UNIFAC”. Thus, statements like (page 10, line 15): “UNIFAC predictions cannot be performed for all amino acids examined here; in particular, the ring structures found in proline and histidine, cannot be represented as subgroups in the current version of UNIFAC.” are not generally correct – the UNIFAC parameterisation by Kuramochi et al. covers most amino acids studied experimentally in this work. However, it is correct that those “specialized” UNIFAC modifications are not implemented in the online versions of AIOMFAC and UNIFAC in E-AIM (see point (1) above), so they are not conveniently available for *calculations, which is likely what is meant by the authors' statement. Such general statements should therefore be revised accordingly and the work by Gupta and Heidemann (1990), Kuramochi et al. (1997) and others mentioned. Consider also that parameter sets that were determined for different UNIFAC model versions are typically not compatible and the use of specific subgroups with only a limited set of interaction parameters determined, e.g. for aqueous mixtures of amino acid solutions only, disqualifies the applicability of such models for predictions of complex, multi-component and multifunctional mixtures of interest in atmospheric aerosol chemistry (as discussed in Section 5.4 of Zuend et al., 2011).*

Response: We have amended section 3.2. P10 L14 now reads: "Amino acids form zwitterions in solution, supressing the vapour pressure of the acid, and this presents a challenge to current thermodynamic models with most not allowing the inclusion of nitrogen amine containing groups (e.g. AIOMFAC-web). AIOMFAC-web only allows for the inclusion of organonitrate and peroxy acyl nitrate sub groups. Hence, model predictions for amino acids were generated using E-AIM, using the UNIFAC model with Peng et al. parameterization (Peng et al., 2001) and Model III (Clegg et al., 1998). Even then UNIFAC predictions cannot be performed for all the amino acids examined here. In particular, the ring structures found in proline and histidine cannot be represented as subgroups in the current version of E-AIM, although these could be represented with the further parametrisations reported by Kuramochi et al. (1997b) or Gupta and Heidemann (1990)."

Specific comments and technical corrections

Referee Comment: *Abstract, first sentence and page 4, line 9: "Hygroscopic data" should be "Hygroscopicity data" (the data itself is likely not hygroscopic).*
Response: Corrected to: 'Hygroscopicity data for 36 organic compounds'

Referee Comment: *P3, line 7: correct spelling of "Köhler"*
Response: Corrected to: 'Köhler'

Referee Comment: *P3, l. 11 – 13: "Values are typically determined from sub-saturated hygroscopic growth measurements and reported at the highest accessible RH (Pajunoja et al., 2015). The value of κ can also be inferred from measurements of the critical supersaturation required for CCN activation, a measurement in a super-saturated regime (Carrico et al., 2008)." It would be appropriate to state that κ values determined at different RH and, to a lesser extent temperature, can vary substantially, especially when comparing κ determined from CCN activation data at water super-saturation compared to sub-saturation conditions, as, e.g., discussed by Hodas et al. (2016) and references mentioned therein.*
Response: P3 L15 We have added 'Further, κ values reported at different RHs can vary significantly and can also differ substantially from measurements in the supersaturated regime (Hodas et al., 2016).'

Referee Comment: *P3, l. 33: correct "(approaching [values] very close to 1)"*
Response: We have amended to read "(approaching values very close to 1)"

Referee Comment: *P4, l. 25: clarify the accuracy statement: "with a greater accuracy (< ± 0.2 % at water activities > 0.8…" do you mean < ± 0.2 % error in water activity or in hygroscopic growth factor or MFS?*
Response: We have clarified the statement to read: "accuracy (<±0.2 % error in water activity at water activities > 0.8 and ±1 % error in water activity at water activities < 0.8) than can be achieved in conventional approaches"

Referee Comment: *P6, l. 5: "with most solutes instead", better: "with most pure organic compounds instead" since this is not about a solution but about the pure components.*
Response: We have amended to read: 'corresponds to that of the pure sub-cooled melt with most pure organic compounds'

Referee Comment: P6, title 2.3: Replace "hygroscopic" by hygroscopicity
Response: We have amended to read '2.3. Extraction of Hygroscopicity properties'

Referee Comment: P7, l. 2: "In this equation, the gradient in water partial pressure is the difference between the RH and aw, the instantaneous water activity at the droplet surface." First, given the evaporation setup with an RH profile dependent on the distance from the droplet, it needs to be stated which RH (and measured where) is meant, i.e. is it the RH at the droplet surface or the RH (sufficiently) far away from the droplet. Second, the difference (RH - aw) or rather saturation ratio S – aw) (as in Rovelli et al., 2016) alone does not constitute a "gradient". Also, since the component subscript "i" in Eq. (5) denotes water (i.e. subscript "w" as in aw), it would seem better to use "w" instead of "i".

Response: We have added the following sentence to clarify that the probe droplet is trapped in exactly the same position as the sample droplet: "In this study, the probe droplets are trapped in exactly the same position within the gas flow as the sample droplets which allows the measurement of the RH in situ. The probe droplets are either pure water (for the RH range 80 – 99 %) or aqueous NaCl (for the RH range 50 – 80 %)."

When referring to gradient in the text, we are referring to the gradient in water partial pressure and we believe this is correct. We do not refer to a gradient formed from (RH-a_w). To be consistent with our previous publications, we have removed the subscript *i* entirely from the equation but not replaced it with *w*.

Referee Comment: P7, l. 9: "is the latent heat of vaporization"; add "of water" at temperature T_∞(?).
Response: Added 'L is the latent heat of vaporization of water at T_∞.'

Referee Comment: P8, l. 10: "using Peng corrections" the meaning of this is unclear. Also, as detailed above, the UNIFAC models likely used by the authors actually include further modifications in terms of the used parameter sets and/or subgroup assignments.
Response: All UNIFAC predictions (with the exception of amino acids) were performed using AIOMFAC-web and we hope we have now made this clear in the manuscript.

Referee Comment: P8, l. 20: "In addition, the UNIFAC predictions become less accurate as the added substituent becomes larger, a consequence of representing all CH, CH2, and CH3 substituents by CHn (Zuend et al., 2008)." There seems to be a misunderstanding about the UNIFAC (AIOMFAC) way of group contribution calculations, see the general comment above. Only group-group interactions in the residual UNIFAC expressions are common for all CHn subgroups (with n = 0,1,2,3), but the volume and surface area terms (combinatorial part) are not. This is the case in all variants of UNIFAC.
Response: We have removed 'a consequence of representing all CH, CH2, and CH3 substituents by CHn (Zuend et al., 2008).'

Referee Comment: P9, l. 20 and l. 17: There are actually more than two distinct UNIFAC group formulas for the different C7-dicarboxylic acids, see the general comment above. Also, given that the UNIFAC (AIOMFAC) model predictions of water activity show a deviation from the CK-EDB data for the straight-chain pimelic acid, the model-measurement deviations shown in Fig. 5b are expected and at least consistent in that sense. Related to the statement on line 17, the observed similarity in hygroscopicity of the different C7-dicarboxylic acids suggests that the degree of branching and/or lengths of alkyl substituents may not always play a substantial role, in particular above a water activity of 0.8. This seems to be a counter-example to the trends observed for the smaller dicarboxylic acids with alkyl substitutions (and a hint for a general underestimation of the hygroscopicity contribution by the CHn groups as represented in UNIFAC/AIOMFAC).

Response: We have now included all functional groups used for AIOMFAC-web predictions in the table in the SI for each compound. The referee makes an interesting observation about the general consequences of the observation of the underestimation of the contribution from CHn groups.

Referee Comment: *P10, l. 15: The sentence should be revised as certain nitrogen containing compounds are available in most UNIFAC models (including in AIOMFAC for organics + water systems) since the parameter set by Hansen et al. (1991) includes amine, amid, nitro, nitrile and pyridine groups and some version include organonitrate groups (Compernolle et al., 2009; Zuend and Seinfeld, 2012) and proline and histidine groups Kuramochi et al. (1997).*

Response: We have amended the section on P10, 3.2. Hygroscopic Response of Amino Acids, to read: "Amino acids form zwitterions in solution, supressing the vapour pressure of the acid, and this presents a challenge to current thermodynamic models with most not allowing the inclusion of nitrogen amine containing groups (e.g. AIOMFAC-web). AIOMFAC-web only allows for the inclusion of organonitrate and peroxy acyl nitrate sub groups. Hence, model predictions for amino acids were generated using E-AIM, using the UNIFAC model with Peng et al. parameterization (Peng et al., 2001) and Model III (Clegg et al., 1998). Even then UNIFAC predictions cannot be performed for all the amino acids examined here. In particular, the ring structures found in proline and histidine cannot be represented as subgroups in the current version of E-AIM, although these could be represented with the further parametrisations reported by Kuramochi et al. (1997b) or Gupta and Heidemann (1990)."

In addition, on P10 L28-29 we have stated: "We used the UNIFAC model with Peng et al. parameterization (Peng et al. 2001), typically run in E-AIM in the Model III mode (Clegg et al. 1998)."

Referee Comment: *P10, l. 22: "except for L-valine"; According to Fig. 8, L-Threonine behaves similar to L-valine even though it contains a hydroxyl group instead of a methyl group. So it seems that L-valine is not an exception or not the only one. Also, the UNIFAC prediction for glycine is missing in Fig. 8a.*

Response: We have added the UNIFAC prediction for glycine to Fig. 8a. We have also amended 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: *P10, l. 30: "is fitted to molality experimental data"; molality of what? The last part of that sentence needs to be rephrased as well.*

Response: We have amended P10 L30 to read: "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: *P11, l. 13: Statement needs to be revised given the above clarification about specific UNIFAC parameterisations for aqueous solutions of amino acids.*

Response: On P11 L15, we have removed: "This is a consequence of the current reliance of the UNIFAC parameterisation on the data of Chan et al. (2005)."

Referee Comment: *P11, l. 15: "This is a consequence of the current reliance of the UNIFAC parameterisation on the data of Chan et al. (2005)." This statement is incorrect, because the UNIFAC models used by the authors do in fact not contain the modified parameters by Chan et al. (2005); rather, they are based on Hansen et al. (1991) and Peng et al. (2001) parameters for the amino acids. Also, as is clearly shown in Chan et al. (2005), their modified UNIFAC parameterisation yields similar results to the Peng et al. version in many cases and the Peng et al. parameterisation is in reasonable agreement with their own experimental data (e.g. for threonine). Therefore, the discrepancies between the new CK-EDB data and the UNIFAC model curves shown*

indicate clear discrepancies among different experimental data sets, as is discussed by the authors in the first paragraph of page 11.
Response: On P11 L15, we have removed "This is a consequence of the current reliance of the UNIFAC parameterisation on the data of Chan et al. (2005)."

Referee Comment: P12, l. 27: "Molecular structures presented in Fig. 10 are the open chain form, which must be used during modelling using UNIFAC."; Why "must"? AIOMFAC also allows you to use the cyclic structure of sugars in aqueous solution, e.g. glucopyranose instead of glucose, if desired.
Response: Cyclic sugar structures do not appear to be available on AIOMFAC-web. Amended P11 L27 to read 'Molecular structures presented in Fig. 10 are the open chain form, which must be used during modelling using AIOMFAC-web.'

Referee Comment: P12, l. 10: and Fig. 11 & 12: replace the compound class labelled "organic acids" by a more appropriate label, e.g. "dicarboxylic acids", since amino acids are also organic acids but not part of that class.
Response: Labels in Figures 11 and 12 have been amended from organic acids to dicarboxylic acids as suggested.

Referee Comment: P12, l. 32: Statement is incorrect, see comment to P11, l. 15.
Response: We have removed the statement: 'this is due to earlier experimental measurements by Chan et al. (2005) which have been used to parametrise UNIFAC'

Referee Comment: P13, first paragraph. With respect to the applicability of the determined component-kappa values from binary data with a simple mixing rule for a complex mixture's total hygroscopicity parameter kappa, I suggest the authors consider in this section that it remains rather uncertain whether the kappa values determined based on binary water + amino acid data apply in multicomponent mixtures of relevance for atmospheric aerosol. This is because the substantial hygroscopicity exhibited by many of the amino acids, due to their zwitterionic nature in aqueous solution, may be affected substantially by the presence of inorganic acids and dissolved salts in aerosol mixtures, altering the partial water uptake contribution by the amino acids in a non-linear manner. This may motivate further experimental investigations for organic-inorganic mixtures with the CK-EDB and other setups.
Response: We agree with the referee's comment and will indeed soon progress to measurements of the hygroscopic response of mixtures.

Referee Comment: Table 1: State the temperature (range) for the measurements. Also the caption text and table header concerning SMILES needs revision.
Response: We have added the temperature of the measurements to caption to read: "Table 1. Experimentally determined κ values at $a_w = 0.95$ for all compounds studied at 293.15 K, presented alongside κ values calculated using UManSysProp and the smile string used for this calculation." We have changed 'smile string' to 'SMILES String'
Referee Comment: Fig. 1: Lower panel, at around 0.9 water activity, the red triangles-up and black triangles-down symbols suggest a larger scatter in experimental data than the binned data and error bars account for. It is unclear why if it is assumed that the different drying rates have similar measurement uncertainty? A brief discussion may be useful.
Response: Each dataset has an associated uncertainty on water activity depending on the RH at which the evaporation occurs (Rovelli et al. 2016). The higher the RH in the gas phase, the slower the evaporation, and there is consequently a greater density of measured data points. This is why the dataset at the higher RH has a higher weighting in the overall averaged data.

Referee Comment: Fig. 2: state the UNIFAC parameterisation used, if AIOMFAC-web was used, then stating that would be sufficiently specific.

Response: AIOMFAC-web was used and this has been stated in the caption on appropriate figures: “UNIFAC predictions using AIOMFAC-web.”

Referee Comment: Fig. 6: the y-axis label “n(water)/n(solute)” would be better written as in Fig. 7 or perhaps in abbreviated form, such as nw/ns.
Response: This has been amended to match that in Figure 7.

Referee Comment: Figs. 8 and 9: The UNIFAC (Peng et al. parameterisation) model curve for Glycine is missing.
Response: The UNIFAC prediction for Glycine has been added in Figures 8 and 9.

Referee Comment: Fig. 9: Comparing this figure to Fig. 1 of Chan et al. (2005), it is clear that many experimental data points from Na et al. are missing, as well as bulk data by Kuramochi et al. (1997) to higher MFS/lower aw than shown and data by Ninni and Mereilles (2001) in Fig. 9b. Including all these measurements in Fig. 9 will provide a better comparison for the discussion concerning the substantial discrepancies found among the experimental data sets and in comparison to model predictions.

Response: As suggested, more data points from Na et al. have been added in Figure 9(a) and (b). It should be noted that in Na et al. the parametrisation of the hygroscopicity data for glycine does not accurately reproduce the experimental data presented in their manuscript. Thus these points in Figure 9(a) were determined by reading a number of points from the graph and a curve with the following formula fit to them MFS = 0.65967 + 0.5305 a_w -1.1458 a_w^2, and this equation was used to generate additional points now plotted on Figure 9a). All available data from Ninni and Mereilles (2001) and Kuramochi et al. (1997) have now been included in both Figure 9(a) and (b).

Referee Comment: Supplementary Information: It would be useful to briefly state at the end of the main text what information is provided in the SI.
Response: This statement has been added on P13 L4-5: ‘The supplementary information provides tabulated hygroscopicity data for all compounds measured in this study, it also details compound purities, density and refractive index parametrisations for all compounds.’

Referee Comment: SI, Table S0: the page numbers for different systems are listed, but the pages in the SI were not numbered. Also, the AIOMFAC subgroups stated for the dicarboxylic acids with CHn groups should be revised, see general comment. The “CHn(OH)” groups stated for citric acid, tartaric acid and other compounds should be stated with OH preferentially in superscript (e.g. CH2[OH] for a CH2 subgroup bonded to an OH group, which is specified separately) to avoid confusion about the number of OH groups present in the molecular structure (see also Table 3 of Zuend et al., 2011).
Response: Supporting Information pages have now been numbered, groups in Table S0 have been labelled according to the suggestions above; an example for tartaric acid is $(COOH)_2$ $(OH)_2$ $(CH)_2{}^{(OH)}$.

Referee Comment: SI, Fig. S8.1: Check the caption text and symbols in the figure. I do not see any coloured curves for data at different temperatures stated in the caption.
Response: S8.1. This caption has been altered to remove any reference to temperature dependent data. This will be reported in a subsequent paper. ‘Hygroscopicity of L-Valine, (Sigma Aldrich, Purity ≥ 98 %), at 293.15 K Open symbols, these CK-EDB experiments; black filled circles, literature data (Kuramochi et al.); solid black line, UNIFAC model (293.15 K).’

Referee Comment: SI, S26 and S27: For aqueous PEG mixtures, much improved interaction parameters have been determined for a PEG-specific version of AIOMFAC, but these are not yet included in AIOMFAC web (see also Hodas et al., 2016).
Response: We are grateful to the referee for highlighting this and will provide a further comparison when the refined parameters are available in AIOMFAC.