Interactive comment on “Hygroscopic Properties of Aminium Sulphate Aerosols” by Grazia Rovelli et al.

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Response to Anonymous Referee #1

The authors would like to thank Anonymous Referee #1 for their generally positive comments on the manuscript. We respond to the specific comments made by the referee below and identify the changes we have to the manuscript.

Specific Comments:

Anonymous Referee #1: *Pg. 2 Line 32: It would be nice to give numbers for seasonal variation here since other numbers are given. Additionally, on P3 line 3 mention the location of the measurements for completeness.*

Response: Line 32 (Page 2) has now been expanded and the revised version reads as follows:

“The ambient concentrations of amines in the gas phase can span wide ranges, depending on the sampling location. For example, concentrations can be up to 140 mg m^{-3} close to a city market (Namieśnik et al., 2003), 110-300 ng m^{-3} in the exhaust gas of a waste disposal site (Kallinger and Niessner, 1999), and of the order of tens of µg m^{-3} inside livestock buildings (Kallinger and Niessner, 1999). Concentrations also depend on the season: for example, single amines in the gas phase at a rural site in Turkey have been reported to be in the range 0.92-7.4 ng m^3 in Winter and 0.29-5.16 ng m^3 in Summer (Akyüz, 2008). Further, Pratt et al. (2009) measured a seasonal volatility dependence of alkylamines depending on the particles pH that affects the amines concentrations in the gas phase. In the condensed phase, amines can account for hundreds of pg m^{-3} or a few ng m^{-3} of aerosol mass.”

The reviews by Ge at al. referenced on Line 3 (Page 3) include data for a large number of studies. Mentioning all the location of the measurements included in Ge’s reviews is probably out of the scope of the overview given here. However, for clarity “at a large number of rural and urban environments” has been added (Page 3), now reading:

“An extensive review of the measured concentrations of a large number of amines both in the gas phase and in aerosols at a great variety of rural and urban environments is given by Ge et al. (2011a, 2011b).”

Anonymous Referee #1: *Pg. 3 line 5: It would be good to discuss the new particle formation in more detail with references.*

Response: We agree with Referee #1 that the role of amines in new particles formation should be discussed in more detail and therefore we added a paragraph at line 5 (Page 3).

"The role of amines in new particles formation and growth has been highlighted by computational studies (DePalma et al., 2012; Loukonen et al., 2010; Ortega et al., 2012), as well as by laboratory (Almeida et al., 2013; Wang et al., 2010b) and field measurements (Kulmala et al., 2013; Mäkelä et al., 2001; Smith et al., 2010). As an example, trimethylamine was found to enhance the formation and growth of new particles (Wang et al., 2010a) because of the favourable heterogeneous neutralisation reactions between the amine gaseous molecules and H_2SO_4-H_2O clusters. Smith et al. (2010) found variable but considerable concentrations of protonated amines in nanoparticles (8-10 nm diameter) during new particles formation events (47% of detected positive ions at an urban site in Mexico, 23% at remote site in Finland and 10-35% at sampling sites in Atlanta and Boulder). Since newly formed secondary particles are estimated to contribute to 45% of cloud condensation nuclei (CCN) (Merikanto et al., 2009), the presence of amines in CCN and their hygroscopic properties need to be taken into account to improve our understanding of the indirect effects of aerosol particles on climate (McFiggans et al., 2005), a key motivator for providing refined characterisation of the hygroscopic growth of aminium salt particles in this work."

Anonymous Referee #1: *Pg. 2 line13: Include the solubility of the amines compared to the salt products.*

Response: The solubility of both the unprotonated amines (data reworked from Ge et al. 2011b) and of five aminium sulphates (data from Clegg et al. 2013) has now been included at page 3.

"The formation of aminium sulphates and other similar aminium salts increases the solubility of short-chained alkylamines from 7-45 wt% for the unprotonated form (calculation from data in Ge et al. (2011b)) to 84-91 wt% for five aminium sulphates in Clegg et al. (2013). This, correspondingly, increases their partitioning from the gas to the condensed phase (Barsanti et al., 2009; Yli-Juuti et al., 2013)."

Anonymous Referee #1:*Pg. 4 line 23: Could you give the RHs used in this experiment here? The only place I saw them was in Figure 1 for the AS experiment.*

Response: This information has now been added at line 16, page 4.

"Temperature and gas phase RH ranges that are accessible with this experimental setup are -25 to 50 °C and 0 to 99%, respectively. All the comparative evaporation kinetics measurements presented here were performed at 20 °C and at gas phase RH values between ~50-90%."

Anonymous Referee #1: *Pg. 6 line 24: What is the difference in any calculations due to less of the amine (e.g. formation of aminium bisulphate) possibly being present?*

Response: Although we have considered that the partial formation of aminium bisulphate could occur, this would increase the discrepancy that already exists between our data and that of Sauerwein et al. (2015) (for example, see Figure 7). Considerable care is taken to ensure that stoichiometric amounts of the sulphuric acid are added to the amine solution.

***Anonymous Referee #1:** Pg. 8 line 5: Mention error again here in regard to the TEAS concentration measurement since you are making a direct comparison and caution that there might be error.*

Response: We agree with Anonymous Referee #1 that mentioning again the possible error on TEAS is appropriate. The following sentences have therefore been added on page 8.

"As indicated in Section 2.2, it is worth reiterating that the results presented here and below for TEAS need to be interpreted cautiously because of the uncertainty of the TEA stock solution. However, the trends that have been observed for TEAS when compared to the other five aminium sulphate systems seem to be completely plausible and this may indicate that the assumed initial TEA concentration is reasonable."

***Anonymous Referee #1:** Pg. 11 line 5: It would be nice to include the trend from Saurwein 2015 somewhere in reference to the GFr and nwater/nsolute since it is not discernable from the comparison graphs in Fig. 5. Are they the same trend as your measurements?*

Response: We agree with Anonymous Referee #1 that from Figures 5 and 6 it is not possible to discern whether or not the trends observed in our work and those from Sauerwein et al. (2015) are similar. However, we already show the comparative trends from our measurements for both the methyl and ethylaminium sulphates series in Figure 3. Very similar trends are seen in the Sauerwein et al. data and we explicitly state on page 11: "However, despite the discrepancies that do exist, results from the two different experimental methods show the same qualitative hygroscopicity trends over the methyl and ethylaminium sulphates series". As a consequence, we do not feel that this merits providing an additional figure.

***Anonymous Referee #1:** Pg. 13 line 15: Section 3.3 (and corresponding fig. 8) does not seem to add to the paper since the method has already been validated in a previous publication and could be moved to the supplemental information.*

Response: We thank the referee for this comment: it has suggested to us that the actual aim of this paragraph was not clearly stated and this has led to some confusion. The main aim of the assessment of reproducibility was not to provide an evaluation of the CK-EDB approach; as Anonymous Referee #1 states, this has already been reported. Instead, the aim of Section 3.3 is to report on the reproducibility of the solution preparation procedures (described in Section 2.2) to ensure that the discrepancies with the results of Sauerwein et al. (2015) are not derived from our the sample preparation. We have added a few sentences in Section 3.3 and improved the clarity of the paragraph to ensure the purpose of the section is more obvious to the reader.

"A full validation of the retrieval of the hygroscopic properties of single trapped solution droplets from CK-EDB experiments has already been presented in a previous publication (Rovelli et al. 2016), where we demonstrated the accuracy of the approach by reporting hygroscopicity measurements for well-characterised inorganic components. In this Section, we evaluate the reproducibility of the solution preparation method (Sect. 2.2) with the aim of demonstrating that the results presented in the previous Sections are not affected by any random error associated with our approach for making the sample solutions. Data obtained from three different datasets of evaporating DMAS solution droplets are compared in Fig. 8. The variation in n_{water}/n_{solute} with a_w (Panel (a)) and the change in osmotic coefficient with square root of sulphate mass fraction (Panel (b)) are calculated from three different data sets, each arising from measurements with 10 droplets and prepared from different starting stock solution of diethylaminium sulphate, obtained separately one from the other by mixing DEA and H_2SO_4

in different days. Data from Sauerwein et al. (2015) (open circles) and calculations for ammonium sulphate (E-AIM model, line) are shown for comparison. Measurements were made with droplet evaporation into a gas phase RH of ~80%. The reproducibility of the data is very satisfactory, giving further evidence that the applied solution preparation procedure coupled to the retrieval of the hygroscopic properties with CK-EDB experiments is reliable. In addition, this consistency in experimental reproducibility strongly suggests that the discrepancies with the data of Sauerwein et al. (2015) do not originate from random errors associated with the CK-EDB experiments."

Anonymous Referee #1: *Figure 1: Note in 'experimental data graph' that you alternate between the sample and a standard (or clarify when it is performed). Some additional description of a, b, c, in the figure caption would be helpful in discerning the use of the figure even though it is described well in text.*

Response: Some more detail is now given in the figure caption and a legend has been added in panel (a) in order to make clearer that sample and probe droplets are alternated.

"Figure 1: Schematics representing the retrieval of hygroscopic growth curves from comparative kinetics experiments in a CK-EDB. An experimental sequence of alternating single evaporating probe and sample droplets is collected (a). For each pair of probe and sample droplets, the gas phase RH is inferred from the evaporation kinetics of the probe (b) and this information is used to analyse the corresponding sample droplet hygroscopic properties as indicated in (c)."

Anonymous Referee #1: Figure 3: Why is there no data for MMAS and TMAS between _0.7-0.8 aw? What is the RH range used for these measurements?

Response: Measurements were taken for a large number of systems over a wide range of conditions and it became apparent only later that measurements were not available for this small range of conditions for two compounds. We concluded that the trends were sufficiently clear that additional measurements were not essential.

Anonymous Referee #1: *Fig. 3,5,6, 8, 10: In description make it explicit that the ammonium sulfate is a model that you already validated earlier in the paper (Fig. 2). On first read through I missed this and was wondering why it was compared to a model and not the experiment.*

Response: To make this clear, we have added a line in the caption of Figure 3 to explicitly say this.

"Note that only E-AIM predictions for $(NH_4)_2SO_4$ are reported in this and subsequent figures with the CK-EDB measurements and the E-AIM model compared in Figure 2."

Anonymous Referee #1: *Fig. S2: Why is the Saurwein et al. 2015 data not included here?*

Response: Data from Sauerwein et al. (2015) come from bulk water activity measurements and, hence, we do not include them in Figure S2 (GF_r vs. a_w plots). In principle, one could convert the data from Sauerwein et al. (2015) into radial growth factors, but we consider that this would not really add much to the discussion in this work.

Anonymous Referee #1: *Pg. 2 line 14: 'Because of this. . .' The 'this' is ambiguous and seemingly refers to solubility, reword sentence for clarity.*

Response: This sentence has now been reworked as follows:

"However, the physicochemical properties of aminium sulphates are much less well characterised than their inorganic counterpart, $(NH_4)_2SO_4$, even though they can play a fundamental role in the nucleation and growth of new particles (DePalma et al., 2012; Loukonen et al., 2010; Wang et al., 2010) and in cloud formation (Lavi et al., 2013)."

Anonymous Referee #1: *P6 line 15: Change the mass fraction to wt% for consistency within paper.*

Response: The mass fraction at line 15, page 6, has now been converted to weight percentage.

Anonymous Referee #1: Figures: Keep the lettering (a,b, etc.) capitalization consistent, Fig. 3 and S1 are capitalized while others are lowercase.

Response: The capitalisation of the letters in all the Figures is now uniform.

Anonymous Referee #1: *Fig. 5/6: note that the Clegg et al. 2013 data is from Qui and Zhang 2012, this was not clear.*

Response: The data plotted in Figure 5 is actually taken from Clegg et al. (2013), who reworked the radial growth factor original H-TDMA measurements from Qiu and Zhang (2012). The same is true for Figure 6, where we converted the data from Figure 5 in terms of osmotic coefficients. For the sake of clarity, we now state in the caption that the data from Clegg et al. (2013) are based on H-TDMA measurements from Qiu and Zhang (2012).

Anonymous Referee #1: *Figures 5, 6, S2, S3: Include lettering in the graphs (a,b etc.) for consistency and ease of reference in text.*

Response: Letters have now been included in the various panels in order to make references in the text clearer.

Interactive comment on “Hygroscopic Properties of Aminium Sulphate Aerosols” by Grazia Rovelli et al.

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Response to Anonymous Referee #2

The authors would like to thank Anonymous Referee #2 for their comments on the manuscript. We respond to the specific comments made by the referee below and identify the changes we have to the manuscript.

Anonymous Referee #2: *This paper describes a new method of CK-EDB which can determine the hygroscopic properties of aerosol particles. In order to validate the method, the authors provided reproducible data for hygroscopic growth factor over the wide range of water activity. The results shown here agreed well with the results of previous studies that were performed with different methods. The manuscript presents in a clear, concise, and well-structured way, but I am afraid whether this paper is suitable for the scope of Atmos. Chem. Phys publication or not. Since the main focus of this work is to validate the new method, it would be better to be in a technical journal. If the authors would still like to publish the manuscript to ACP, the authors should address and implement my comments as below.*

Major comments: The measurements of hygroscopic properties of six aminium sulfate aerosols over the water activity range of 0.5 _ 1.0 are in remarkably good agreement with the calculations and the previous studies. However, I do wonder to where/for what we could apply these results? To understand why this work is important in the area of atmospheric chemistry and physics, please describe atmospheric implications in more detail with a separate section.

Response: In order to address the concerns of Referee #2 about the atmospheric relevance of this study, we have added some considerable detail in the Introduction section about the different processes aminium sulphates are involved in, together with a number of references to the literature. In particular, we added more detail about the role of gaseous amines molecules in the formation of new particles. In addition, we now clearly stress the fact that nanoparticles deriving from such new particles formation events and containing aminium sulphates have the potential ability to act as cloud condensation nuclei (CCN). For this reason, investigating and quantifying precisely the hygroscopic properties of aminium sulphates is particularly atmospherically relevant, since this information is valuable in understanding of the role of such compounds in cloud activation and therefore in the indirect effects of atmospheric aerosols on climate. Please refer to the Introduction (specifically the modifications already requested by Referee #1) and to the Summary and Conclusions (section 4), which is now titled “Atmospheric Importance and Conclusions”. To highlight the atmospheric relevance, we now write at the beginning of Section 4:

"Quantifying the hygroscopic properties of aminium sulphates is important for understanding and modelling of the atmospheric processes in which they are involved. In particular, the role of short-chained alkylamines in the formation of new particles has been investigated in recent literature studies and found to be significant (Section 1). Aminium sulphate-rich nanoparticles that derive from new particles formation events can potentially act as CCN, and their hygroscopic properties must be well-characterised with the aim of reducing the overall uncertainties that currently affect our understanding of the indirect effects of atmospheric aerosols on climate. Robust and accurate data are essential for improving microphysical models of aerosol hygroscopicity; this study presents an extensive data set for an homologous series of six compounds, compared to ammonium sulphate, extending over a wide range in RH. In addition, it represents the most comprehensive characterisation of the hygroscopic response of aminium sulphate aerosol so far, complementing previous bulk phase measurements (comparable in accuracy but limited to higher water activity) and aerosol measurements at lower RH (with lower accuracy than achieved here). Previously, the bulk and aerosol measurements reported in the literature were in disagreement. Here, we report aerosol measurements that are in good agreement with the previously most accurate bulk phase data, resolving this discrepancy."

In addition, we already state later in this section the significance of these new data when compared with the earlier bulk phase data, stating:

"The main differences in approaches are that: we perform aerosol measurements that cover a wider range in water activity as compared with the bulk measurements of Sauerwein et al. (2015); and we provide direct measurement at amine-to-sulphate ratios of exactly 2:1, whereas Sauerwein et al. (2015) performed a ZSR fitting on data from solutions with variable amine-to-sulphates ratios and extrapolated water content for the exact 2:1 ratio. These new CK-EDB measurements suggest a higher level of hygroscopic growth for the aminium sulphates than previously reported by Sauerwein and co-workers when inferred from measurements over a range of amine-to-sulphates ratios; we have provided a refined parameterisation for all compositions."

Minor comments

Anonymous Referee #2: *1. Page 4, line 23, Please add the RH and temperature values.*

Response: This information has now been added at line 16, page 4.

"Temperature and gas phase RH ranges that are accessible with this experimental setup are -25 to 50 °C and 0 to 99%, respectively. All the comparative evaporation kinetics measurements presented here were performed at 20 °C and at gas phase RH values between ~50-90%."

Anonymous Referee #2: *2. Page 6, line 13, Remove the comma after "mixed, "*

Response: This comma has now been removed.

Anonymous Referee #2: *3. Page 6, line 18, Please state at what temperature the amine solution was kept in an ice bath.*

Response: We have now explicitly said that the temperature was 0 °C.

“During both the titration of the amine stock solution with HCl and the preparation of the aminium sulphates solutions with H_2SO_4, the amine solution was kept in an ice bath (0 °C) and the addition of the acid was performed slowly and dropwise, in order to dissipate the heat generated by the neutralisation reaction and to avoid any possible amine volatilization.”

Anonymous Referee #2: *4. Page 8, line 12, Cite only once (Qiu and Zhang, 2012)*

Response: The double citation has now been removed.

Anonymous Referee #2: *5. I wonder why there is no data point for MMAS and TMAS from _0.7 to _0.8 aw in Fig. 3.*

Response: We have responded to this issue in our response to the comments made by Referee #1. Measurements were taken for a large number of systems over a wide range of conditions and it became apparent only later that measurements were not available for this small range of conditions for two compounds. We concluded that the trends were sufficiently clear that additional measurements were not essential.

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Response to Anonymous Referee #3

The authors would like to thank Anonymous Referee #3 for their helpful comments on the manuscript. We respond to the specific comments made by the referee below and identify the changes we have to the manuscript.

Anonymous Referee #3: *In this paper Grazia et al. describe the use of a Comparative Kinetic Electrodynamic Balance for investigation of the hygroscopic properties of Aminium Sulfate aerosols in comparison with water and Sodium Chloride solution drops with the same system and data collected by a number of other studies and methods. The experiments presented within are well thought out, the uncertainties in the data have been well investigated, and the results thoroughly compared with pervious data. However, I feel the tie to atmospheric chemistry, although present, is lacking. To be accepted for publication the authors should present more of a link to atmospheric processes and clearer indications of where this data this data will be most useful. Below are more detailed comments on the manuscript.*

Response: A similar comment was made by Referee #2 to which we have already responded. More specifically, we have added some considerable detail in the Introduction section about the different processes aminium sulphates are involved in, together with a number of references to the literature. In particular, we added more detail about the role of gaseous amines molecules in the formation of new particles. In addition, we now clearly stress the fact that nanoparticles deriving from such new particles formation events and containing aminium sulphates have the potential ability to act as cloud condensation nuclei (CCN). For this reason, investigating and quantifying precisely the hygroscopic properties of aminium sulphates is particularly atmospherically relevant, since this information is valuable in understanding of the role of such compounds in cloud activation and therefore in the indirect effects of atmospheric aerosols on climate. Please refer to the Introduction (specifically the modifications already requested by Referee #1) and to the Summary and Conclusions (section 4), which is now titled “Atmospheric Importance and Conclusions”. To highlight the atmospheric relevance, we now write at the beginning of Section 4:

“Quantifying the hygroscopic properties of aminium sulphates is important for understanding and modelling of the atmospheric processes in which they are involved. In particular, the role of short-chained alkylamines in the formation of new particles has been investigated in recent literature studies and found to be significant (Section 1). Aminium sulphate-rich nanoparticles that derive from new particles formation events can potentially act as CCN, and their hygroscopic properties must be well-characterised with the aim of reducing the overall uncertainties that currently affect our understanding of the indirect effects of atmospheric aerosols on climate. Robust and accurate data are essential for improving microphysical models of aerosol hygroscopicity; this study presents an extensive data set for an homologous series of six compounds, compared to ammonium sulphate, extending over a wide range in RH. In addition, it represents the most comprehensive characterisation of the hygroscopic response of aminium sulphate aerosol so far, complementing previous bulk phase measurements (comparable in accuracy but limited to higher water activity) and aerosol measurements at lower RH (with lower accuracy than achieved here). Previously, the bulk and aerosol measurements reported in the literature were in disagreement. Here, we report aerosol measurements that are in good agreement with the previously most accurate bulk phase data, resolving this discrepancy."

In addition, we already state later in this section the significance of these new data when compared with the earlier bulk phase data, stating:

"The main differences in approaches are that: we perform aerosol measurements that cover a wider range in water activity as compared with the bulk measurements of Sauerwein et al. (2015); and we provide direct measurement at amine-to-sulphate ratios of exactly 2:1, whereas Sauerwein et al. (2015) performed a ZSR fitting on data from solutions with variable amine-to-sulphates ratios and extrapolated water content for the exact 2:1 ratio. These new CK-EDB measurements suggest a higher level of hygroscopic growth for the aminium sulphates than previously reported by Sauerwein and co-workers when inferred from measurements over a range of amine-to-sulphates ratios; we have provided a refined parameterisation for all compositions."

Anonymous Referee #3: *Page 2 line 30: Rework the sentence starting with 'Their ambient conditions...'*

Response: This sentence has now been reworded as follow: "The ambient concentrations of amines in the gas phase can span wide ranges, depending on the sampling location. For example, concentrations can be up to 140 mg m^{-3} close to a city market (Namieśnik et al., 2003), 110-300 ng m^{-3} in the exhaust gas of a waste disposal (Kallinger and Niessner, 1999), and of the order of tens of µg m^{-3} inside livestock buildings (Kallinger and Niessner, 1999). Concentrations also depend on the season: for example, single amines in the gas phase at a rural site in Turkey have been reported to be in the range 0.92-7.4 ng m^3 in Winter and 0.29-5.16 ng m^3 in Summer (Akyüz, 2008)."

Anonymous Referee #3: *Introduction overall: This is meant to bring everyone up to speed but I found it lacking. Consider including more information on atmospheric relevance, in situ particle formation, etc. For instance your mention of aminium sulfates role in cloud particle nucleation seems forced. If you go to the Lavi et al. paper you find right in their abstract that "Alkyl aminium sulfates have been postulated to constitute important components of nucleation and accumulation mode atmospheric aerosols." and "We infer that these species have very high CCN activity . . ."*

Response: We thank the referee for this suggestion. As indicated in our response to their first comment, the Introduction section has now been reworked and expanded in order to make include more information on the atmospheric relevance of the investigation of the hygroscopic properties of aminium sulphates. In particular, we state on page 3:

"The role of amines in new particles formation and growth has been highlighted by computational studies (DePalma et al., 2012; Loukonen et al., 2010; Ortega et al., 2012), as well as by laboratory (Almeida et al., 2013; Wang et al., 2010b) and field measurements (Kulmala et al., 2013; Mäkelä et al., 2001; Smith et al., 2010). As an example, trimethylamine was found to enhance the formation and growth of new particles (Wang et al., 2010a) because of the favourable heterogeneous neutralisation reactions between the amine gaseous molecules and H_2SO_4-H_2O clusters. Smith et al. (2010) found variable but considerable concentrations of protonated amines in nanoparticles (8-10 nm diameter) during new particles formation events (47% of detected positive ions at an urban site in Mexico, 23% at remote site in Finland and 10-35% at sampling sites in Atlanta and Boulder). Since newly formed secondary particles are estimated to contribute to 45% of cloud condensation nuclei (CCN) (Merikanto et al., 2009), the presence of amines in CCN and their hygroscopic properties need to be taken into account to improve our understanding of the indirect effects of aerosol particles on climate (McFiggans et al., 2005), a key motivator for providing refined characterisation of the hygroscopic growth of aminium salt particles in this work."

Anonymous Referee #3: *Page 4 Line 6: It would be of benefit to the reader if a diagram of the EDB were included in the paper.*

Response: Because of the considerable length of the manuscript, and since 10 figures have already been included, we prefer not to include a diagram of the EDB instrument here; such diagrams already appear in our earlier papers. However, a schematic of the EDB setup has now been included in the supporting information and referred to in the text.

Anonymous Referee #3: *Page 4 line 16: How are you controlling the RH?*

Response: Different RHs are obtained by mixing a wet and a dry nitrogen flow in different ratios. This information has now been included on page 4. For completeness, how the temperature is controlled in this experimental setup has also been included. These details were not included in the original version of the manuscript, instead choosing to refer the reader to previous publications (Rovelli et al., 2016; Davies et al., 2013) for a detailed description.

"The gas flow RH is modified by mixing different ratios of a humidified and a dry nitrogen flow and is inferred from the evaporation kinetics of probe droplets, as described below in this section. The temperature within the trapping chamber is controlled by a circulating a 1:1 volume mixture of water and ethylene glycol, through the lid and the bottom of the chamber."

Anonymous Referee #3: *Page 4 line 22: You never explicitly state the range of RH and temperatures you are conducting your experiments at, over. Please include for completeness and link to atmospherically relevant conditions.*

Response: This information has now been added on page 4. Although a wide range in atmospherically relevant RHs is addressed in the measurements we present here, we have not yet performed a temperature dependence for these measurements. This will be addressed in a subsequent publication.

"Temperature and gas phase RH ranges that are accessible with this experimental setup are -25 to 50 °C and 0 to 99%, respectively. All the comparative evaporation kinetics measurements presented here were performed at 20 °C and at gas phase RH values between ~50-90%."

Anonymous Referee #3: *Page 4 line 26: You mention it once (on the noted line) but I think it would help to clarify that your droplets are alternatingly injected into the system as it is possible to have multiple particles or drops trapped in an EDB simultaneously. One question I had – You're residence timescale for a single particles is less than 30 s so the RH it is exposed to is arguably constant, but to what degree does the RH change over the course of the 10+ particle runs?*

Response: To make sure that it is clear that all evaporation kinetics experiments are performed by alternating single probe droplets to single sample droplets, "single" (droplets) has been added at lines 15, 23, 24 (page 4) and "singly-trapped" (probe and sample droplets) has been added at line 28 (page4).

With respects to Referee #3's concerns about the stability of the gas phase RH over a run of 10+ particles, first we would like to point out that the evaporation kinetics of each sample droplet is analysed using the RH value coming from the fitting of the previous probe droplet. This ensures that even when there are very slight fluctuations in the gas phase RH, they would be taken into account in the retrieval of the hygroscopic properties of the sample droplets. That said, RH fluctuations over a typical run of 20 droplets (10 probe/10 samples) are of the order of 0.2% and never exceed 0.5% RH. In order to clarify this aspect, a few sentences have been added on page 5.

"RH fluctuations over the run of ten pairs or more of probe and sample droplets are very slight, typically of the order of 0.2% RH and never exceeding 0.5% RH. However, it should be noted that slight RH fluctuations are taken into account in our approach: the gas phase RH is monitored before every sample droplet by injecting a probe droplet and data from this probe droplet are directly used in the sample droplet evaporation analysis."

Anonymous Referee #3: *Page 8 line 13: I've seen this throughout the paper: '. . . estimated by Qiu and Zhang (2012) (Qiu and Zhang, 2012) is . . .' You have essentially cited the paper twice and the second citation should be removed. Other instances can be found on page 3 line 3 and page 15 line 29. There may be others I missed.*

Response: Thank you for identifying this problem. The double references mentioned have now been removed and we have also checked throughout the manuscript to make sure there are no other double references remaining.

Anonymous Referee #3: *Page 12 line 19: I think this is the first time you introduce ZSR, make this acronym explicit in line 16 where you introduce Zdanovskii-Stokes-Robinson expression.*

Response: We have added the definition of the acronym on page 12 where it is used for the first time.

Anonymous Referee #3: *Page 15 line 22: Quantify fine variations.*

Response: 'Fine variations' at line 22, page 15, is now quantified as follows.

"Measurements from our new approach provide a level of accuracy that reveals clearly the fine variations in hygroscopic growth (down to discernible difference is GF_r of order 0.01-0.02) that occur with molecular structure and substitution, and avoids the additional complexity of volatilisation of semi-volatile components during hygroscopic growth with measurements complete in a matter of a few seconds.”

Anonymous Referee #3: *Page 16 last paragraph: This doesn’t seem to fit. Your previous paragraph starts with ‘As a final remark . . .’ then this is thrown in. This goes back to my main issue of making the paper more atmospherically relevant.*

Response: Thank you for this comment. We agree that having “As a final remark..” at the start of the second to last paragraph is a little misleading, so we have now changed this. However, we think that the considerations in the last paragraph are quite important, because this is the first one of a series of papers where we will report measurements of the hygroscopic properties of increasingly more complex organic and mixed inorganic-inorganic aerosol systems. We have addressed the question of atmospheric relevance earlier in our response.

Anonymous Referee #3: *Figure 4: You can remove legend from caption text.*

Response: The legend has now been removed from the caption.

Anonymous Referee #3: *Figures 5 & 6: Consider labeling your subplots a-f as done in other multi-plot figures.*

Response: Figures 5 and 6 are now labelled with a-f to indicate each subplot. References to these labels have also been included in the main text.

Hygroscopic Properties of Aminium Sulphate Aerosols

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Abstract. Alkylaminium sulphates originate from the neutralisation reaction between short-chained amines and sulphuric acid and have been detected in atmospheric aerosol particles. Their physicochemical behaviour is less well characterised than their inorganic equivalent, ammonium sulphate, even though they play a role in atmospheric processes such as the nucleation and growth of new particles and cloud droplet formation. In this work, a comparative evaporation kinetics experimental technique using a cylindrical electrodynamic balance is applied to determine the hygroscopic properties of six short-chained alkylaminium sulphates, specifically mono-, di- and tri-methylaminium sulphate and mono-, di- and tri-ethyl aminium sulphate. This approach allows the retrieval of a water activity dependent growth curve in less than 10 s, avoiding the uncertainties that can arise from the volatilisation of semi-volatile components. Measurements are made on particles >5 μm in radius, avoiding the need to correct equilibrium measurements for droplet surface curvature with assumed values of the droplet surface tension. Variations in equilibrium solution droplet composition with varying water activity are reported over the range 0.5 to >0.98, along with accurate parameterisations of solution density and refractive index. The uncertainties in water activities associated with the hygroscopicity measurements are typically <±0.2% at water activities >0.9 and ~±1% below 0.9, with maximum uncertainties in diameter growth factors of ±0.7%. Comparison with previously reported measurements show deviation across the whole water activity range.

1. Introduction

Quantifying the response of aerosol particles to variations in relative humidity (RH) in the atmosphere is important for predicting the impact of aerosols on climate through both direct and indirect radiative forcings (Albrecht, 1989; Kanakidou et al., 2005; Kolb et al., 2010), for understanding the mechanisms of heterogeneous chemistry (Dennis-Smither et al., 2014; Lee et al., 2012) and the partitioning of products in the condensed phase (Dusek et al., 2006; Topping et al., 2013a), and for inferring the deposition and loss mechanism of aerosols on surfaces and on inhalation into the respiratory tract (Broday and Georgopoulos, 2001; Haddrell et al., 2015). With an increase in RH, solution droplets must absorb water to maintain an equilibrium balance of water between the gas and condensed phases, leading to the dilution of solutes, increase in mass of condensed phase water and hygroscopic growth in particle size. The hygroscopic response of a wide range of inorganic and organic solutes of varying solubility often present as complex mixtures, must be quantified. Thus, the influence of interactions between multiple solutes of varying charge, acidity and hydrophilicity must be understood through predictions of activity coefficients that reflect the departure of solution composition from ideality (Dutcher et al., 2013; Shiraiwa et al., 2013).

Measurements of the hygroscopic growth of ambient aerosol are routinely made: the extent of growth at high RH or the critical supersaturation for activation as cloud condensation nuclei are often represented by a single parameter, such as the κ parameter in κ-Köhler theory (Petters and Kreidenweis, 2007). Resorting to such a reduced parameter model is a consequence of the complex chemical composition of ambient aerosol and the intractability of providing accurate predictions based on a detailed chemical speciation. However, laboratory measurements are essential for exploring the complex details often obscured in measurements of ambient aerosol. These include the roles of pH, liquid-liquid phase separation and mixing state (Topping et al., 2013c; You et al., 2014) and the co-condensation of semi-volatile organic species with varying RH (Topping et al., 2013b). When considered alongside measurements of hygroscopic response and change in particle composition with RH for aerosol of well-known chemical composition, detailed predictive tools can be benchmarked and improved, providing a crucial framework for interpreting field measurements. We present here measurements of the hygroscopic response of a class of compounds, aminium sulphates, with the objective of providing accurate data to refine predictive tools of their equilibrium hygroscopic response.

Low molecular weight amines are mostly emitted into the atmosphere as gaseous compounds by a number of different sources, both anthropogenic (animal husbandry, food processing and cooking, combustion, pesticides) and natural (oceans, biomass burning, vegetation) (Ge et al., 2011a). These chemical species are basic (with pK_a values from 9.8 to 10.84) (Lide, 2005), highly water-soluble and have high pure liquid vapour pressures (up to hundreds of kPa at 298.15 K) (Ge et al., 2011b). ~~Their~~The ambient concentrations of amines in the gas phase ~~in the environment~~ can span wide ranges, depending on the sampling location. ~~(f~~For example, concentrations can be up to 140 mg m^{-3} close to a city market (Namieśnik et al., 2003), 110-300 ng m^{-3} in the exhaust gas of a waste disposal site (Kallinger and Niessner, 1999), and of the order of tens of µg m^{-3} inside livestock buildings (Kallinger and Niessner, 1999).~~)~~ Concentrations also depend ~~and~~ on the season: for example, single amines in the gas phase at a rural site in Turkey have been reported to be in the range ~~(e.g.,~~ 0.92-7.4 ng m^3 in Winter and ~~,~~ 0.29-5.16 ng m^3 in Summer~~, for single amines in the gas phase at a rural site in Turkey~~ (Akyüz, 2008)~~;~~. Further, ~~(~~Pratt et al.~~,~~ (2009) measured a seasonal volatility dependence of alkylamines depending on the particles pH that affects the amines concentrations in the gas phase~~)~~ ~~(Akyüz, 2008; Pratt et al., 2009)~~. In the condensed phase, amines can account for hundreds of pg m^{-3} or a few ng m^{-3} of aerosol mass~~;~~. ~~an~~ An extensive review of the measured concentrations of a large number of amines both in the gas phase and in aerosols at a ~~great variety~~large number of rural and urban environments is given by Ge et al. (~~Ge et al.,~~ 2011a, 2011b).

The role of amines in new particles formation and growth has been highlighted by computational studies (Loukonen et al., 2010; DePalma et al., 2012; Ortega et al., 2012), as well as by laboratory (Wang et al., 2010b; Almeida et al., 2013) and field measurements (Mäkelä et al., 2001; Smith et al., 2010; Kulmala et al., 2013). As an example, trimethylamine was found to enhance the formation and growth of new particles (Wang et al., 2010a)~~,~~ because of the favourable heterogeneous neutralisation reactions between the amine gaseous molecules and H_2SO_4-H_2O clusters. Smith et al. (2010) found variable but considerable concentrations of protonated amines in nanoparticles (8-10 nm diameter) during new particles formation events (47% of detected positive ions at an urban site in Mexico, 23% at remote site in Finland and 10-35% at sampling sites in Atlanta and Boulder). Since newly formed secondary particles are estimated to contribute to 45% of cloud condensation nuclei (CCN) (Merikanto et al., 2009), the presence of amines in CCN and their hygroscopic properties need to be taken into account to ~~go towards an increased~~improve our understanding of the indirect effects of aerosol particles on climate (McFiggans et al., 2005), a key motivator for providing refined characterisation of the hygroscopic growth of aminium salt particles in this work.

In addition, d~~D~~espite the volatility of short-chained alkylamines, these compounds can undergo gas-to-particle partitioning due to a variety of chemical processes (Ge et al., 2011a): direct solubilisation, oxidation reactions that lead to the formation of secondary organic aerosols, acid-base reactions similar to those of ammonia (Seinfeld and Pandis, 2006) with both inorganic (sulphuric, nitric and hydrochloric acids) and organic acids (Lavi et al., 2015; Liu et al., 2012), and displacement reactions of ammonium cations with aminium cations (Bzdek et al., 2010; Qiu and Zhang, 2013). ~~With respect to these last two types of chemical reactions,~~ The product of these last two types of chemical reactions and the salts formed by ~~the~~ protonated amines following to new particles formation are aminium sulphates, ~~are the products of~~ which result from the neutralisation of sulphuric acid and short-chained alkylamines:

$$H_2SO_4 + 2R_3N \rightleftarrows (R_3NH)_2SO_4 \qquad (1)$$

where R can be either $-CH_3$, $-CH_2CH_3$ or $-H$. The formation of aminium sulphates and other similar aminium salts increases ~~their solubility~~the solubility of short-chained alkylamines ~~(~~from 7-45 wt% for the unprotonated form (calculation from data in Ge et al. (2011b)) to 84-91 wt% for five aminium sulphates in Clegg et al. (2013)~~)~~. This, correspondingly, increases~~and, thus,~~ their partitioning from the gas to the condensed phase (Barsanti et al., 2009; Yli-Juuti et al., 2013). ~~Because of this, and because~~

~~of their relative abundance in the atmosphere, aminium sulphates~~ However, ~~their~~ the physicochemical properties of aminium sulphates are much less well characterised than their inorganic counterpart, $(NH_4)_2SO_4$, even though they can play a fundamental role in the nucleation and growth of new particles (DePalma et al., 2012; Loukonen et al., 2010; Wang et al., 2010b) and in cloud formation (Lavi et al., 2013). Some recent work has attempted to fill this gap, reporting the densities (Clegg et al., 2013; Lavi et al., 2013; Qiu and Zhang, 2012), CCN activity, optical properties (Lavi et al., 2013), hygroscopicity and phase transitions of aminium sulphates (Chu et al., 2015; Clegg et al., 2013; Lavi et al., 2013; Qiu and Zhang, 2012; Sauerwein et al., 2015), specifically for the methyl and ethylaminium sulphates (or subsets of these six compounds). In this work, we report measurements of the hygroscopic behaviour of the three methylaminium sulphates (methylaminium sulphate, MMAS; dimethylaminium sulphate, DMAS; trimethylaminium sulphate, TMAS) and the three ethylaminium sulphates (ethylaminium sulphate, MEAS; diethylaminium sulphate, DEAS; triethylaminium sulphate, TEAS) from water evaporation experiments made using a comparative kinetic Electrodynamic Balance (CK-EDB) (Rovelli et al., 2016). In Section 2 we review the experimental details and procedures for performing hygroscopic growth measurements using the CK-EDB. In Section 3, we present measurements of the hygroscopic growth of the six aminium sulphate salts, comparing our measurements with literature values and considering the accuracy and reproducibility of measurements with the CK-EDB.

2 Experimental

We first describe the CK-EDB technique and the data analysis before describing the method for preparing aqueous starting solutions of the aminium sulphates.

2.1 Hygroscopic Properties from Comparative Kinetics Measurements in a CK-EDB

Electrodynamic trapping of single charged droplets has been used to investigate various properties of confined particles, including optical properties (Barnes et al., 1997), vapour pressures of low volatility compounds (Pope et al., 2010), hygroscopic properties of atmospherically-relevant aqueous solutions (Choi and Chan, 2002; Chu et al., 2015; Peng et al., 2001; Rickards et al., 2013) and of pharmaceutical aerosols (Haddrell et al., 2013; Peng et al., 2000), and evaporation dynamics of aqueous droplets (Heinisch et al., 2009; Shulman et al., 1997; Zobrist et al., 2011). The experimental setup used in this work has been presented in previous publications (Davies, 2014; Davies et al., 2012a, 2012b, 2013; Haddrell et al., 2012; Miles et al., 2012) and a schematic of it can be found in the Supplementary Information (Fig. S1). In particular, the approach used to quantify the hygroscopic properties of single confined particles from comparative kinetics measurements using a CK-EDB has also been previously discussed (Davies et al., 2013) and its application over a wide solution water activity range from 0.5 to >0.99 has been extensively validated (Rovelli et al., 2016).

In a CK-EDB single charged droplets from two solutions with known chemical composition and concentration can be sequentially dispensed on-demand by means of two alternatively operated microdispensers and trapped within the electrodynamic field generated by a set of concentric cylindrical electrodes. This electrode geometry guarantees a stable and tight trapping of single droplets within 100 ms from their generation. Single d~~D~~roplets are confined in the trapping chamber within a nitrogen stream with controlled mass flow, temperature and relative humidity. The gas flow RH is modified by mixing different ratios of a humidified and a dry nitrogen flow and is inferred from the evaporation kinetics of probe droplets, as described below~~ in this section~~. The temperature within the trapping chamber is controlled by a circulating a 1:1 volume mixture of water and ethylene glycol, through the lid and the bottom of the chamber. Temperature and gas phase RH ranges that are accessible with this experimental setup are -25 to 50 °C and 0 to 99%, respectively. All the comparative evaporation kinetics measurements presented ~~in this work~~here were performed at 20 °C and at gas phase RH values between ~50-90%. Trapped droplets are illuminated by laser light (532 nm) and the resulting elastic scattering light pattern is collected every 0.01 s by means of a CCD camera and used to keep track of changes in size of a single levitated droplet using the geometrical optics approximation (Glantschnig and Chen, 1981). Note that the variations in refractive index due to water evaporation from each droplet are taken into account for an accurate determination of droplet size, as described in a previous publication (Davies et al., 2012b).

The evaporation rate of water from a droplet containing one or more solutes at a certain RH and temperature depends on the hygroscopic properties of the solution. In comparative kinetics experiments, the evaporation rate of single probe droplets with known composition and known evaporation kinetics (either pure water or a NaCl solution) is compared to that of single sample droplets in order to determine the hygroscopic properties of the solution droplet being studied (Davies et al., 2013; Rovelli et al., 2016). To do so, typical CK-EDB experiment are composed of a series of at least ten alternating single probe and sample droplets (Fig. 1a).

The retrieval of the hygroscopic properties from the radius (a) vs. time evaporation profiles of a sequence of singly-trapped probe and sample droplets is shown schematically in Fig. 1. Different analyses are carried out for probe (Fig. 1b) and sample droplets (Fig. 1c). Either pure water (as shown in Fig. 1a) or NaCl solution droplets with known initial salt concentration can be used as a probe. The evaporation profiles of the probe droplets are compared with simulations obtained from the evaporation/condensation kinetics model by Kulmala et al. (1993). By doing so, the gas phase RH can be inferred, either from fitting the a^2 vs. time evaporation profile of pure water droplets or from the equilibrated radius of the NaCl solution droplets. Both methods, together with their associated uncertainties and their RH ranges of applicability, have been discussed previously (Davies et al., 2013; Rovelli et al., 2016). RH fluctuations over the run of ten pairs or more of probe and sample droplets are very slight, typically ~~in~~of the order of 0.2% RH and never exceeding 0.5% RH. However, it should be noted that~~, please note that possible~~ slight RH fluctuations are taken into account in our approach: the gas phase RH is monitored before every sample droplet by injecting a probe droplet and data from this probe droplet are directly used in the sample droplet evaporation analysis.~~, since the gas phase RH is monitored before the run of every sample droplet by injecting a probe droplet; successively, for the retrieval of hygroscopic properties of sample droplets (described in the following paragraph), the RH inferred from the previous probe droplet is directly used in the sample droplet evaporation analysis.~~

For the analysis of the radius (*a*) vs. time data of sample droplets, the radius data (Fig. 1c, inset panel i) are converted to droplet mass (inset ii) by using a 3rd order polynomial parameterisation of density as a function of the solute mass fraction, which is discussed below. The mass flux of water leaving the droplet during evaporation (d*m*/d*t*) is then calculated and, knowing the gas phase RH from the probe droplet analysis, Kulmala's equations for evaporation kinetics are applied to calculate the temporal variation of water activity (a_w) in the droplet (inset iii). In addition, knowing the initial concentration and size of the droplet at generation, the radius of the dry particle (a_{dry}) can be estimated and a radial growth factor ($GF_r = a / a_{dry}$) can be calculated for each of the measured radii (inset iv). Results from inset panels (iii) and (iv) are then combined and typical GF_r vs a_w growth curves are obtained. The key thermodynamic quantities that describe the hygroscopic properties of the tested solution (moles of water per mole of solute in solution, n_{water}/n_{solute}; osmotic coefficients, ϕ_{st}) can be calculated if the densities of the aqueous solutions are also known (see below). Details of the treatment of the experimental uncertainties and their influence on each of the computed quantities are described in the Supplementary Information (Table S1). When error bars are not shown in the figures in the following sections, the reader can assume that they are smaller than the size of the corresponding data point.

A previous study (Cai et al., 2016) showed that the molar refraction mixing rule, together with a 3rd order polynomial parameterisation of density as a function of the square-rooted mass fraction of solute (*mfs*), represent the best approach to predicting refractive indices (*m*) and densities (ρ) of solutions of organic compounds for which bulk data of such quantities is available for solute mass fractions up to at least 0.4. In this work the densities of at least ten solutions with different concentrations for each aminium sulphate were measured with a density meter (Densito 30PX, Mettler Toledo, accuracy of ±0.001 g cm^{-3}, calibrated with pure water before each use). Densities were measured at ambient temperature, which varies in the laboratory between 293 K and 295 K; temperatures were always registered together with the measured density values. In addition, refractive indices of the same solutions were measured at 589 nm by means of a refractometer (Palm Abbe II, Misco, precision of ±0.0001, calibration with pure water before each use). The measured density and *m* values for each aminium sulphate solution are provided in the Supplementary Information (Table S2), together with the 3rd order polynomial and the molar refraction mixing rule fittings for each compound (Table S3 and Fig. ~~S1~~S2). A brief description of the molar refraction mixing rule application is also provided in the Supplementary Information. These data have been presented previously and discussed by Cai et al. (2016) along with measurements from a large number of organic aqueous solutions.

2.2 Preparation of the Solutions

Aminium sulphate stock solutions were prepared by the neutralization of solutions of each of the six amines with aqueous sulphuric acid. The commercial amines stock solutions (Sigma Aldrich, MMA, ~ 40 wt%; DMA, ~ 40 wt%; TMA, ~ 45 wt%; MEA, ~ 66.0-72.0 wt%; DEA ≥ 99.5 wt%; TEA ≥ 99 wt%) were titrated with standardised HCl (1 M, SLS) to determine their mass concentrations accurately. Three repetitions were performed for each titration and the pH was measured throughout by means of a pH-meter (HI 8314, Hanna Instruments), which was calibrated with standard pH 7 and pH 4 solutions. Before the titration, the amine stock solutions were always diluted down to 1-5 wt% in order to minimize the heat generated by the neutralisation reaction and to minimise volatilisation of the amine. In addition, the HCl (and later the H_2SO_4) used for the standardisation of the commercial amine solutions were titrated with Na_2CO_3 (≥ 99.5%, Alfa Aesar), which was first dried at 225°C for 3 h before weighing to make sure that no water was adsorbed on it. Three repetitions were performed in these cases.

For the preparation of the aminium sulphates stock solutions, stoichiometric amounts of the standardised H_2SO_4 and amine solutions were mixed~~,~~ with an initial concentration of both solutions around 40 wt%. The pH of the solution mixture was monitored for the whole duration of the reaction to ensure that all of the amine in the solution had reacted. The concentrated stock solutions of the salts that result from this procedure were subsequently diluted down to a~~ mass fraction of ~0.05~~ weight percentage of ~5%, in order to obtain a suitable starting concentration for the CK-EDB comparative kinetics measurements. During both the titration of the amine stock solution with HCl and the preparation of the aminium sulphates solutions with H_2SO_4, the amine solution was kept in an ice bath (0 °C) and the addition of the acid was performed slowly and dropwise, in order to dissipate the heat generated by the neutralisation reaction and to avoid any possible amine volatilization. Phase separation was observed when titrating the TEA commercial solution and its concentration was determined to be 81.6 wt% (0.52 wt% standard deviation over 3 repetitions), which is considerably lower than the ≥ 99 wt% concentration value given by the manufacturer. This is possibly due to the much lower solubility of TEA (0.7 mol kg^{-1}) than the other amines (Ge et al., 2011b), leading to incomplete solvation of the amine in water and an inaccurate measurement of pH during the titration. Thus, we instead assumed that the commercial TEA solution was a 99 wt% concentration and note that the results for the TEA system should be interpreted with some caution. This experimental procedure ensured that the concentrations of the reagents were well known and, consequently, that the concentrations of the stock solutions prepared for aminium sulphates were similarly well known. The uncertainties in the commercial solution concentrations of the reagents, as determined from the repeated titrations, were taken into account for the calculation of the overall experimental uncertainties indicated in the Supplementary Information (Table S1).

To validate the procedure for solution preparation described above, the steps were carried out for the preparation of $(NH_4)_2SO_4$ from the reaction of ammonia and sulphuric acid. The resulting salt solution was then used in comparative kinetics measurements and the hygroscopicity of the ammonium sulphate from reaction was compared with calculations from the

Extended Aerosol Inorganics Model (E-AIM) (Wexler and Clegg, 2002). Figure 2 shows the hygroscopic properties of $(NH_4)_2SO_4$ droplets prepared in this way from the direct reaction of ammonia and sulphuric acid, reporting values of n_{water}/n_{solute}, vs. a_w (Panel (a)) and osmotic coefficients (ϕ_{st}) plotted against the square-root of the sulphate molality ($m(SO_4^{2-})^{0.5}$, Panel (b)). Osmotic coefficients are useful parameters to represent the deviation of a solution from an ideal behaviour and they are defined as indicated in Eq. (2):

$$\boldsymbol{\phi_{st} = -\frac{\ln(a_w)}{M_w 3m/1000}} \qquad (2)$$

where M_w is the molecular weight of water, m is the molality of the solute and 3 is the stoichiometric number of ions in the salt. The value of ϕ_{st} tends to 1.0 in the limit of an infinitely dilute solution, in accordance with the Debye-Hückel limiting law (Robinson and Stokes, 1970).

In a previous publication (Rovelli et al., 2016) we showed that it is possible to achieve very good agreement with predictions from the E-AIM model for well-characterised inorganic compounds with the CK-EDB experimental technique within an uncertainty in a_w of ±0.002. The plots in Fig. 2 show the averaged data obtained from two datasets of ten droplets of aqueous $(NH_4)_2SO_4$ (black and open circles). In Fig. 2b the effect of a ±0.002 error on a_w on the modelled osmotic coefficients values is shown with dashed lines. The osmotic coefficients agree well with calculations from the E-AIM model and lie within the envelope associated with this previous estimate of typical experimental uncertainty for the CK-EDB technique. This demonstrates that the volatility of ammonia is not a significant problem when the neutralisation reaction with H_2SO_4 is performed. In addition, since the vapour pressure of ammonia (1956 kPa at 298.15 K) (Lide, 2005) is even higher than the vapour pressure of the most volatile of the six considered amines (methylamine, 336 kPa at 298.15 K) (Ge et al., 2011b), it is likely that there is also no evaporative loss of amines from solution during the preparation of the aminium sulphate solutions. This result confirms that the estimated concentrations of the $(NH_4)_2SO_4$ solutions prepared from NH_3 and H_2SO_4 are accurate, and that the preparation method is reliable for both $(NH_4)_2SO_4$ and all the six aminium sulphates.

3 Results and Discussion

We first report our measurements of the hygroscopic response of the sequence of six aminium salts before comparing our results with previous studies and assessing the accuracy and reproducibility of our data.

3.2 Hygroscopic Properties of Aminium Sulphate Droplets

The hygroscopic properties of the series of six aminium sulphates were characterised by means of comparative kinetics measurements and using the density and refractive index parameterisations discussed for the CK-EDB data treatment, as described in Sect. 2.1. First, the radial growth curves are shown in Fig. 3a. Considering the compound with the lowest molecular weight first, the hygroscopic behaviour of MMAS is the most similar to ammonium sulphate, in terms of GF_r. Continuing in the methylaminium sulphates series, a slight decrease in GF_r is observed in the high water activity region (a_w>0.8) for DMAS and TMAS, while at lower water activities, the hygroscopic properties of these compounds converge to $(NH_4)_2SO_4$ within the uncertainties of the measurements as the amount of water in the particles decreases. With respect to the ethylaminium sulphates series, a more evident decreasing trend in the radial growth curve is observed with increasing number of C atoms in the cation (MEAS > DEAS > TEAS), once again especially in the upper part of the curves. If the mono-, di- and tri- pairs within the two different series are compared, the methyl compound always presents higher values of radial growth factor than its equivalent in the ethylaminium sulphates series. As indicated in Section 2.2, it is worth reiterating that the results presented here and below for TEAS need to be ~~taken~~interpreted cautiously because of the uncertainty of the TEA stock solution. However, the trends that have been ~~individuated~~observed for TEAS ~~(both in terms of GF_r here and below)~~ when compared to the other five aminium sulphate~~s~~ systems seem to be completely plausible and this may indicate that the assumed initial TEA concentration is reasonable.

For the calculation of the dry radius reference state in the denominator of GF_r, the pure melt density is used (Sect. 2.1); if the pure solid density values were known and used, one could expect that the calculated radial growth curve would be slightly higher, a consequence of the solid densities having higher values than the melt density (Clegg et al., 2013). A comparison of the pure melt densities (ρ_{melt}) from our work and from Clegg et al. (2013) and solid densities (ρ_{solid}) estimated by Qiu and Zhang (2012) ~~(Qiu and Zhang, 2012)~~ is provided in Table S4 in the Supplementary Information, with our data previously published in Cai et al. (2016). As an example, if a hypothetical increase of 5% from ρ_{melt} to ρ_{solid} as a rough estimate is considered for DMAS, the obtained GF_r curve would increase by less than 1% (less than 0.01 in GF_r); this would not affect the trends shown in Fig. 3a, although it would marginally change the relative position of the aminium sulphates curves to that of ammonium sulphate.

The same datasets shown in Fig. 3a have been converted to n_{water}/n_{solute} vs. a_w and are shown in Fig. 3b. Note that the y-axis is displayed on a logarithmic scale for clarity. Different trends can be recognised: the primary factor influencing how many moles of water are absorbed per mole of solute is the number of alkyl groups in the cation and not the length of the carbon chains (i.e. mono- vs. di- vs. tri-methyl or ethyl). In fact, when the n_{water}/n_{solute} curves (Fig. 3b) are compared with the hygroscopic behaviour plotted as GF_r (Fig. 3a), more significant differences are apparent in Fig. 3b within each series (e.g. among MMAS, DMAS and TMAS) rather than between analogous compounds belonging to the two series (e.g. between TMAS and TEAS), even though the ethylaminium sulphate in a pair always has slightly higher values of n_{water}/n_{solute} (i.e. MMAS ≈ MEAS < DMAS ≈ DEAS < TMAS ≈ TEAS).

The seemingly different trends found for the hygroscopic properties of aminium sulphates when reported either as GF_r or n_{water}/n_{solute} as a function of a_w originate in the different physicochemical properties that each quantity is dependent on. When

GF_r is calculated, the density and molecular weight of each compound are central to its determination. For example, if particles with a dry radius of 1 µm for each of the six aminium sulphates are considered, the moles of salt in each droplet decreases with increase in molecular weight and decrease in density, as shown in Fig. 4. Therefore, if hygroscopicity is represented by a radial growth factor, GF_r is determined not only by the ability of a compound to absorb water at a certain relative humidity, but also by the number of solute molecules present in the droplet itself. For this reason, a decreasing hygroscopic growth trend with increasing molecular weight of the aminium sulphates is apparent in Fig. 3a for GF_r.

Growth factor curves are widely used in the aerosol literature, especially when the optical properties and radiative forcing or the climatic effects of atmospheric aerosols are investigated, because these properties largely depend on particle size. The quantification of the hygroscopic properties of a compound in terms of GF_r is therefore useful for such applications and is reported in this work. However, n_{water}/n_{solute} vs. a_w curves allow the thermodynamic characterisation of the water uptake of a substance and the decoupling of its hygroscopic properties from its density and molecular weight, with the water uptake 'normalised' to the moles of solute in the particle. This representation – effectively water activity as a function of concentration – is mostly used when focusing on chemical reactivity or on the thermodynamic properties of compounds in the aerosol phase. The increasing trend apparent in Fig. 3b for n_{water}/n_{solute} curves with increasing number of carbon atoms in the cation is related to the size of the cation itself: the bigger the cation, the larger the number of water molecules required to solvate the cation at a particular water activity. It is perhaps worth noting here the high level of accuracy in retrieving hygroscopic growth by this method and the opportunity it provides to resolve such fine trends in growth factor.

3.2 Comparisons with Previous Studies

As described in the Introduction, there have been some recent reports of the physicochemical properties of aminium sulphate aerosols and aqueous solutions, motivated by the increasing understanding of their role in atmospheric processes (Bzdek et al., 2010; Ge et al., 2011a; Lavi et al., 2015; Liu et al., 2012; Qiu and Zhang, 2013). With respect to the determination of their hygroscopic properties, the approach presented here differs from the earlier reports in either the preparation method of the solutions or in the experimental measurement technique. We now compare our measurements using a CK-EDB with the results of these previous studies.

Qiu and Zhang (2012) were the first to measure diameter growth curves for these compounds (excluding MEAS) by means of an HTDMA (Hygroscopicity Tandem Differential Mobility Analyser). They inferred hygroscopic growth factors from the ratio of the mobility diameters measured at a variable RH (up to 90%) and at an RH of ~12%. A monotonic increase in the particle size with RH for each compound was observed and no deliquescence/efflorescence behaviour was observed. If their growth curves are compared with the GF_r shown in Fig. 3a (Fig. ~~S2~~ S3 in Supplementary Information), a systematically smaller growth factor is reported from the HTDMA measurements. The largest deviations are for TEAS (-16% on average in the a_w range where the two datasets overlap, from ∼ 0.5 to 0.9) and for TMAS (-13%), a deviation of -10% is observed for DEAS and DMAS and of -7% for MMAS. These discrepancies are most likely due to the presence of some residual water at the conditions at which the reference diameter was measured in the HTDMA experiments (RH ∼12%), which would result in an overestimated reference ‘dry’ size and in underestimated growth factor values. This explanation is supported by the studies of Chan and Chan (2012) who reported the presence of water for some aminium sulphates even at an RH of ∼3%. In addition, the possible volatilisation of the amine during the drying step in the HTDMA would alter the chemical composition of the particles (Chan and Chan, 2012, 2013), not only artificially reducing the apparent dry size recorded but shifting the dry particle towards an aminium bisulphate composition (1:1 molar ratio of sulphuric acid to amine), which has been shown to be less hygroscopic than its sulphate counterpart (Sauerwein et al., 2015).

Consistent with the above discussion, the two compounds with the biggest deviation between the GF_r values reported here and by Qiu and Zhang (TMAS and TEAS) are those that were found to be affected by the largest evaporative losses of amine by Chan and Chan (2012). They reported studies of ammonium displacement reactions by alkylamines by levitating single droplets in an EDB and evaluating the changes in the recorded Raman spectra during an experiment. After TEAS solution droplets were levitated at RH<3% for more than 5 h, TEAS was found to have converted to TEA bisulphate almost completely, indicating that half of the amine in the initial solution droplet had evaporated. Similar behaviour was observed for TMAS, while DMAS and DEAS showed a smaller degree of evaporation of the amine (∼25% and ∼5%, respectively); MMAS and MEAS did not show any relevant evaporation over the experimental timescales. These results support the hypothesis of possible evaporation of the amine from the drying solution droplets during HTDMA experiments, and at the same time represent an interesting comparison to evaluate the timescales over which the evaporative loss of amine is significant. The hygroscopic growth measurement of each droplet of aminium sulphate solution in CK-EDB studies extends over 30 s at the longest: this allows the effective decoupling of the fast water evaporation and the slow amine evaporation, since these two processes occur over different timescales. In addition, the hygroscopicity measurements in the present work were carried out at RHs in excess of 50% at all times; for this reason, the evaporation of the amines are necessarily smaller than those measured by Chan and Chan (2012).

Clegg et al. (2013) have converted the size growth curves measured by Qiu and Zhang to n_{water}/n_{solute} vs. a_w. The growth curves that resulted did not show any discernible trends in the hygroscopicity of aminium sulphates. Indeed, the results were essentially similar to the water uptake of ammonium sulphate in the lower a_w range. At higher a_w above 0.7, the scatter in the data limited the identification of any apparent trend apart from the suggestion that the methylaminium sulphates absorb fewer moles of water per moles of solute than the compounds in the ethyl series. Fig. 5 shows the large differences between the water uptake determined from the results of Qiu and Zhang, and that from the work in this study. Because of the uncertainties associated with the HTDMA GF_r values, it is hard to draw conclusions the comparison with our results.

Sauerwein et al. (2015) have recently reported bulk water activity measurements with an activity meter (Aqua lab Series 3TE) for various amine-to-sulphate ratios and over a concentration range of dissolved electrolyte up to 9 mol kg^{-1} at 25°C. (Note that TEAS was not considered in their study.) Using a bulk measurement technique for the determination of hygroscopic properties of aminium sulphates has the advantage of limiting possible evaporative losses of the amine during the experiments, especially compared to accumulation-mode aerosol measurements with an HTDMA for which timescales of evaporative loss/equilibration are assumed very short. As a first comparison, the hygroscopic growth curves previously shown in Fig. 3b in terms of n_{water}/n_{solute} vs. a_w are compared with results from Sauerwein et al. (2015) (Fig. 6a in their paper) in Fig. 5. The hygroscopic growth curves determined from the two different experimental methods differ marginally, but these discrepancies are considerably smaller than the differences between the results of both studies – CK-EDB and bulk water activity measurements – and HTDMA data from Clegg et al. (2013).

A comparison of the two datasets represented in terms of osmotic coefficients (Eq. (2)) can provide further insight, see Fig. 6. Notably, the measurements reported here extend to both more dilute and concentrated solutions and include measurements for TEAS. If the errors associated with each dataset are considered, the two sets of measurements overlap over some of the range in $m(SO_4^{2-})^{0.5}$, especially in the low molality limit (high water activity region) for MMAS, TMAS, MEAS and DEAS ($m(SO_4^{2-})^{0.5} < 1$, approximately), but also in the region $m(SO_4^{2-})^{0.5} > 2$ for DMAS and TMAS. A comparison with the uncertainty in the osmotic coefficients that arises from an uncertainty of ±0.002 in water activity (same as in Fig. 2b) indicates that the observed discrepancies are larger in magnitude than this typical experimental uncertainty of our technique, except for very low sulphate molality values (below ~0.8). However, despite the discrepancies that do exist, results from the two different experimental methods show the same qualitative hygroscopicity trends over the methyl and ethylaminium sulphates series. For further comparison, the results of Clegg et al. (2013) (from the HTDMA data) were converted to stoichiometric coefficients and are plotted in Fig. 6. These values are broadly comparable for all of the compounds, and close to those for ammonium sulphate as noted earlier. They do not agree with either the results of the experiments reported here, or the bulk measurements of Sauerwein et al. (2015).

We now consider the differences that exist between the data of Sauerwein et al. (2015) and our measurements. It is worth stating here that the evaporation kinetics measurements at the core of the CK-EDB approach have been validated in a previous publication (Rovelli et al., 2016) by means of the determination of the hygroscopic properties of well-characterised inorganic compounds and their mixtures. In addition, we have performed sensitivity tests to evaluate possible effects of random experimental errors associated with the proposed experimental method. The reproducibility of our measurements and the uncertainties associated with the treatment of densities are discussed below in Sect. 3.3 and 3.4, where they are shown not to affect significantly the determined hygroscopic properties of a compound.

If the differences between our measurements and the results of Sauerwein et al. (2015) were caused by partial volatilisation of the amine from the droplets evaporating in the CK-EDB, the observed bias between the two datasets would be reversed, i.e. an underestimation of n_{water}/n_{solute} and of osmotic coefficients would be expected, similar to what has been discussed in the case of the HTDMA size-based measurements of Qiu and Zhang (2012) when converted to a molar basis by Clegg et al. (2013). Another potential significant source of error could be inaccuracies in the starting concentrations of the aminium sulphate solutions. In this respect, the solution preparation and measurement method described in Sect. 2.2 has been validated through the reaction of ammonia and sulphuric acid and the measurements of the hygroscopic properties of the obtained $(NH_4)_2SO_4$. If the volatilisation of NH_3 during the neutralisation reaction was not an issue in preparing the solution of $(NH_4)_2SO_4$ it is unlikely to present a problem for the alkylamine solutions, with all alkylamines characterised by lower vapour pressures than ammonia (Ge et al., 2011b). Furthermore, in order to achieve complete agreement with the data from Sauerwein et al. (2015) the aminium sulphates solutions should be 5-10% more concentrated than calculated from the titration of the commercial stock solutions and from the amount of the reagents. Not only does this percentage seem unrealistically high, but the solute concentrations would be overestimated and not underestimated if any volatilisation of the amine occurred during the preparation of the solutions.

Sauerwein et al. (2015) provide a framework for the estimation of the water content in mixtures (in this case ternary mixtures of H_2O-H_2SO_4-amine) at any molar ratio of solutes. This allows a calculation of the water content (in terms of kg of water per mole of solute, or molality) and the stoichiometric osmotic coefficients (Eq. (2)) for the relevant aminium:sulphate ratio of 1:1 (bisulphate) and 2:1 (sulphate). However, it should be noted that unlike the study presented here, measurements were not explicitly made for the 2:1 molar ratio aqueous aminium sulphate solution. Instead, Sauerwein et al. used a modified Zdanovskii-Stokes-Robinson expression (ZSR, Eq. (3) of Sauerwein et al.) to represent the water uptake of the different mixtures of aqueous aminium sulphates and H_2SO_4; these fits are shown in Fig. 7 along with the actual measured points. x_{salt} can be considered as the degree of neutralisation of sulphuric acid. x_{salt}=0 corresponds to pure H_2SO_4 and the water content in this case is well-known (Clegg and Brimblecombe, 1995); the ZSR fit is therefore constrained to this value. A value at x_{salt}=1 corresponds to the completely neutralised aminium sulphate. The results of the fit were used to estimate the water uptake of each solution of aqueous aminium sulphate (i.e. the 2:1 molar ratio at x_{salt}=1) and it is these values that are shown in Fig. 6. In order to compare our data with that of Sauerwein et al., values at the same water activities must be compared (0.8 and 0.925 are chosen here) and a linear interpolation between actual measurement points is required to achieve this. Normally, the data from CK-EDB measurement are calculated with a_w steps of 0.01 for a_w > 0.8 where hygroscopic growth curves are the steepest, with a spacing of 0.02 for the water activity range ~0.65 - 0.8 and of 0.03 for a_w < 0.65. As in Sauerwein et al. (2015), the uncertainty of the interpolated points is set as the largest uncertainty among the experimental points used for the interpolation. The discrepancies between the estimations from bulk and CK-EDB measurements shown in Fig. 5 are apparent in Fig. 7 too at x_{salt}=1: the amount of water associated with each mole of aminium sulphate is systematically higher from the CK-EDB measurements when compared with the bulk measurements at both a_w with the discrepancy higher at the higher water activity.

In view of the differences between our measurements at $x_{\mathrm{salt}} = 1.0$ and the extrapolations from the fits of Sauerwein et al., we include a second fit to the ZSR model used previously but including our own measurements of the water uptake. The fit equations and parameters are provided in Supplementary Information (Table S6). As well as the fitted values more closely reflecting our measured values for the pure aminium sulphates at x_{salt} equal to unity, the revised fit does not significantly worsen the fit to the measurements of Sauerwein et al. for the acidified mixtures when $x_{\mathrm{salt}} < 0.6$). We therefore suggest that the discrepancies seen in terms of n_{water}/n_{solute} (Fig. 5), osmotic coefficients (Fig. 6) and kg of water per mole of solute in Fig. 7 can be attributed, in part, to the uncertainties associated with the ZSR fits and interpolation necessary to estimate the water uptake of the pure aqueous aminium sulphates from the results of Sauerwein et al. (2015). Certainly there is no physical reason why a simple relation such as the modified ZSR equation (Eq. (3) of Sauerwein et al.) should exactly represent the relationship between water activity and chemical composition in such systems, especially considering the large and unquantified influence of the sulphate-bisulphate equilibrium on the thermodynamic properties of the solutions.

A possible constant error in measured water activity could be the origin of the differences, but this seems unlikely. Such an offset in water activity results in a large change in the osmotic coefficient at the lowest concentrations for which measurements were made, but a much smaller change at the highest concentrations. This is not consistent with the differences in ϕ_{st} shown in Fig. 6. As a final consideration, we now explore the reproducibility of the CK-EDB measurements and the sensitivity of the retrieved hygroscopicity to the chosen treatment for solution density.

3.3 Reproducibility of Measurements

A full validation of the retrieval of the hygroscopic properties of single trapped solution droplets from CK-EDB experiments has already been presented in a previous publication (Rovelli et al. 2016), where we demonstrated ~~its~~the accuracy of the approach ~~by testing it against~~by reporting hygroscopicity measurements for well-characterised inorganic components. In this Section, we ~~want to In order to~~ evaluate the reproducibility of the solution preparation method (Sect. 2.2) ~~and ofcoupled to the retrieval of hygroscopic properties of a compound from the CK-EDB measurementthe CK-EDB method. T~~ with the aim ~~is that~~ of demonstrating that the results presented in the previous Sections are not affected by any random error associated ~~to~~with our approach~~ and they are therefore reliable~~for making the sample solutions. D~~, d~~ata obtained from three different datasets of evaporating DMAS solution droplets are compared in Fig. 8. The variation in n_{water}/n_{solute} with a_w (Panel (a)) and the change in osmotic coefficient with square root of sulphate mass fraction (Panel (b)) are calculated from three different data sets, each arising from measurements with 10 droplets and prepared from different starting stock solution of diethylaminium sulphate, obtained separately one from the other by mixing DEA and H_2SO_4 in different days. Data from Sauerwein et al. (2015) (open circles) and calculations for ammonium sulphate (E-AIM model, line) are shown for comparison. Measurements were made with droplet evaporation into a gas phase RH of ~80%. The reproducibility of the data is very satisfactory, giving further evidence that the applied solution preparation procedure coupled to the retrieval of the hygroscopic properties with CK-EDB experiments ~~the experimental method~~ is reliable. In addition, this consistency in experimental reproducibility strongly suggests that the discrepancies with the data of Sauerwein et al. (2015) do not originate from random errors associated with the CK-EDB experiments.

3.4 Sensitivity to Parameterization of Solution Density

A knowledge of the solution density as a function of solute concentration is needed to the process CK-EDB evaporation radius profiles (Sect. 2.1). The effect of uncertainties in the density parameterization used is here evaluated for DMAS, in order to estimate how potential errors in the density measurements and uncertainties in the extrapolation of ρ_{melt} at *mfs* equal to unity could affect the hygroscopicity data retrieved from comparative kinetics measurements. In Fig. 9, the densities of bulk DMAS solutions measured in this work are shown together with their 3rd order polynomial fit, which is the parameterization used in all the calculations for this compound in this work (Table 1). As shown in a previous work (Cai et al., 2016), a ±2% uncertainty is typical for the estimated melt density (*mfs* = 1.0) predicted from with a 3rd order polynomial fit of measured solution densities (Sect. 2.1), while the error is decreases with $mfs^{0.5}$ for the rest of the curve as shown in Fig. 9. More generally, the aminium sulphates are very soluble compounds and it was possible to directly measure the density of their bulk solutions over a wide range of solute mass fractions (up to $mfs^{0.5}$ values of 0.67-0.85, depending on the compound, see Table S2). Consequently, the $mfs^{0.5}$ range over which the extrapolation for the calculation of ρ_{melt} is needed is small and an uncertainty of ±2% (Fig. 9) is large for the evaluation of its effects. The two 3rd order polynomials (called 'Error+' and 'Error-' in Table 1, respectively) were applied together with the molar refraction mixing rule to explore the sensitivity of the data analysis of the original DMAS evaporation kinetics datasets to the representation of the solution density. Density data from Clegg et al. (2013) are also shown in Fig. 9 for comparison. A small discrepancy between their measurements and the data presented in this work is observed, not only for DMAS but also for the other 4 aminium sulphates they considered; but no clear pattern to these differences. Figure ~~S3~~ S4 shows a further comparison of density data from this work and from Clegg et al. (2013) converted in terms of apparent molar volumes; both measured and fitted apparent molar values are provided and the coefficient of the fitted equations can be found in Table S5. They may be attributable to the different preparation procedures of the aminium sulphates solutions and to the different experimental techniques for the measurement of densities.

The hygroscopic properties of DMAS obtained from the treatment of the evaporation kinetics data with the 'original' density parameterization and with the upper and lower bounds on the density treatment are shown in Fig. 10. Data from Sauerwein et al. (2015) and calculations for ammonium sulphate (E-AIM model) are plotted for comparison. When the hygroscopic properties of DMAS are represented either in terms of the dependence of either n_{water}/n_{solute} or GF_r on water activity (Panels (a) and (b)), the three curves deriving from the three different density treatments are virtually undistinguishable; thus the uncertainty in the applied density parameterisation does not significantly alter the analysis. In the case of the osmotic coefficients plot (Panel (c)) some very slight deviations between the three treatments can be distinguished at the two extremes of the plot. With respect to the low sulphate molality region, these small differences are due to the fact that a small variation in the sulphate molality results in more significant variations in the osmotic coefficients, because m_{st} appears in the denominator in the osmotic coefficient expression (Eq. (2)). If the high sulphate molality region is considered, the variations among the three curves are more significant because the simulated error on the density parameterisation is larger for more concentrated solutions (i.e. the size of the grey envelope in Fig. 9).

It is clear that the hygroscopic properties of aminium sulphates determined from CK-EDB measurements are relatively insensitive to reasonable variations in the extrapolated ρ_{melt} value (±2%) and to the applied density parameterisation. In addition, the variations introduced by different density parameterisations are very small compared to the differences from the results of Sauerwein et al., who obtain lower values of the hygroscopicity and osmotic coefficient. We conclude that these differences cannot be caused by inaccuracies in the approaches for treating variations of the density of evaporating droplets.

4 ~~Summary and~~ Atmospheric Importance and Conclusions

Quantifying the hygroscopic properties of aminium sulphates is important for ~~an accurate~~ understanding and modelling of ~~some~~ the atmospheric processes in which they are involved. ~~(e.g. formation and growth of new particles, activation of cloud droplets).~~ In particular, the role of short-chained alkylamines in the formation of new particles has been investigated in recent literature studies and found ~~considerable~~to be significant (Section 1). Aminium sulphate~~s~~-rich nanoparticles that derive from new particles formation events can potentially act as CCN, and their hygroscopic properties ~~need to~~must be well-characterised ~~in the optic of~~with the aim of reducing the overall uncertainties that currently affect our understanding of the indirect effects of atmospheric aerosols on climate. Robust and accurate data are essential for improving microphysical models of aerosol hygroscopicity; this study presents an extensive data set for an homologous series of six compounds, compared to ammonium sulphate, extending over a wide range in RH. In addition, it represents the most comprehensive characterisation of the hygroscopic response of aminium sulphate aerosol so far, complementing previous bulk phase measurements (comparable in accuracy but limited to higher water activity) and aerosol measurements at lower RH (with lower accuracy than achieved here). Previously, the bulk and aerosol measurements reported in the literature were in disagreement. Here, we report aerosol measurements that are in good agreement with the previously most accurate bulk phase data, resolving this discrepancy.

In order to measure their hygroscopic properties with a CK-EDB, the dependence of aminium sulphates solution densities and refractive indices on mass fraction of solute are reported. The experimental technique together with the application of the molar refractive mixing rule and a 3rd order polynomial parameterisation of density for the representation of the refractive indices and densities of solutions with variable solute mass fractions were presented and validated in previous works (Cai et al., 2016; Davies et al., 2013; Rovelli et al., 2016).The procedure for preparation of the aminium sulphates stock solutions was validated by using it for the preparation of ammonium sulphate solutions from the direct reaction of ammonia and sulphuric acid. The hygroscopic properties of the obtained $(NH_4)_2SO_4$ solutions retrieved from CK-EDB measurements were in very good agreement with calculations from E-AIM model and we demonstrated that the uncertainty of such measured values was comparable with a typical uncertainty of ±0.002 on a_w, which was previously shown to be typical for CK-EDB measurements (Rovelli et al., 2016). This result demonstrated that the used preparation procedure is robust and reliable.

The experimental results for the aminium sulphates were compared with the few studies available in the literature and the observed discrepancies were discussed in the light of the different experimental approaches. Measurements from our new approach provide a level of accuracy that reveals clearly the fine variations in hygroscopic growth (down to discernible difference is GF_r ~~in~~of ~~the~~ order ~~of~~ 0.01-0.02) that occur with molecular structure and substitution, and avoids the additional complexity of volatilisation of semi-volatile components during hygroscopic growth with measurements complete in a matter of a few seconds. The largest discrepancies with previous data were found when comparing the CK-EDB results with H-TDMA measurements (Clegg et al., 2013; Qiu and Zhang, 2012). These differences can be attributed to a possible overestimation of the dry size of particles due to residual water in the reference dry state in HTDMA measurements and/or to a shift of the chemical composition of particles towards the bisulphate composition because of partial volatilization of the amines from solution. ~~More~~ Closer comparability was found with the bulk water activity measurements by Sauerwein et al. (2015) ~~(Sauerwein et al., 2015)~~. The main differences in approaches are that: we perform aerosol measurements that cover a wider range in water activity as compared with the bulk measurements of Sauerwein et al. (2015); and we provide direct measurement at amine-to-sulphate ratios of exactly 2:1, whereas Sauerwein et al. (2015) performed a ZSR fitting on data from solutions with variable amine-to-sulphates ratios and extrapolated water content for the exact 2:1 ratio. These new CK-EDB measurements suggest a higher level of hygroscopic growth for the aminium sulphates than previously reported by Sauerwein and co-workers when inferred from measurements over a range of amine-to-sulphates ratios; we have provided a refined parameterisation for all compositions.

~~As a final remark, i~~It is worth noting that the characterization of the hygroscopic properties of aminium sulphates up to a_w of 0.99 was possible with the CK-EDB technique. The other literature approaches that were discussed in this Section were able to cover larger a_w ranges (down to 0.1) but none of them could be applied to obtain any data for a_w>0.9. Thus, the comparative kinetics measurements in a CK-EDB provide a powerful tool for investigating a water activity region that is otherwise hard to characterise with such accuracy, but which is of great importance for the understanding of the activity of aerosol particles as cloud condensation nuclei (Wex et al., 2009).

As a final remark, a~~A~~minium sulphates are the first class of mixed inorganic-organic aerosol systems to be investigated by means of the CK-EDB comparative kinetics technique, described in Rovelli et al. (2016), over a wide range of water activities. Therefore, besides the atmospheric relevance of these compounds, this study also provides a deeper understanding of the possible effects caused by random errors in the experimental procedure, and by uncertainties on the representation of the density of a compound. We demonstrated that the CK-EDB measurements are characterised by a very good level of reproducibility and that a typical ±2% uncertainty on the value of the extrapolated melt density only marginally affect the measured hygroscopic properties.

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Tables

	3rd order polynomial density coefficients				Melt	Melt ρ /
	a	***b***	***c***	***d***	**R.I.**	g cm^{-3}
DMAS	0.99847	$-2.55\cdot10^{-3}$	0.34103	-0.05191	1.4725	1.2850
Error+	0.99847	0.017256	0.342053	-0.04702	1.4665	1.3108
Error-	0.99847	-0.02231	0.339909	-0.05675	1.4783	1.2593

Table 1: Parameters of the 3rd order polynomial parameterisation for density and for the molar mixing rule (Sect. 2.1). DMAS is the original fitting of experimental data (black circles in Fig. 9), while 'Error+' and 'Error-' are calculated supposing a ±2% error on the extrapolated ρ_{melt}, as described in the text.

Figures

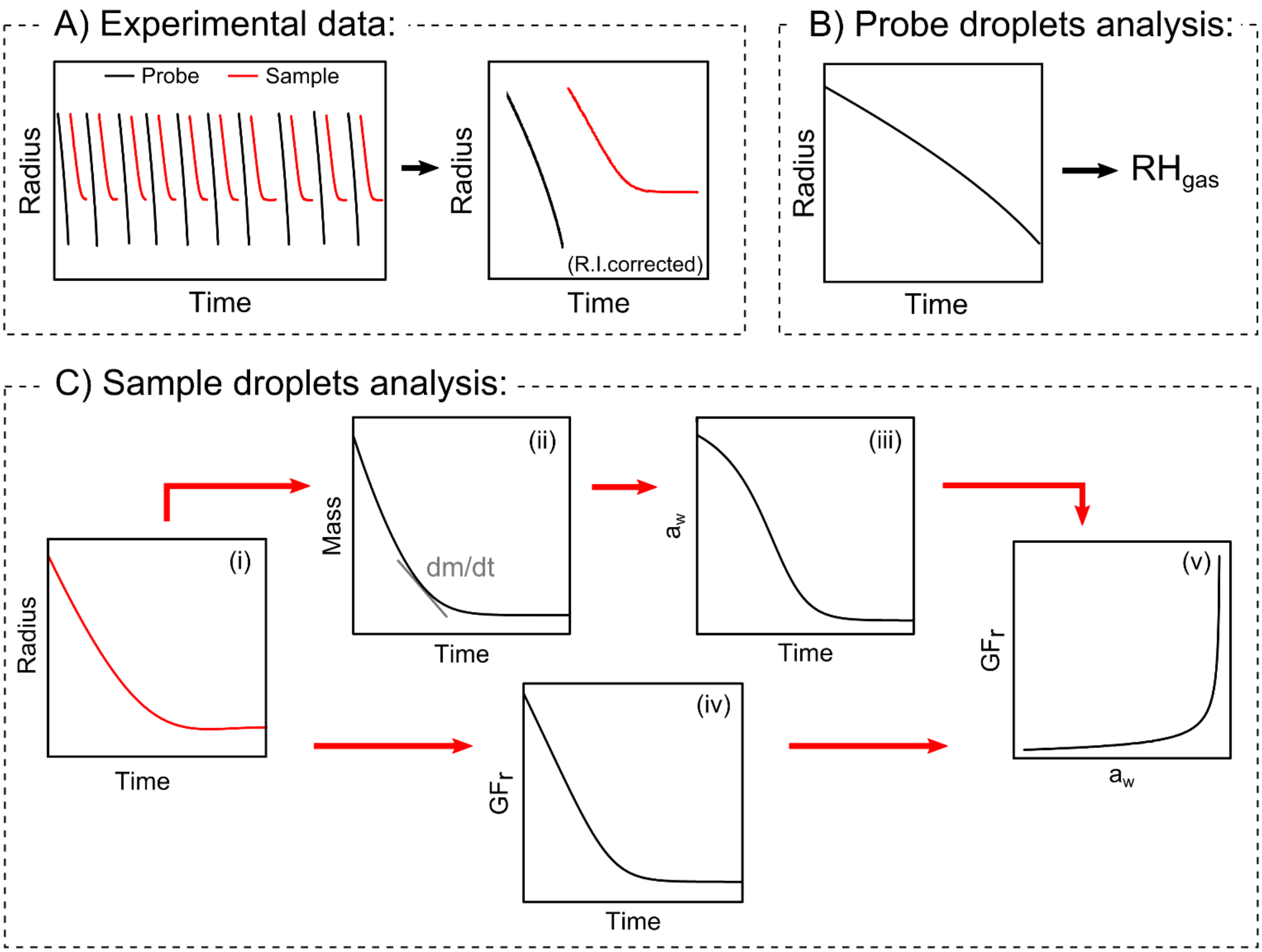


Figure 1: Schematics representing the retrieval of hygroscopic growth curves from comparative kinetics experiments in a CK-EDB. **An experimental sequence of alternating single evaporating probe and sample droplets is collected (a). For each pair of probe and sample droplets, the gas phase RH is inferred from the evaporation kinetics of the probe (b) and this information is used to analyse the corresponding sample droplet hygroscopic properties as indicated ~~as schematised~~ in (c).**

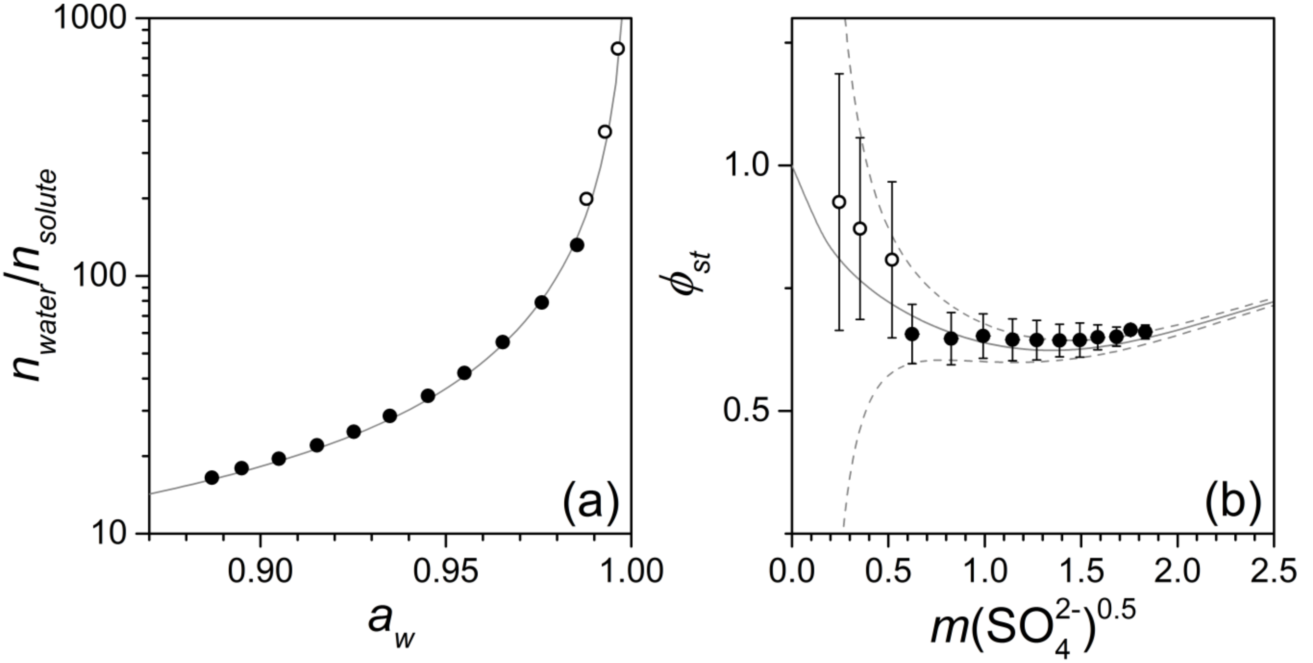


Figure 2: Measured n_{water}/n_{solute} vs. a_w (Panel (a)) and osmotic coefficients (ϕ_{st}) vs. the square root of sulphate molality ($m(SO_4^{2-})^{0.5}$) (Panel (b)) of ammonium sulphate solution obtained from the reaction between NH_3 and H_2SO_4. Symbols: black dots – 0.03 *mfs* of $(NH_4)_2SO_4$ in the initial solution, 88.5% RH in the gas phase; open circles – 0.004 *mfs* of $(NH_4)_2SO_4$ in the initial solution, 90% RH in the gas phase; solid lines – calculations from E-AIM model; dashed lines – uncertainty on the osmotic coefficients corresponding to an error in a_w of ±0.002.

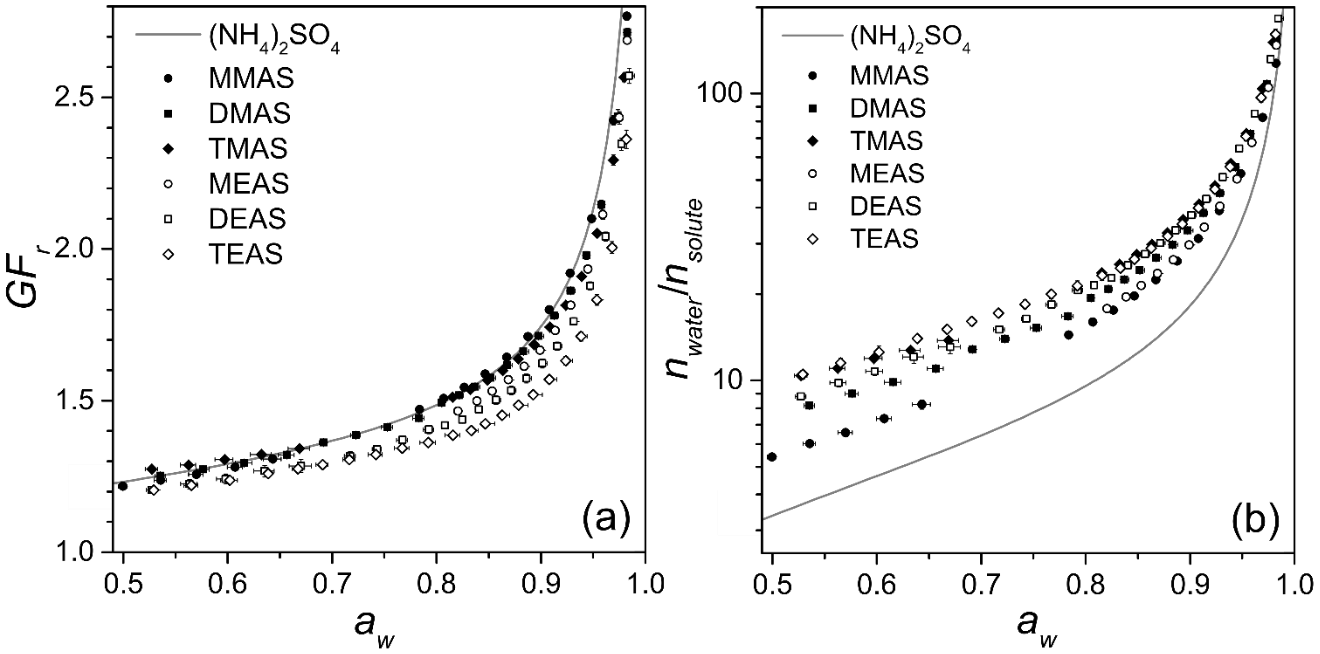


Figure 3: Aminium sulphates GF_r vs. a_w (Panel (a)) and n_{water}/n_{solute} vs. a_w (Panel (b)) hygroscopic growth plots from CK-EDB experiments. Symbols: ● – MMAS; ■ – DMAS; ♦ – TMAS; ○ – MEAS; □ – DEAS; ◊ – TEAS; line, E-AIM model calculation for $(NH_4)_2SO_4$. Note that ~~for simplicity from this figure on the~~ only E-AIM ~~data~~predictions for $(NH_4)_2SO_4$ ~~is~~are reported in this and subsequent figures with the CK-EDB measurements and the E-AIM model compared in Figure 2.

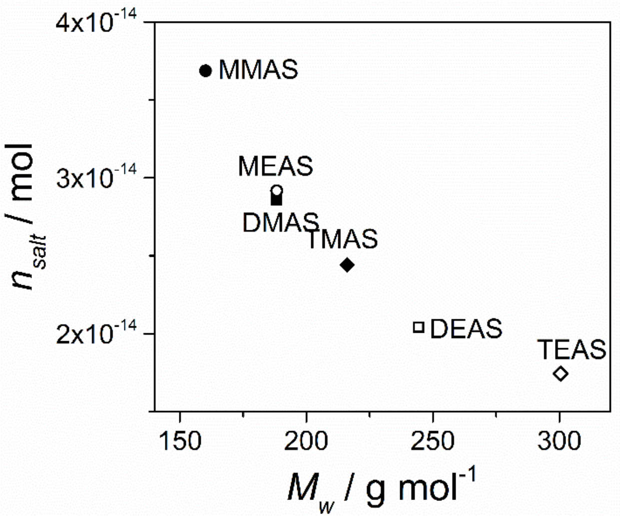


Figure 44: Moles of salt (n_{salt}) in a 1 μm radius solid particle as a function of the molecular weight (M_w) of each aminium sulphate. ~~**Symbols: ● – MMAS; ■ – DMAS; ♦ – TMAS; ○ – MEAS; □ – DEAS; ◊ – TEAS.**~~

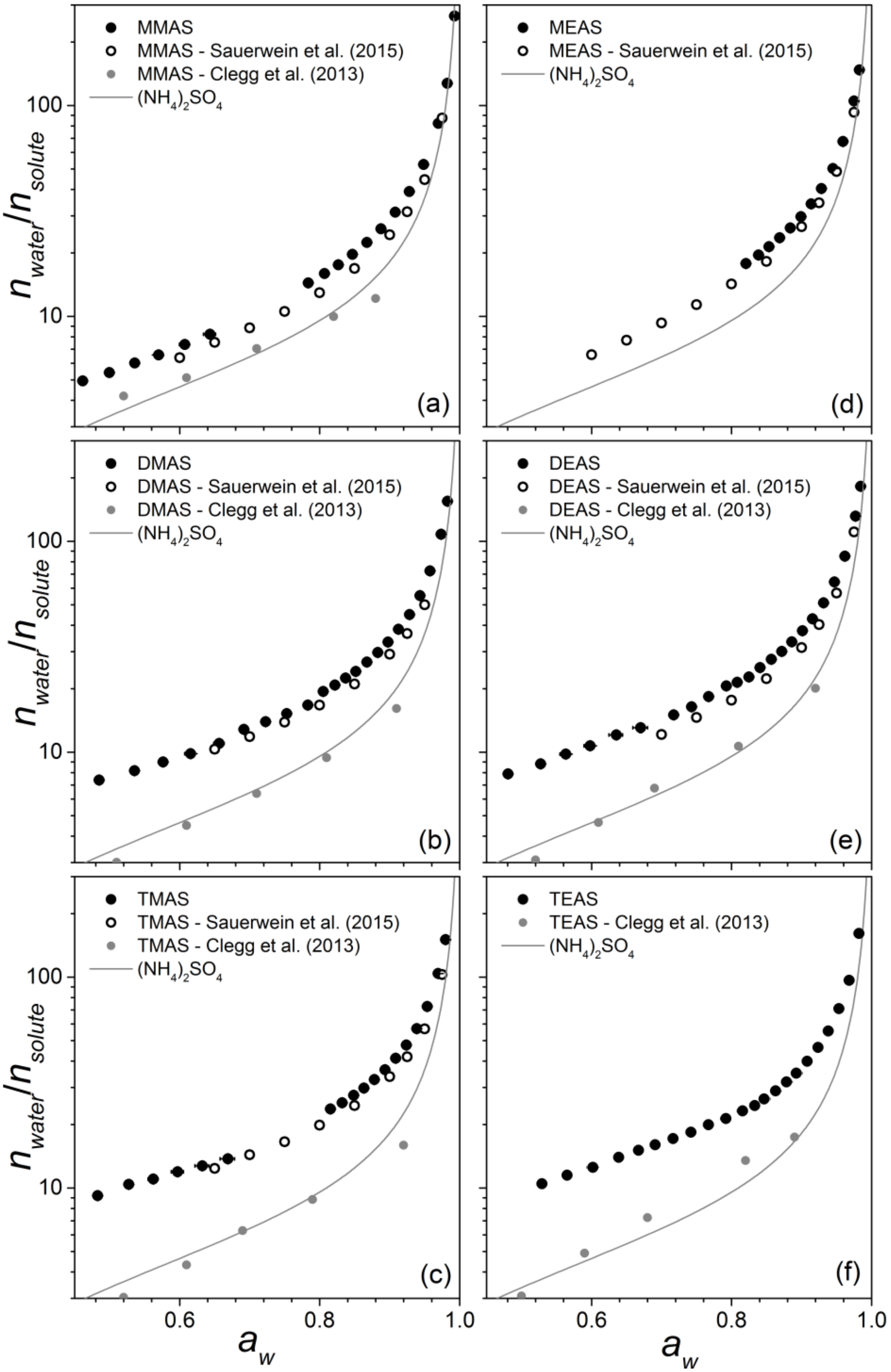


Figure 5: n_{water}/n_{solute} vs. a_w plots for the six aminium sulphates. Symbols: black circles – CK-EDB comparative kinetics measurements; open circles – Sauerwein et al. (2015); grey dots – Clegg et al. (2013) (based on measurements from Qiu and Zhang (2012)); line – $(NH_4)_2SO_4$ calculation from E-AIM model.

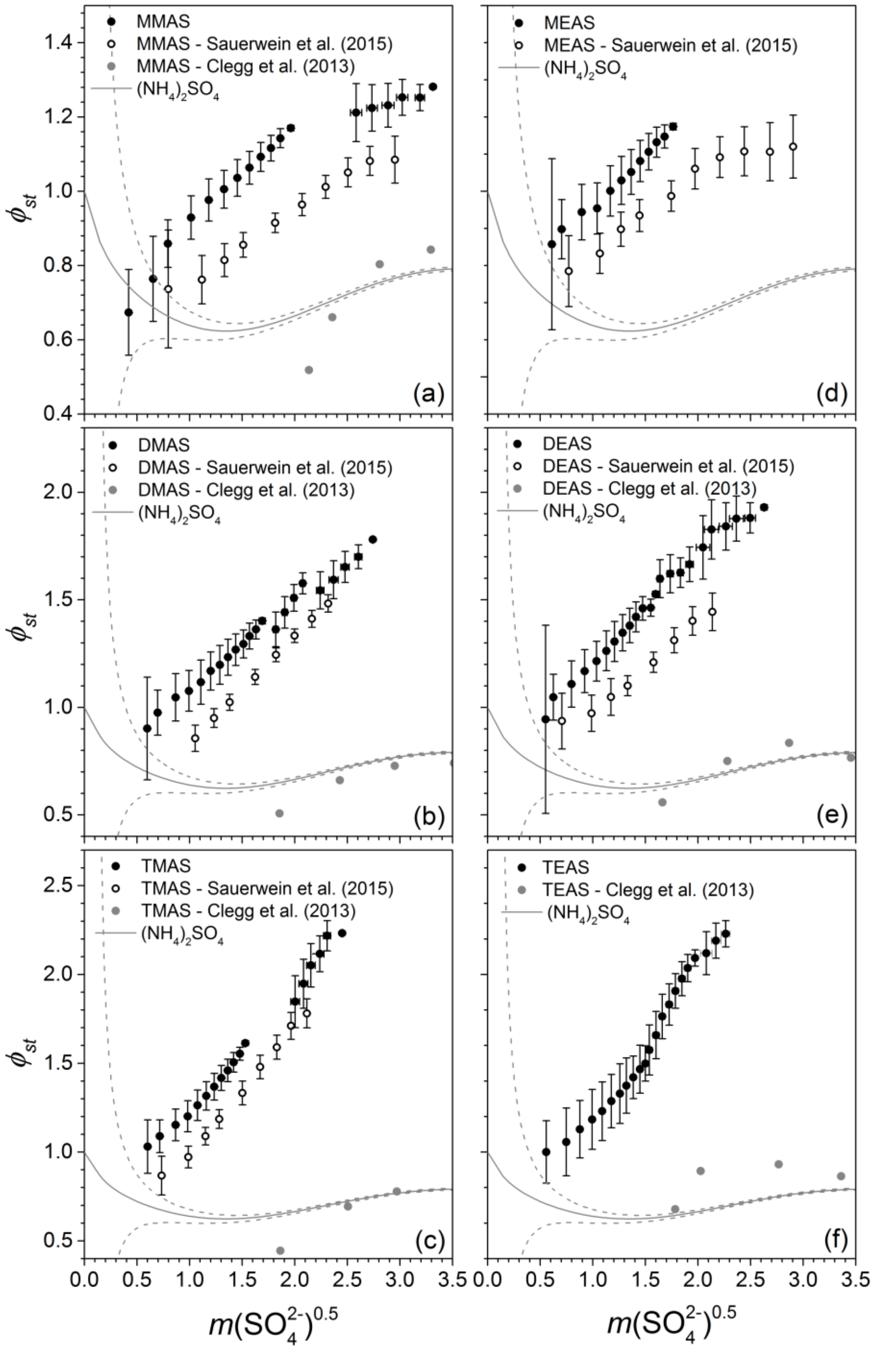
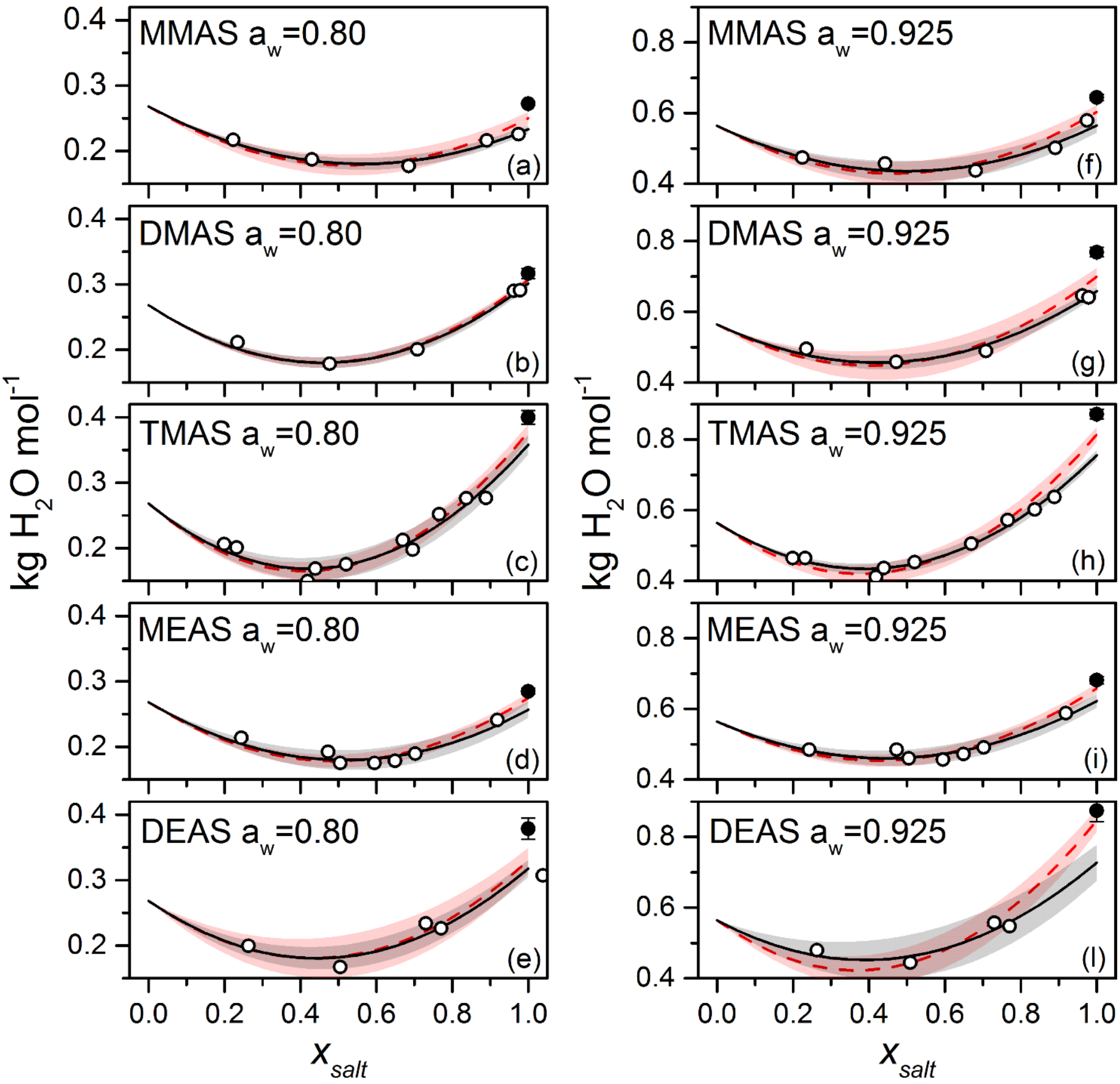


Figure 6: Osmotic coefficients (ϕ_{st}) vs. square root of sulphate mass fraction ($m(SO_4^{2-})^{0.5}$) for the six aminium sulphates. Symbols: black circles – CK-EDB comparative kinetics measurements; open circles – Sauerwein et al. (2015); grey circles – Clegg et al. (2013) (based on measurements from Qiu and Zhang (2012)); solid line – $(NH_4)_2SO_4$ calculation from E-AIM model; dashed lines – uncertainty of the osmotic coefficients for $(NH_4)_2SO_4$ corresponding to an error in a_w of ±0.002, included to provide a guide as to the level of expected error in the osmotic coefficient with varying molality.



5 **Figure 7: Mass of H_2O (kg) per mole of solute as a function of the degree of neutralisation of sulphuric acid by amine (x_{salt}). Symbols: solid circles – data from this work; open circles – data from Sauerwein et al. (2015). Lines: black – ZSR fitting of the data in Sauerwein et al. (2015); red dashed – same ZSR fitting but including the CK-EDB data point for each a_w; shaded envelopes – uncertainty associated to the fitting.**

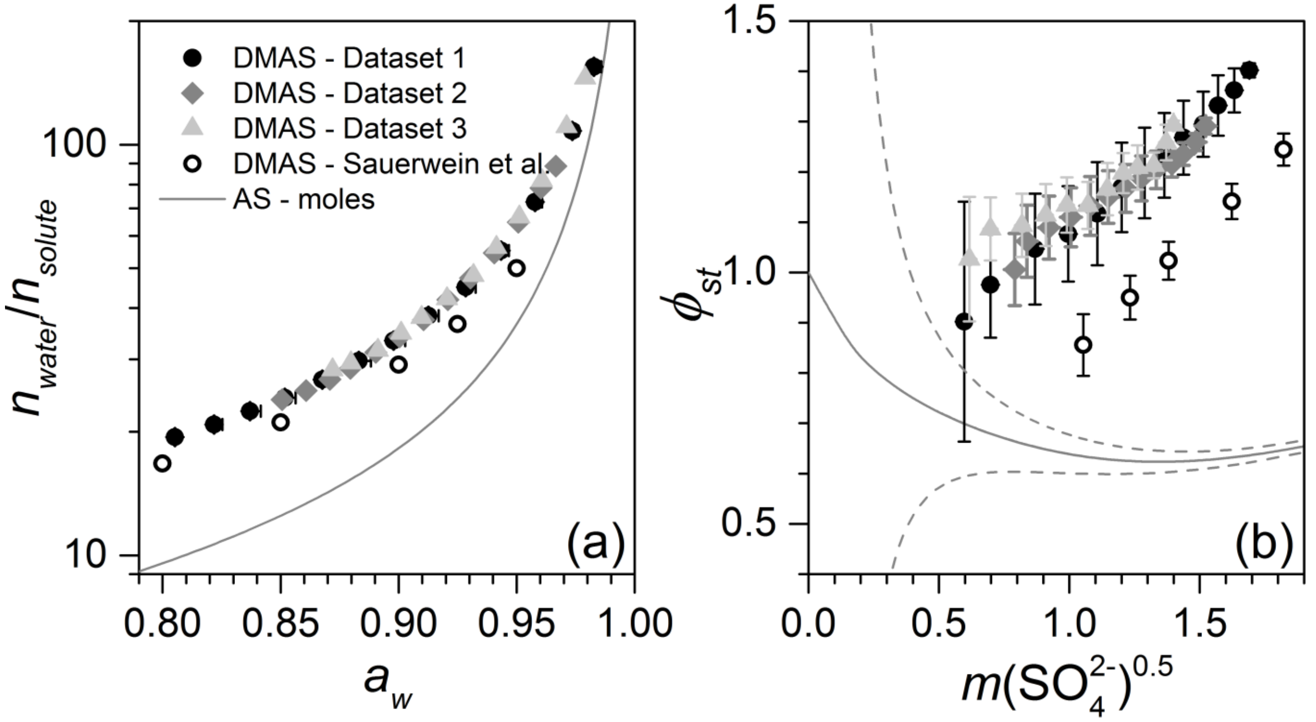


Figure 8: Evaluation of the reproducibility of measurements of the hygroscopic properties of DMAS. Symbols: black dots, dark grey diamonds, light grey triangles – different datasets measured with the CK-EDB from DMAS solutions obtained indipendently; open circles – data from water activity measurements in Sauerwein et al. (2015); solid lines – $(NH_4)_2SO_4$ calculations from the E-AIM model; dashed lines – uncertainty on $(NH_4)_2SO_4$ osmotic coefficients corresponding to an error in a_w of ±0.002.

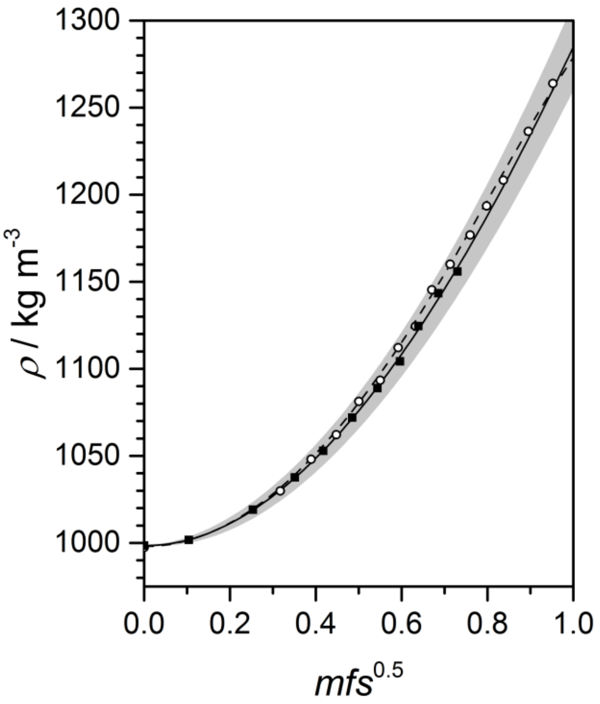


Figure 9: DMAS density (ρ) dependence on mass fraction ($mfs^{0.5}$) of solute. Symbols: black squares – measured densities, this work; solid line – 3rd order polynomial fit of measured ρ values; grey shaded area – evaluated uncertainty of the density parameterisation (calculated as discussed in the main text); open circles – measured densities from Clegg et al. (2013); dashed line – densities from the apparent molar volumes fitting by Clegg et al. (2013).

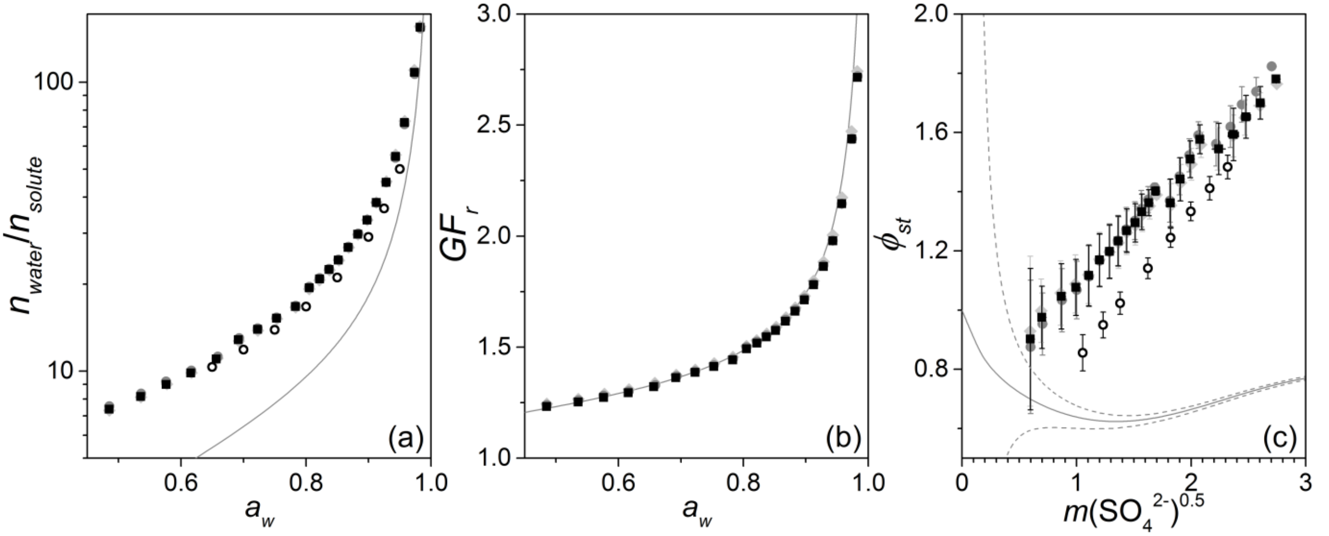


Figure 10: Hygroscopic properties of DMAS obtained from the treatment of the CK-EDB kinetics evaporation data with the three different set of parameters in Table 1 for treating solution density. Symbols: black squares – original data; dark grey dots – obtained with 'Error+' parameters; light grey diamonds – obtained with 'Error-' parameters; open circles – Sauerwein et al. (2015); solid lines – E-AIM model for $(NH_4)_2SO_4$; dashed lines – uncertainty on $(NH_4)_2SO_4$ osmotic coefficients corresponding to an error in a_w of ±0.002.

Supplementary Information for:
Hygroscopic Properties of Aminium Sulphate Aerosols

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Supplementary Information outline:

- **Table S1:** List and description of the uncertainties taken into account when calculating the hygroscopicity properties of aerosols from comparative kinetics experiments in a CK-EDB.
- **Table S2:** Measured densities and refractive indices of aminium sulphates solutions.
- **Table S3:** 3rd order polynomial fitted parameters for densities, calculated melt densities and melt refractive indices calculated with molar refraction mixing rule for the six considered aminium sulphates.
- **Table S4:** Comparison of pure melt densities from this work and from Clegg et al. (2013) and solid densities from Qiu and Zhang (2012).
- **Table S5:** Coefficients of the fitted equations of the measured apparent molar volumes.
- **Table S6:** Extended ZSR fitted coefficients at two fixed water activities (a_w, 0.80 and 0.925) for mixtures of aminium sulphate salts and sulphuric acid.

- **Figure S1:** Schematics of the EDB experimental setup used in this work.
- **Figure S2:** Measured densities of aminium sulphates solutions and 3rd order polynomial fittings of data and measured refractive indices as a function of mass fraction and the corresponding molar refraction mixing rule fitting.
- **Figure ~~S2~~S3:** Comparison of measured GF_r from CK-EDB experiments and GF_r data from H-TDMA measurements by Qiu and Zhang (2012)

- **Figure ~~S3~~S4:** Measured and fitted apparent molar volumes of aminium sulphates in aqueous solutions from this work and from Clegg et al. (2013).

Table S1: List and description of the uncertainties taken into account when calculating the hygroscopicity properties of aerosols from comparative kinetics experiments in a CK-EDB.

Quantity	Symbol/Formula	Uncertainties
Water activity	a_w	- a_w: uncertainty from RH determination in the EDB measurements (Davies et al., 2013): - RH>80% (pure water used as a probe): $RH = {RH_w}^{+(0.169{RH_w}^2-0.364RH_w+0.194)}_{-(-0.020RH_w+0.021)}$ - RH<80% (NaCl used as a probe): $RH = {RH_{eq}}^{+\left(-0.0175{RH_{eq}}^2-0.0005RH_{eq}+0.017\right)}_{-\left(-0.0266{RH_{eq}}^2+0.0086RH_{eq}+0.017\right)}$
Radial growth factor	$GF_r = \frac{a}{a_{dry}}$	- a (measured): ±100 nm (Davies, 2014), <1% for droplets bigger than 10 μm.^(a) - a_{dry}: uncertainty on the initial radius extrapolation at t_0 (${a_{dry}}^{+150\,nm}_{-100\,nm}$); uncertainty on the initial solution concentration.
Mass fraction	$mfs = \frac{m_{solute}}{m_{tot}}$	- m_{solute} (dry mass from the initial concentration): ${a_{dry}}^{+150\,nm}_{-100\,nm}$; uncertainty on the initial solution concentration.^(b) - m_{tot}: uncertainty from radius determination.
Mole curves	$\frac{n_{\mathrm{water}}}{n_{solute}}$	- n_{water}, calculated from $m_{water} = m_{tot} - m_{solute}$ (see uncertainties indicated above for *mfs*).
Stoichiometric osmotic coefficient	$\phi_{st} = \frac{-\ln(a_w)}{(m_{st} \cdot M_w/1000)}$	- m_{st} (stoichiometric molality): uncertainties on n_{solute} and m_{water} (see uncertainties indicated for *mfs* and for n_{water}/n_{solute}).

Symbols: a_w; water activity; GF_r – radial growth factor; a – droplet radius; a_{dry} – dry particle radius; mfs – mass fraction of solute; m_{solute} – mass of solute in the particle; m_{tot} – total particle mass; n_{water} – moles of water; n_{solute} – moles of solute; ϕ_{st} – stoichiometric osmotic coefficients; m_{st} – stoichiometric molality; M_w – molecular mass of water.

Notes:

(a) The optical phase function measurements in the CK-EDB used to estimate the size of a levitated droplet are taken at a wavelength of 532 nm; however, the wavelength dependence of refractive index was considered negligible (e.g. for pure water m=1.333 at 589 nm and m=1.335 at 532 nm) and introduced negligible error in the determination of droplet size when compared with other experimental uncertainties that must be accounted for (Rovelli et al., 2016).

(b) No uncertainties on the applied density parameterisations are taken into account. However, the sensitivity of the hygroscopic properties retrieved by means of CK-EDB measurements to potential uncertainties in the parameterisation of solution density have been evaluated in Section III.d of the main manuscript.

Table S2: Measured densities and refractive indices of aminium sulphates solutions.

MMAS

mfs			ρ (kg m^{-3})		*m*	
				σ		σ
0	±	0	998.1	0	1.333	-
0.0021	±	8.90E-06	999.0	0.1	1.3334	-
0.0070	±	3.00E-05	1001.4	0.1	1.3342	-
0.0178	±	0.0001	1006.3	0.1	1.3359	-
0.0406	±	0.0002	1016.8	0	1.3394	-
0.0675	±	0.0003	1028.8	0.1	1.3436	-
0.1061	±	0.0005	1045.8	0.2	1.3494	-
0.1487	±	0.0006	1064.8	0.1	1.3561	-
0.1995	±	0.0009	1087	0	1.3638	-
0.2579	±	0.0011	1111.5	0.4	1.3724	-
0.3002	±	0.0013	1127.6	0.1	1.3778	5.77E-05
0.3657	±	0.0016	1154.7	0.1	1.3872	5.77E-05
0.4411	±	0.0019	1186.8	1.2	1.3981	-
0.5482	±	0.0023	1231.3	0.6	1.4145	1.53E-04

MEAS

mfs			ρ (kg m^{-3})		*m*	
				σ		σ
0	±	0	998.2	0.1	1.333	-
0.0073	±	3.00E-05	1000.6	0.1	1.3342	-
0.0129	±	5.30E-05	1002.8	0.1	1.3350	-
0.0345	±	0.0001	1010.6	0.1	1.3382	5.77E-05
0.0776	±	0.0003	1026.1	0	1.3444	-
0.1393	±	0.0006	1047.3	0.2	1.3531	-
0.2087	±	0.0009	1071.1	0.4	1.3632	5.77E-05
0.3097	±	0.0013	1107.1	0.1	1.3778	-
0.4178	±	0.0017	1144.2	0.2	1.3934	1.15E-04
0.5295	±	0.0022	1180.6	0.2	1.4091	5.77E-05
0.7687	±	0.0031	1247.6	1.2	1.4413	2.00E-04

DMAS

mfs			ρ (kg m^{-3})		*m*	
				σ		σ
0	±	0	998.5	0.1	1.333	-
0.0108	±	0.0001	1001.8	0.1	1.3345	-
0.0643	±	0.0005	1019.1	0.1	1.3421	-
0.1232	±	0.0010	1037.6	0.1	1.3502	-
0.1742	±	0.0015	1052.9	0.6	1.3573	-
0.2351	±	0.0020	1071.9	0.1	1.3657	1.53E-04
0.2956	±	0.0025	1088.9	1.2	1.3737	2.65E-04
0.3557	±	0.0031	1104.3	4.7	1.3823	2.00E-04
0.4082	±	0.0035	1124.5	0.4	1.3898	5.77E-05
0.4699	±	0.0040	1143.4	0.4	1.3985	5.77E-05
0.5330	±	0.0045	1156.0	1.1	1.4067	1.15E-04

DEAS

mfs			ρ (kg m^{-3})		*m*	
				σ		σ
0	±	0	998.1	0.1	1.333	-
0.0024	±	4.70E-05	998.3	0.1	1.3335	5.77E-05
0.0124	±	2.50E-04	1000.5	0.1	1.3347	5.77E-05
0.0291	±	0.0006	1004.1	0.1	1.3371	-
0.0690	±	0.0014	1012.7	0.1	1.3426	-
0.1126	±	0.0022	1026.7	0.1	1.3518	-
0.2094	±	0.0041	1043.3	0.1	1.3629	1.15E-04
0.3061	±	0.0061	1064.9	0.1	1.3773	5.77E-05
0.4292	±	0.0085	1092.2	0.1	1.3962	1.15E-04
0.5622	±	0.0111	1117.3	1.4	1.4152	9.87E-04
0.6667	±	0.0132	1134.5	0.2	1.4309	4.16E-04

TMAS

mfs			ρ (kg m^{-3})		m	
				σ		σ
0	±	0	998.0	0.1	1.333	
0.0017	±	1.70E-05	998.5	0	1.3334	-
0.0039	±	3.70E-05	999.2	0.1	1.3336	-
0.0109	±	0.0001	1001.2	0.1	1.3346	-
0.0197	±	0.0002	1003.5	0.1	1.3359	-
0.0331	±	0.0003	1007.3	0.1	1.3378	-
0.0515	±	0.0005	1012.1	0.2	1.3404	-
0.0786	±	0.0007	1019.4	0.1	1.3444	-
0.1027	±	0.0010	1025.7	0.1	1.3477	5.77E-05
0.1303	±	0.0012	1032.9	0.1	1.3517	-
0.1450	±	0.0014	1036.8	0.1	1.3539	5.77E-05
0.1828	±	0.0017	1046.6	0.2	1.3593	5.77E-05
0.2104	±	0.0020	1053.4	0.1	1.3634	-
0.2557	±	0.0024	1065.3	0.1	1.3701	-
0.3074	±	0.0029	1078.6	0.2	1.3778	5.77E-05
0.3638	±	0.0035	1094.0	0.2	1.3864	-
0.4580	±	0.0044	1118.1	1.6	1.4006	1.53E-04

TEAS

mfs			ρ (kg m^{-3})		m	
				σ		σ
0	±	0	998.0	0.2	1.333	
0.0025	±	3.20E-04	998.5	0.1	1.3336	-
0.0129	±	7.30E-04	1001.3	0.1	1.3354	5.77E-05
0.0335	±	0.0012	1006.9	0.2	1.3392	-
0.0637	±	0.0016	1014.9	0.2	1.3447	-
0.1236	±	0.0023	1030.8	0.1	1.3558	-
0.1884	±	0.0028	1048.9	0.1	1.3683	1.53E-04
0.2747	±	0.0034	1075.1	0.1	1.3864	-
0.3807	±	0.0040	1104.8	1.2	1.4082	1.00E-04
0.4999	±	0.0046	1135.6	1.6	1.4298	1.18E-03
0.6008	±	0.0050	1158.2	1.8	1.4480	4.54E-03

Symbols: *mfs* – mass fraction of solute; ρ – measured density of solution; m – measured refractive index of solution; σ – standard deviation arising from the averaging of three repeated measurements.

Table S3: 3rd order polynomial fitted parameters for densities (ρ), calculated melt densities (ρ_{melt}) and melt refractive indices (m_{melt}) calculated with molar refraction mixing rule for the six considered aminium sulphates.

	a_0	a_1	a_2	a_3	ρ_{melt} (kg m^{-3})	m_{melt}
MMAS	998.10	5.12	447.11	-40.19	1410.1	1.4771
DMAS	998.47	-2.55	341.03	-51.91	1285.0	1.4725
TMAS	998.03	4.64	252.17	4.82	1259.7	1.4921
MEAS	998.17	-19.25	459.22	-127.00	1311.1	1.4708
DEAS	998.10	-10.09	285.60	-82.47	1191.1	1.4810
TEAS	998.50	-25.09	378.58	-100.86	1251.1	1.5357

Parameterisations used:

3rd order polynomial parameterization for densities (ρ) as a function of the square-rooted mass fraction (*mfs*) of solute:

$$\rho = a_0 + a_1(mfs^{0.5}) + a_2(mfs) + a_3(mfs^{1.5}) \qquad \text{Eq. S1}$$

Molar refraction mixing rule for the representation of the refractive index (m) of a solution. The molar refraction (R) of a species is defined as (Liu and Daum, 2008):

$$R = \frac{(m^2-1)M}{(m^2+2)\rho} \qquad \text{Eq. S2}$$

where M is the compound's molecular mass and ρ is its pure density (melt density in case of a solute, pure liquid density in the case of the solvent, i.e. water). The molar refraction for a mixture of different components is defined as the sum of the molar refractions of each compound (i) weighted by their mole fractions (x_i):

$$R = \sum_i x_i R_i \qquad \text{Eq. S3}$$

Therefore, in the case of a binary solution composed of water and a generic solute:

$$\frac{({m_{solution}}^2-1)M_{solution}}{({m_{solution}}^2+2)\rho_{solution}} = x_{H_2O}\frac{({m_{H_2O}}^2-1)M_{H_2O}}{({m_{H_2O}}^2+2)\rho_{H_2O}} + x_{solute}\frac{({m_{melt}}^2-1)M_{solute}}{({m_{melt}}^2+2)\rho_{melt}} \qquad \text{Eq. S4}$$

where $m_{solution}$ and $\rho_{solution}$ are measured, $M_{solution}$ is calculates as $M_{solution} = \sum_i x_i M_i$ (Liu and Daum, 2008), the mole fractions of water and solute are known from the concentration of the prepared solution, density and refractive index of pure water are known, ρ_{melt} is calculated from the density parameterisation at *mfs*=1. Therefore, the only unknown is m_{melt} and a least squares fit of the experimental refractive index data is performed with Eq. S4 to calculate it.

When correcting the obtained radius vs. time data from CK-EDB experiments, the iterative procedure proposed in a previous work (Davies et al., 2012) is applied, but the variation in refracting index with the variation of the solution concentration is calculated with the molar refraction mixing rule.

Table S4: Comparison of pure melt densities (ρ_{melt}) from this work and from Clegg et al. (2013) and solid densities (ρ_{solid}) from Qiu and Zhang (2012).

Compound	ρ_{melt} **(this work)** (g cm^{-3})	ρ_{melt} **(Clegg et al., 2013)** (g cm^{-3})	ρ_{solid} **(Qiu and Zhang, 2012)** (g cm^{-3})
MMAS	1.410	1.451 (±0.0029)	1.485 ± 0.089
DMAS	1.285	1.278 (±0.0022)	1.408 ± 0.084
TMAS	1.259	1.289 (±0.0031)	1.342 ± 0.081
MEAS	1.311	-	-
DEAS	1.191	1.212 (±0.0030)	1.268 ± 0.076
TEAS	1.251	1.190 (±0.0018)	1.247 ± 0.075

Table S5: Values of the coefficients of the fitted equations of measured apparent molar volumes (V^{ϕ}) of aminium sulphates in aqueous solutions (displayed in Figure S3). The used fitting equation is the same used by Clegg et al. (2013):

$$V^{\phi} = V^{\phi\infty} + a_1 \cdot (wt\%)^{0.5} + a_2 \cdot (wt\%)^{0.75} a_3 \cdot (wt\%) + a_3 \cdot (wt\%)^{1.5}$$

where $V^{\phi\infty}$ is the apparent molar volume of the aminium salt taken from literature (as in Clegg et al.) and *wt%* is the weight percentage of salt in solution. Note that the fitted equation is constrained at *wt%* = 0 to the $V^{\phi\infty}$ literature value.

	$V^{\phi\infty}$	a_1			a_2			a_3			a_4		
MMAS	86.27	-0.542	±	0.276		0		0.792	±	0.099	-0.0507	±	0.00882
DMAS	123.83	2.039	±	0.150		0			0		0.00266	±	0.00367
TMAS	159.47	-8.051	±	0.962	6.866	±	0.883	-1.318	±	0.201		0	
MEAS	120.8	-1.043	±	0.238	1.062	±	0.088		0			0	
DEAS	191.91		0			0		0.115	±	0.009		0	
TEAS	256.16	-22.759	±	1.264	7.080	±	0.495		0			0	

Table S6: Extended ZSR fitted coefficients (Eq. 3 in Sauerwein et al. (2015)) at two fixed water activities (a_w, 0.80 and 0.925) for mixtures of aminium sulphate salts and sulphuric acid, as in Figure 7 in the main manuscript. The coefficients refer to the ZSR fitting of data from Sauerwein et al. (2016) together with the CK-EDB datapoint (red dashed lines in Figure 7 in the main manuscript). Symbols: w^o_a – water associated to H_2SO_4 in an aqueous solution at the same water activity as the mixture; w^o_{as} – water associated to the aminium salt in an aqueous solution at the same water activity as the mixture; A^o – fitted empirical parameter.

$a_w = 0.80$

	$\boldsymbol{w^o_a}$	$\boldsymbol{w^o_{as}}$			$\boldsymbol{A^o}$		
MMAS	0.2682	0.2501	±	0.0092	-0.3218	±	0.0447
DMAS	0.2682	0.3072	±	0.0047	-0.4272	±	0.0240
TMAS	0.2682	0.3782	±	0.0112	-0.6147	±	0.0388
MEAS	0.2682	0.2747	±	0.0076	-0.3733	±	0.0256
DEAS	0.2682	0.3299	±	0.0195	-0.4655	±	0.0882

$a_w = 0.925$

	$\boldsymbol{w^o_a}$	$\boldsymbol{w^o_{as}}$			$\boldsymbol{A^o}$		
MMAS	0.5641	0.6035	±	0.0194	-0.6155	±	0.0934
DMAS	0.5641	0.6997	±	0.0248	-0.7095	±	0.1273
TMAS	0.5641	0.8143	±	0.0215	-1.0166	±	0.0749
MEAS	0.5641	0.6587	±	0.0140	-0.6166	±	0.0476
DEAS	0.5641	0.8472	±	0.0325	-1.0603	±	0.1233

Figure S1: Schematics of the EDB experimental setup used in this work (view from top).

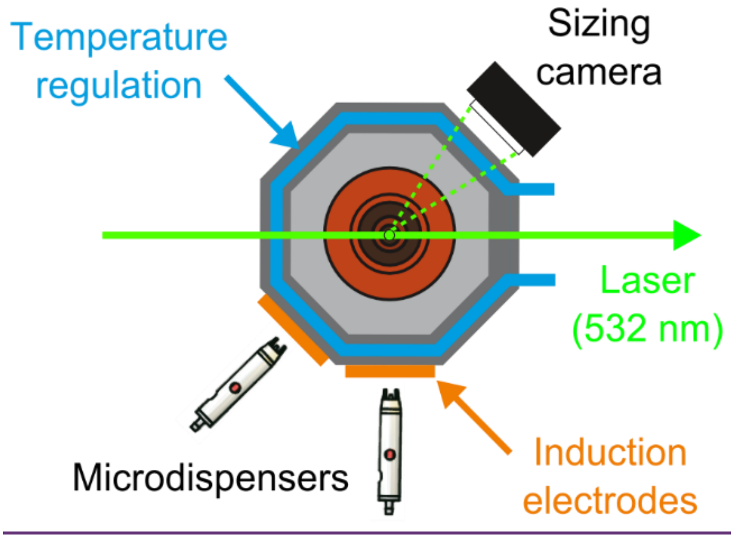


Figure ~~S1~~S2: Measured densities of aminium sulphates solutions and 3rd order polynomial fittings of data (Panel ~~A~~(a)). Measured refractive indices as a function of mass fraction and the corresponding molar refraction mixing rule fitting (Panel ~~B~~(b)).

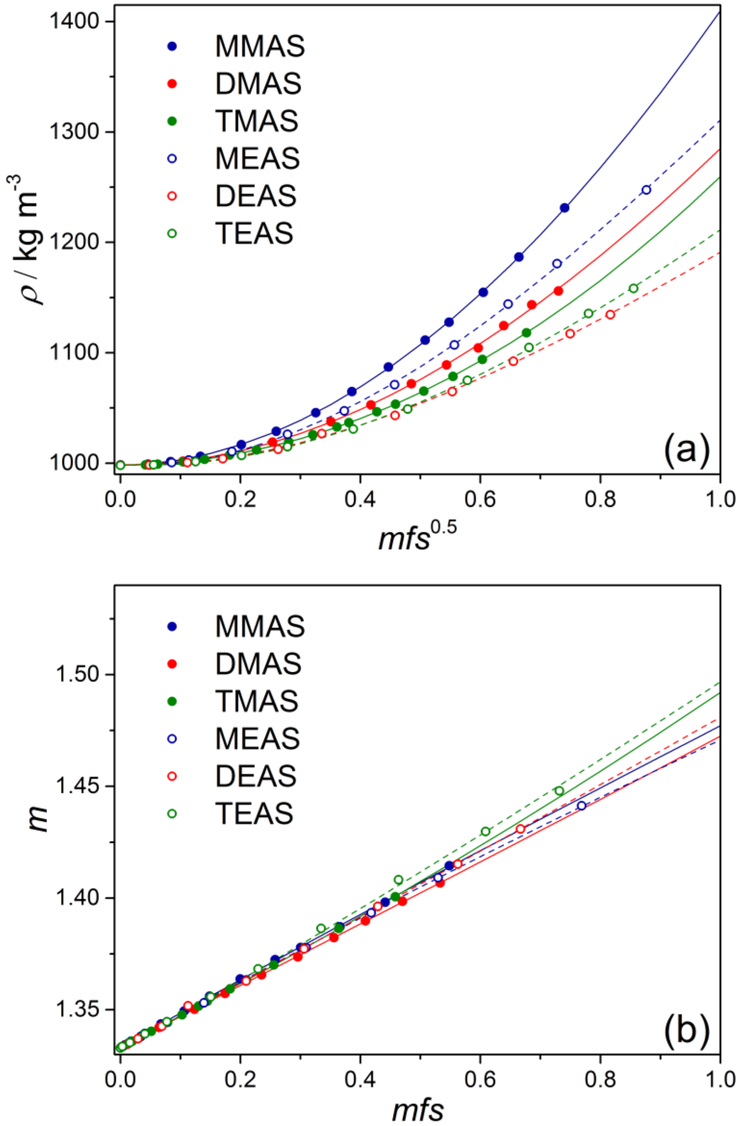


Figure ~~S2~~S3: Comparison of measured GF_r from CK-EDB experiments and GF_r data from H-TDMA measurements by Qiu and Zhang (2012).

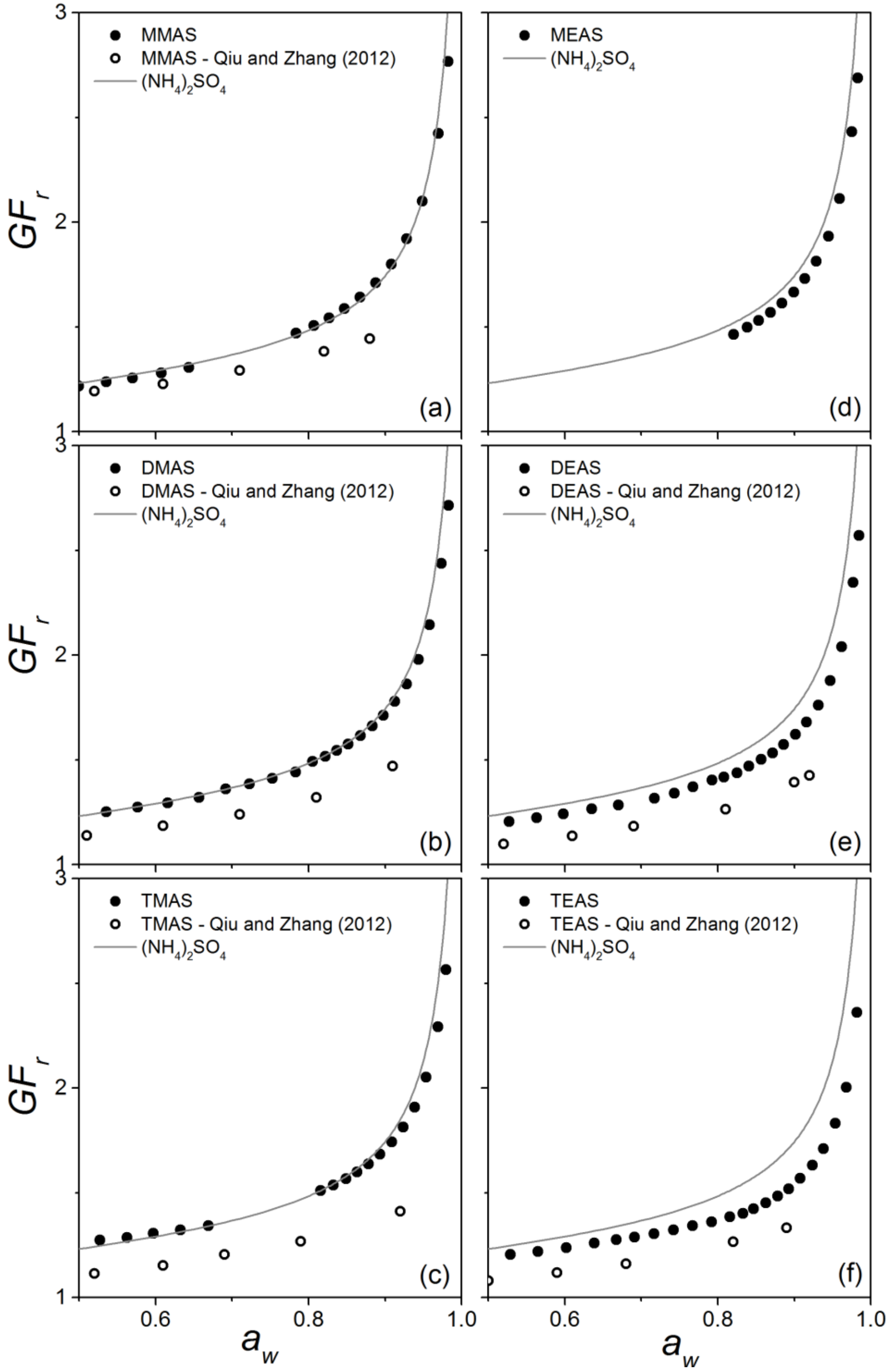
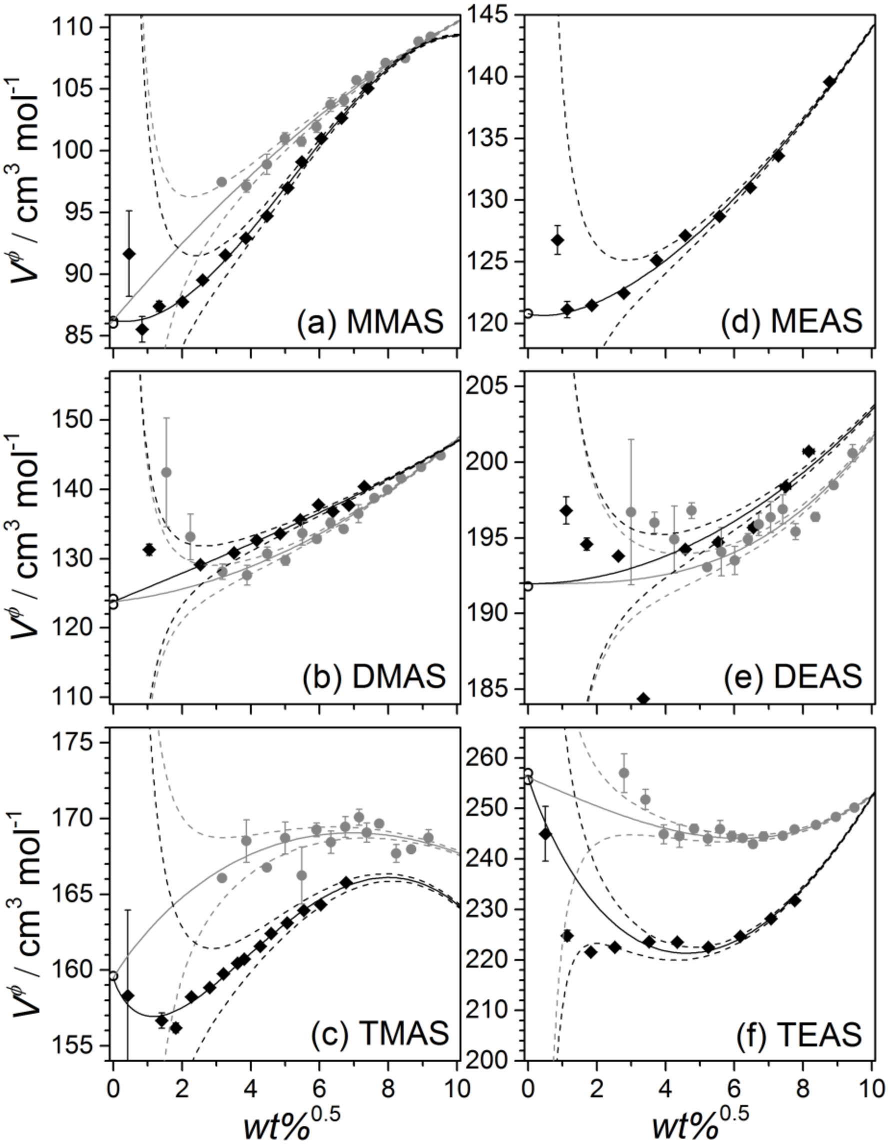


Figure ~~S3~~S4: Apparent molar volumes (V^{ϕ}) of aminium sulphates in aqueous solutions as a function of the square root of the solute weight percentage (*wt%*). Symbols: black diamonds – measured values, this work; black line – fitted equations (coefficients in Table S5); grey dots – measured values by Clegg et al. (2013); grey lines – fitted equations of mrasured data in Clegg et al. (2013); dashed lines – uncertainty on apparent molar volumes when a ±0.001 g cm^{-3} uncertainty on the measured density is considered; open circles – apparent molar volumes at infinite dilutions from literature (as in Fig. 1 in Clegg et al. (2013)).



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