

Anonymous Referee #2

Received and published: 14 September 2015

Summary: This work demonstrates the application of Nano-HTDMA to measure the hygroscopicity of nanoparticles in the frame of the CLOUD experiments. The manuscript fits well to the scope of ACP and presents valuable results. Thus I recommend it to be published after the following moderate/minor comments listed below have been adequately addressed.

Comments:

Referee's comment: 1. In the abstract (page 19805, lines 8-9) and introduction (page 19806, lines 9-10), it is not accurate to state: "Water uptake constrains their chemical composition". On the contrary, the chemical composition of aerosol particles defines their ability to take up water. Please reconsider this.

Authors' response, changes in MS: Thank you for your suggestion. We modified a text as: "Water uptake is useful information to indirectly study the chemical composition of aerosol particles" in the abstract and "Hygroscopicity, the ability of particles to take up water, is important when considering aerosol climate effects. Hygroscopicity of a particles is defined by the particle's composition and, therefore, hygroscopicity can be used for indirectly estimating chemical composition of size-resolved nanoparticles" in the introduction.

Referee's comment: 2. What does the value refer to in Table 1? Are they peak/mean/median values?

Authors' response, changes in MS: We used mean values in Table 1.

Referee's comment: 3. Page 19810, lines 4-5, please describe the calibration results in the text / supplementary. How you considered the shape factor in the calibration, especially for sodium chloride nanoparticles?

Authors' response, changes in MS: The actual calibration was done by using ammonium sulfate and only some supporting calibration measurements were done using sodium chloride. The sodium chloride calibration data wasn't used in the analysis. We removed the word "sodium chloride" in the text and also added the short description of the calibration measurements: "The size and RH calibration of the nano-HTDMA was carried out by using ammonium sulfate nanoparticles before, during and after the CLOUD7 experiments. The RH calibration was done by measuring the efflorescence and deliquescence RH of ammonium sulfate particles and by comparing the value to the theoretical values."

Referee's comment: 4. Page 19811, lines 16-20 and Page 19813 lines 10-20. The ammonium seems like a significant contaminant, can we simply treat the Exp. A listed in Table 1 as the H₂SO₄-NH₃ nucleation? Also, if the CIMS observed significant sulfate and ammonium signals, maybe the author can compare the HGF (Exp. A) with previous studies (Biskos, G., Paulsen, D., Russell, L. M., Buseck, P. R., and Martin, S. T.: Prompt deliquescence and efflorescence of aerosol nanoparticles, *Atmos Chem Phys*, 6, 4633-4642, 10.5194/acp-6-4633-2006, 2006.).

Authors' response, changes in MS: In the experiment A ammonia concentration was low (below 5 pptV, which is the detection limit of the ion chromatograph.) and DMA also remained as contaminants in the chamber (Bianchi et al., 2014). Even if these low levels of ammonia and DMA as contaminants would have some effect on the nucleation, they are not expected to affect substantially the subsequent growth. However, the measured kappa for experiment A was smaller than the pure kappa for sulfuric acid, suggesting possibly a small contamination in the particles (see reply to question 5).

Referee's comment: 5. Page 19811, lines 24-25, which value do you use as the kappa to calculate the DMAS volume fraction in eq.4 for Exp. B-D? For me it seems you use kappa value of ammonium sulfate (0.47) or I misunderstand something. Page 19813, lines 14-15, the ammonium also exists in Exp. A, why the authors only compare the kappa values to sulfuric acid, not the ammonium sulfate as stated in Page 19811, lines 24-25?

Authors' response, changes in MS: To estimate a volume of DMAS, we used κ values of inorganic sulfate and DMAS as shown in Eq. (4). We assumed that the inorganic sulfates in the particles are either sulfuric acid or ammonium sulfate. The κ values of sulfuric acid and ammonium sulfate were assumed as 0.70 (Sullivan et al., 2010) and 0.47 (Topping et al., 2005), respectively. The κ value of DMAS was assumed as 0.28 (Qiu and Zhang, 2012). In the revised manuscript we have clarified the use of different κ values of the inorganic sulfate in the context of discussion of revised Fig. 3.

First of all, because we supplied only sulfuric acid to the chamber during experiment, we compared kappa values between our results and pure sulfuric acid. However, the measured κ values are slightly lower than results for pure sulfuric acid and therefore we compared results from our other experiments (with DMA or organics) to the experiment A instead of the literature value of kappa of sulfuric acid. As we mentioned in our manuscript, measurements from Api-TOF and TDCIMS showed existence of trace levels of contaminants in the cluster and nanoparticles. We also added kappa of ammonium sulfate in the Figure 2. The measured κ values of 10 and 15 nm particles in the presence of sulfuric acid (Exp. A) are lower than results from pure sulfuric acid and higher than those of pure ammonium sulfate as shown in Fig. 2.

Referee's comment: 6. For Fig.2. I would suggest the authors also plot the kappa of ammonium sulfate.

Authors' response, changes in MS: It is a good comment. We modified the figure 2.

Referee's comment: 7. It seems the kappa values used in the calculation mostly refer to the large particles (100 nm). Since this work was mainly focus on the 10 nm and 15 nm nanoparticles, are these kappa values still representative? How did the authors consider the uncertainties of kappa values? How much it can influence the results and conclusions?

Authors' response, changes in MS: The reviewer raises a good question here. So far kappa values reported for the compounds have been determined for larger particles, and although in theory these values should be applicable for smaller particles, provided that the Kelvin effect is considered appropriately, this has not been tested and is a topic of our follow-up study. Another source of

uncertainty in our calculations is the actual value of the κ of the inorganic sulfate. First, the experimentally determined κ and κ calculated with E-AIM are 0.7. Second, there observation on ammonia could indicate that the inorganic sulfate was ammonium sulfate which has κ of 0.47. The choice of κ for the inorganic fraction affects the calculated DMAS volume fraction. In the revised manuscript we have included in Fig. 3 the volume fractions calculated with different values of the κ for the inorganic fraction and discussion about the effect of the inorganic hygroscopicity value. Even though the different values for the inorganic κ result in different DMAS volume fractions with each value of κ_{inorg} there is a clear increase in DMAS volume fraction from 10 nm to 15 nm. Hence our measurements support the view that the contribution of dimethylamine to particle growth increases with increasing particle size.

Referee's comment: 8. The authors listed the standard deviations of HGF and kappa values in Table 1 and Fig.2. How many scans of each diameter were performed? Have you repeated the experiments?

Authors' response, changes in MS: We got data from at least 15th scans of each diameter and experiment. We didn't have repeated experiments, however the experimental conditions in the CLOUD chamber are well controlled and therefore we believe that it is possible to draw conclusions based on this dataset without repeated experiments.

Referee's comment: 9. Page 19816, lines 9-11, dose the dimethylamine concentration (like Exp. B) influence this conclusion?

Authors' response, changes in MS: This a good point. In experiment B the DMA gas phase concentration was indeed smaller than in experiments C and D and therefore it's not straightforward to compare exp. B to C and D regarding the effect of sulfuric acid gas phase concentration changes. However, in exp. C and D the DMA gas phase concentrations were the same. We have modified the conclusion made in the text: "It suggests that the composition of 10 nm particles does not change significantly over this range of sulfuric acid and DMA gas-phase concentrations."

Referee's comment: 10. Could the authors compare the results with previous studies (Keskinen et al., 2013)? I think they reported kappa values of more particle sizes.

Authors' response, changes in MS: It is a good comment. The straightforward comparison of result reported here and in Keskinen et al. (2013) is not possible. This is because the experimental conditions of two studies were different. In Keskinen et al. (2013), the ammonia concentrations were clearly higher as ammonia was injected into the chamber and also the organics used were different. In this study, we focused on hygroscopicity of particles in the presence of sulfuric acid, amines and organics from oxidation of α -pinene without ammonia.

Referee's comment: 11. Page 19817, lines 12-14, does the CIMS observed more α -pinene oxidation products contributed to the mass?

Authors' response, changes in MS: From TDCIMS measurements, we found that there is a large increase in the oxidized organics in the α -pinene experiments compared to the DMA+sulfuric acid only experiments.

Reference

Bianchi, F., Praplan, A. P., Sarnela, N., Dommen, J., Kürten, A., Ortega, I. K., Schobesberger, S., Junninen, H., Simon, M., Tröstl, J., Jokinen, T., Sipilä, M., Adamov, A., Amorim, A., Almeida, J., Breitenlechner, M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hakala, J., Hansel, A., Heinritzi, M., Kangasluoma, J., Keskinen, H., Kim, J., Kirkby, J., Laaksonen, A., Lawler, M. J., Lehtipalo, K., Leiminger, M., Makhmutov, V., Mathot, S., Onnela, A., Petäjä, T., Riccobono, F., Rissanen, M. P., Rondo, L., Tomé, A., Virtanen, A., Viisanen, Y., Williamson, C., Wimmer, D., Winkler, P. M., Ye, P., Curtius, J., Kulmala, M., Worsnop, D. R., Donahue, N. M., and Baltensperger, U.: Insight into acid-base nucleation experiments by comparison of the chemical composition of positive, negative, and neutral clusters, *Environ. Sci. Technol.*, 48, 13675–13684, 2014.

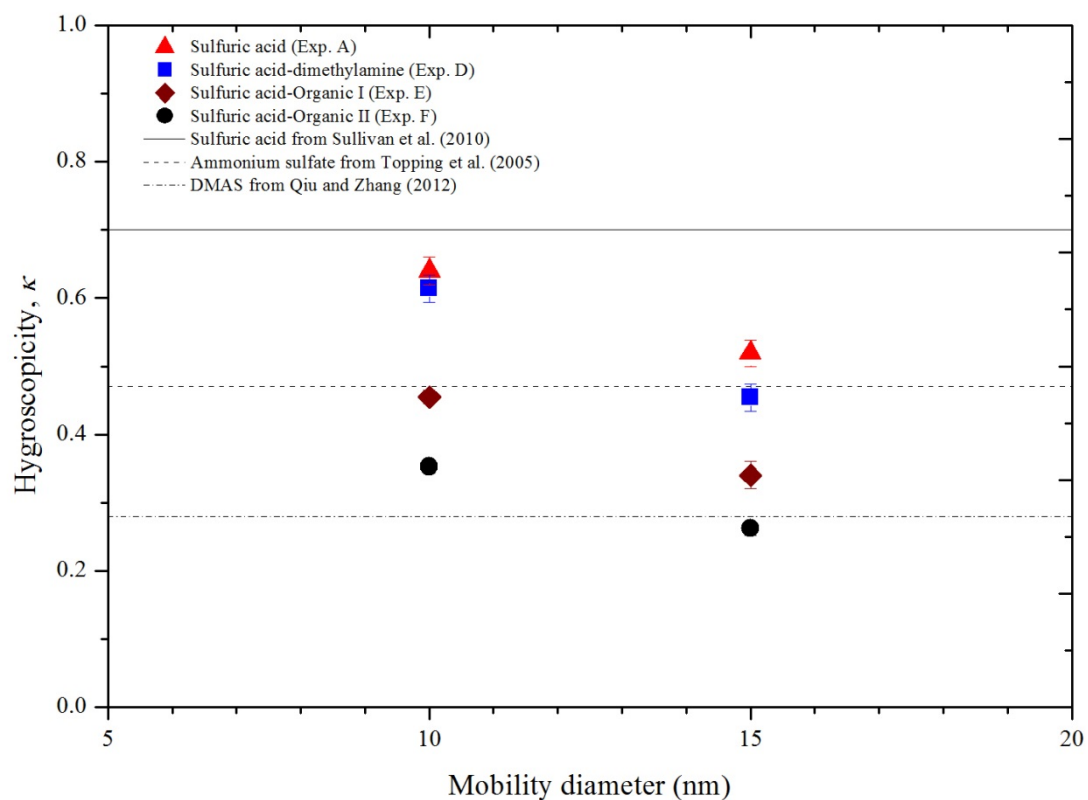


Fig. 2. Comparison of hygroscopicity (κ) for 10 and 15 nm particles in the presence of sulfuric acid (Exp. A), sulfuric acid-dimethylamine (Exp. D), and sulfuric acid-organics produced by α -pinene oxidation with OH scavenger (Exp. E-F). The theoretical κ of sulfuric acid (solid line) from Sullivan et al. (2010), κ of ammonium sulfate (dashed line) from Topping et al. (2012), and κ of DMAS (dashed dotted line) from Qiu and Zhang (2012) are also presented. The α -pinene concentrations during sulfuric acid-organic I and sulfuric acid-organic II were 420 and 910 ppt, respectively, as can be seen in Table 1. Error bars show a standard deviation from measurements data.

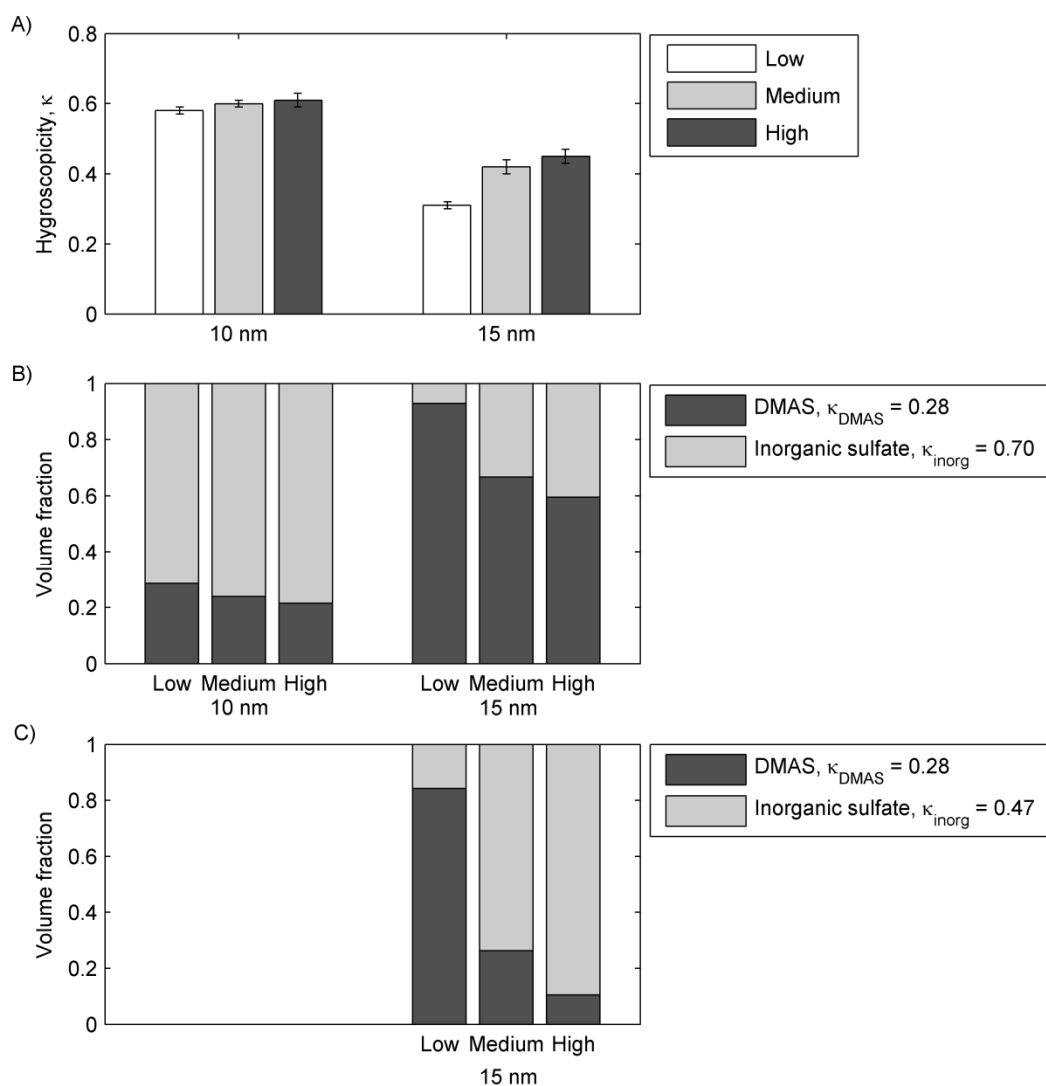


Fig. 3. (A) Comparison of hygroscopicity of 10 and 15 nm particles produced from sulfuric acid and dimethylamine; (B-C) Estimated volume fractions in the particles depending on UV aperture (Exp. B-D) assuming the inorganic fraction was (B) sulfuric acid and had a hygroscopicity $\kappa = 0.70$ and (C) ammonium sulfate and had a hygroscopicity $\kappa = 0.47$. The concentrations of sulfuric acid were 5.1×10^6 , 7.6×10^6 , and 12.3×10^6 molecules cm^{-3} for low, medium, and high, respectively.

Anonymous Referee #1

Received and published: 3 September 2015

This manuscript presents nano-HTDMA measurements of freshly nucleated particles in the presence of sulphuric acid, sulphuric acid-dimethylamine, and sulphuric acid-organics mixtures. This work is well presented, and the conclusions logical. I have only very minor comments:

Referee's comment: Page 19814, line 11: "the observed increases in k values"– do the authors mean "decreases"?

Authors' response, changes in MS: Yes, you are right. It is my mistake. Our data showed that κ values decreased with increasing particle size. Text was corrected accordingly.

Referee's comment: Page 19815, line 3: Can the authors also confirm that this evaporation does not account for the difference in acidity between particle sizes?

Authors' response, changes in MS: In order to estimate the impact of evaporation of DMA in the sampling tube on the acidity of particles with different size, the thermodynamic condensation model simulations were conducted using the MABNAG (Ahlm et al., 2015). These simulations showed decreases in DMA to SA ratio of 15% and 17% for 10 nm and 20 nm particles, respectively. This suggests that evaporation of DMA can only explain a minor fraction of the discrepancies in acidity of particles regardless of particle sizes. As the relative change in DMA to SA ratio due to evaporation in sampling line was larger for larger particle size, this also suggests that the effect of evaporation would tend to weaken the size dependence of DMA to SA ratio, not strengthen it.

Referee's comment: Page 19815, line 24: "at a constant paste" – do you mean "rate"?

Authors' response, changes in MS: Yes, you are right. It is my mistake. Text was corrected accordingly.

Referee's comment: Page 19816, line 10: Have the authors done any statistical significance testing to confirm this?

Authors' response, changes in MS: No statistical testing was done, as we didn't have repeated experiments for the different SA gas phase concentrations (only one experiment per SA gas phase concentration). The uncertainty range given for each SA concentration is the standard deviation between different scans (at least 15th scans of each diameter and experiment). The changes in κ between the three SA concentration cases are larger than the uncertainties of each value suggesting that there might be real difference in particle composition between these three cases, however the difference is small.

Referee's comment: Finally, I believe the figures would be much clearer if they were in colour, particularly figure 2 making the points more distinguishable.

Authors' response, changes in MS: We modified size and color of points in Figure 2.

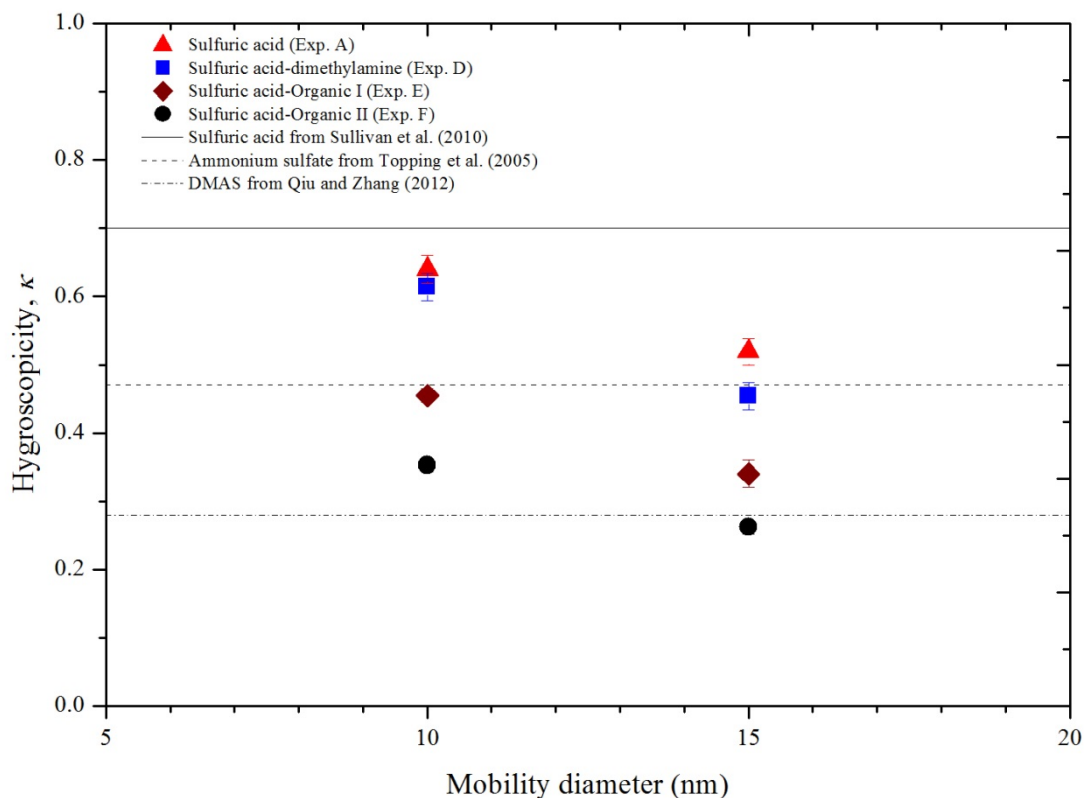


Fig. 2. Comparison of hygroscopicity (κ) for 10 and 15 nm particles in the presence of sulfuric acid (Exp. A), sulfuric acid-dimethylamine (Exp. D), and sulfuric acid-organics produced by α -pinene oxidation with OH scavenger (Exp. E-F). The theoretical κ of sulfuric acid (solid line) from Sullivan et al. (2010), κ of ammonium sulfate (dashed line) from Topping et al. (2012), and κ of DMAS (dashed dotted line) from Qiu and Zhang (2012) are also presented. The α -pinene concentrations during sulfuric acid-organic I and sulfuric acid-organic II were 420 and 910 ppt, respectively, as can be seen in Table 1. Error bars show a standard deviation from measurements data.