

Response to Anonymous Referee # 2

This is a nicely performed study with very clearly explained measurements. My only suggestions are for revision of the discussion section, where I think the authors may be speculating a bit too much on the implications of their data:

We thank the reviewer for their generous and frank assessment. To summarize our responses below, we concede that there is not enough evidence to conclude that a phase change occurred over the measured size range. However, we continue to assert that the data demonstrate a size-dependent composition change.

1. Section beginning with: “The TDCIMS data overall indicate a large increase of base fraction as the particles grew from 10 to 20 nm.” I think the authors should be bit more cautious in interpreting their data in this section. Aside from 3 data points, it appears that the base:acid ratios in figure 11 are bound between 0.2 and 0.5 for all measurements. While the results presented are very interesting I think it is premature to conclude that the chemical composition of particles is unquestionably changing as they grow from 10-20 nm.

In the absence of HTDMA data, there might be reason to doubt the change in particle composition from 10-20 nm. In that case we might state that only sub-13 nm particles ever showed base:acid ratios below about 0.2. However, the HTDMA observations, based on entirely different measurement principles, show the same direction and particle size region for the compositional change.

We modified the following sentence (non-italicized part) to emphasize the agreement between instruments:

“The direction of this composition change over this range of diameter is corroborated by aerosol hygroscopicity results from the same experiments”

Based on the Cheng et al. (2015) results, there could also be a phase transition taking place close to this size, and we have added text to that effect, citing Cheng et al.’s results for ammonium sulfate nanoparticles:

“At the slightly lower temperature in the present study (273 K), this [phase] transition occurs at a slightly smaller particle diameter, closer to 9 nm. For the dimethylammonium-ammonium-sulfate nanoparticles studied here, a similar size-dependent transition seems plausible.”

The TDCIMS observations on their own suggest a size-dependent change, and the additional pieces of evidence support this idea. While the possibility of a phase transition may be speculative, the HTDMA observations confirm the size-dependent composition change.

Cheng, Y., Su, H., Koop, T., Mikhailov, E. and Pöschl, U.: Size dependence of phase transitions in aerosol nanoparticles, Nat. Commun., 6, 5923, doi:10.1038/ncomms6923, 2015.

2. Similarly, there is no evidence in the measurements reported here for a phase transition in particles as they grow from 10-20 nm. They do show that 10-20 nm particles sampled are more acidic than basic, and are composed of slightly more ammonia than dimethylamine. More analysis seems necessary to examine the phase of the detected particles.

The only observational evidence for a phase transition in these experiments is the size-dependent composition change, and we concede that there may be other explanations for this composition change. We argue that since there is a phase change for ammonium sulfate in this size range, it is possible that a similar sulfate salt also has such a transition. The methods used by Cheng et al. to identify the phase state of ammonium sulfate at different sizes can't be applied in the same way in this case, largely because much less is known about the thermodynamics of salts formed from amine-ammonia-sulfuric acid mixtures, and they appear to have properties unique to the individual amines (Chan and Chan, 2013). We have modified the manuscript (described below) to reflect that a phase transition at these sizes is possible but not verifiable using the information currently at hand. We added this discussion to the text:

“At the slightly lower temperature in the present study (273 K), this [phase] transition occurs at a slightly smaller particle diameter, closer to 9 nm. For the dimethylammonium-ammonium-sulfate nanoparticles studied here, a similar size-dependent transition seems plausible. However, less is known about the thermodynamics of these mixed ammonium-aminium sulfate salts. Even for large droplets, where size-dependent effects are not important for phase state, pure dimethylaminium sulfate does not form a solid phase, even at < 3 % RH. However, the exposure of such an amorphous liquid droplet to ammonia results in the formation of a solid phase which contains ammonium and aminium and is resistant to further exchange (Chan and Chan, 2013).”

We added this statement to the Conclusions as a caveat about the suggested phase change:

“However, further work is needed to characterize the phase states of mixed ammonium-aminium-sulfate nanoparticles to assess these possibilities and to understand the growth pathways of such particles.”

We also removed the statement about a possible phase transition from the Abstract.

Chan, L. P. and Chan, C. K.: Role of the Aerosol Phase State in Ammonia/Amines Exchange Reactions, Environ. Sci. Technol., 47, 5755–5762, doi:10.1021/es4004685, 2013.

Minor Comment:

1. The manuscript refers to “Kim et al 2016”. However, this citation does not appear in the references section. Also, I do not believe the “Alhm et al, 2016” citation is published in Aerosol Science and Technology (perhaps it is in review).

Thanks for pointing out these oversights. We added the Kim et al. reference, and Ahlm et al. has now been published.