

Interactive comment on “Amine reactivity with charged sulfuric acid clusters” by B. R. Bzdek et al.

Anonymous Referee #1

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This work looks at cluster distributions of electrospray generated ammonium sulfate clusters and their reactivity with amines using a FTICR mass spectrometer. It is a direct continuation of several previously published papers by the authors on the subject, and in this paper the important addition is the extension of the study to negative ions. As expected, the cluster distributions, especially at the smallest cluster sizes, differ considerably between positive and negative ions. Nevertheless, the substitution of amines for ammonia seems to be nearly collision-limited also for the negative ions.

This paper is an important addition to the ongoing work of understanding the initial cluster formation leading to new aerosol particles in the atmosphere. It is well-written, concise, and fits into the scope of ACP, and should therefore be accepted for publication. However, I do have some comments that I wish the authors would take into

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account, my major concern being the applicability of these results to real ambient cluster formation.

Major comments:

Although electrospray ionization produces cluster distributions far from equilibrium, the ions will quickly (milliseconds or less) revert to a distribution with only semi-stable clusters present, mainly due to collisions and charge transfer with other molecules. At reasonable temperature and RH the resulting cluster distribution should be close to the one expected in the atmosphere. On the other hand, measurements made in vacuum, may be distorted in comparison with ambient cluster formation. RH will be practically zero and the temperature is not very well-defined. As the authors point out the atmospheric implications as one of the major results of the paper, I feel more discussion is needed on the representativeness of these measurements, at least in chapter 4: Atmospheric implications. Naturally, clusters can not be measured by any other means than mass spectrometry, which requires vacuum, and the possible perturbations caused by this should always be kept in mind. This paper discusses reactions occurring over time periods up to 40s in vacuum, and the authors should therefore be extra careful in the interpretation.

One specific point that is mentioned in the paper is the instability of dimethylammonium sulfate clusters upon mass selection, but this is not discussed any further. If the substitution of DMA for NH₃ in the clusters is so highly favorable, why are the DMA clusters not more stable than the ones with NH₃? I feel this should be discussed in a bit more detail, as it may relate directly to the conclusions of the paper.

Possibly relating the above point, figure 1b shows a similar amount of the sulfuric acid tetramer as of the dimer, but no data is presented on the DMA or NH₃ addition to the tetramer. This might have been a very interesting cluster as DMA substitutes NH₃ and adds 3 additional molecules onto the pentamer, but does not react at all with the trimer. Was the tetramer also not stable upon mass selection, just as the DMA sulfate

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clusters? And again, what does that mean?

Page 10, line 17-18. The authors state that NH_3 did not add onto the $(\text{H}_2\text{SO}_4)_5(\text{NH}_3)_1$ cluster, but in figure 1b $(\text{H}_2\text{SO}_4)_5(\text{NH}_3)_2$ is of the same order as $(\text{H}_2\text{SO}_4)_6(\text{NH}_3)_2$. Can the authors comment on this? Is this perhaps due to the difference between ambient and vacuum conditions, or do the authors have some other explanation?

Other comments:

Where does the sodium contamination come from? Is the sodium source also present during the ammonium sulfate production? If it is, then what is the reason for sodium not substituting NH_3 ? A benefit of all the recently developed MS techniques to measure small clusters is that it has become evident that contaminations of some sort are almost always present, although most earlier studies have assumed them to be zero. It is understandable that the authors do not wish to have an extensive discussion on the contaminations of their experiment, but I would like to believe that this community has come far enough to understand that contaminations are practically always present in one form or another, and it is better to discuss them openly (and perhaps even learn from them) than to sweep them under the rug or just ignore them (to make it clear, I am not suggesting this was done in this paper). In this case, if sodium substitutes DMA in the clusters, does that suggest that sodium, although not atmospherically relevant in this context, would enhance cluster stabilization of H_2SO_4 even better than DMA?

Why does DMA never add to a cluster with NH_3 , but always starts by substituting all NH_3 and then adding to the DMA cluster? Do the authors have any ideas on this?

Could the residence time between the ESI and MS be varied? Did/would this change the measured distribution presented in figures 1 and 2, or are they already "close enough" to equilibrium and thus not changed remarkably?

Page 10 line 14. This should be Table 2.

Page 11, lines 8-13. Please move the Junninen reference earlier in the sentence, and

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possibly add "in this work" to the end. The sentence now suggests that Junninen et al made the electrospray of amm.sulf., but I assume the authors are referring to their own data?

Without taking a stand in the debate of the importance of ion-induced nucleation, somewhere in chapter 4 I feel there should be a sentence or two also on the implications of these results on the neutral clusters (if any). As it is, nucleation is discussed, as are ion clusters, but neutral clusters are not mentioned at all, even though they might be much more important. This should at least be acknowledged somewhere.

The major nucleating compound is commonly believed to be H_2SO_4 , with some stabilization needed from base compounds. How does the fact that amines seem to produce more stable clusters impact on the further growth of the particles? Is the more stable DMA cluster more likely to grow further by H_2SO_4 addition than the one with NH_3 , or has the cluster become so stable that H_2SO_4 no longer attaches as readily to it as to a NH_3 cluster? In the latter case amines would thus inhibit particle formation. Could the experimental setup be used to study also growth by H_2SO_4 to different clusters by bleeding in H_2SO_4 ? I do not suggest that the authors do this for this paper, only state that these results might also be interesting. . .

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14637, 2011.

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