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Atmospheric Chemistry and Physics Discussions

Interactive comment on "On the formation of sulphuric acid-amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation" *by* P. Paasonen et al.

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We would like to thank the referee for his comments. In the following we give our responses.

1) What is behind the DACM model? Is it a kinetic solver for the ODE system resulting from the addition/decomposition steps for all intermediates/clusters including sink terms or are equilibrium conditions generally assumed or what is considered else?

DACM model is a kinetic solver for the ODE system which is run with Matlab-program.

It is formed by time derivative equations for the concentration of each different cluster. Each time derivative includes source terms related to those collisions of smaller clusters/molecules and evaporations from larger clusters that result in the cluster, and sink terms due to the collisions and evaporations of the cluster as well as the coagulation with larger particles. A more detailed description of DACM has been added to the description of the model in Sect 2.1.1.

2) The chemical structure of the clusters "2 SA x 2 DMA" and "2 SA x 2 TMA" should be given allowing the readership to get a visual impression. Here it could be explained where a third SA could be attached in both cases.

The structure of these clusters has been added to Supplementary Material. Information on where the next attaching acid molecule would be added cannot be shown with the methods applied in this study. This is because we do not take into account in what exact location of the cluster the colliding molecule/cluster hits, but assume that each collision has a sticking probability of 1 and that the collision product rearranges immediately into its minimum energy conformation. Due to the rapid rearrangement of the collision product, it would also be somewhat misleading to let the readers imagine the structure of the next cluster, which would not eventually be the one that represents the most stable and thus most abundant structure in reality.

3) I guess there is a shortcoming in the discussion of the RH dependence. The authors found a drop of cluster formation with increasing RH or the cluster formation was nearly unaffected by RH depending on the amine considered in the cluster. This finding should be discussed with respect to atmospheric observations and lab results, if possible!

In addition to the Hamed el al. (2011) paper investigating the role of RH in atmospheric new particle formation (NPF) measurements, laboratory studies (Berndt et al., 2010; Brus et al., 2011; Zollner et al., 2012) are now mentioned in the revised manuscript. However, the comparison with the laboratory results cannot be directly made, because during the RH experiments conducted in these articles the base(s) participating in NPF

have not been identified.

4) DMA and TMA, a secondary and a tertiary aliphatic amine, were chosen as the model amines in this study. Other amines with atmospheric relevance are for instance pyridine and aniline and derivatives. What can we expect for the process of cluster formation and growth from an aromatic amine, or from a primary amine with a relatively large phenyl group (steric hindrance)? Are some explanations possible with the current state of knowledge?

While pyridine and its derivatives (and other similar molecules such as aniline) are all fairly strong bases and thus bind to single sulphuric acid molecules quite strongly, they are very likely somewhat less efficient at promoting nucleation than small aliphatic amines such as DMA. This is due to the steric issues mentioned by the reviewer: the bulky ring structures limit the number of acids that can cluster effectively with pyridine and its derivatives. Thus, pyridine, aniline etc. are less effective at decreasing acid evaporation rates from larger clusters. In case of pyridine, the lack of hydrogen atoms bound to the nitrogen prevents the formation of hydrogen bonds to bind with more than one sulphuric acid, which further decreases pyridines capacity of forming nucleating clusters.

References:

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