Hydration of Sulfuric Acid Clusters and the Impact of Bases

H. Henschel[1], I. K. Ortega[1], O. Kupiainen[1], T. Olenius[1], T. Kurtén[2] and H. Vehkamäki[1]

[1]Division of Atmospheric Sciences, Department of Physics, P.O. Box 64, 00014 University of Helsinki, Finland
[2]Laboratory of Physical Chemistry, Department of Chemistry, P.O. Box 64, 00014 University of Helsinki, Finland
Keywords: sulfuric acid, ammonia, water, quantum chemistry, nucleation.
Presenting author email: henning.henschel@helsinki.fi

The formation of new particles in the atmosphere is generally agreed to involve sulfuric acid and water. However, it is known that these alone can not explain the observed particle formation rates. Therefore, other substances must be invoved in the process. One substance known to enhance the formation rate is ammonia, though not either this can fully explain the observed rates.

An important goup of substances that could explain the elevated nucleation rates are amines. Especially dimethylamine has been found to be involved in particle formation events (Mäkelä, 2001).

We present here a study of the hydration of clusters formed by sulfuric acid, and sulfuric acid together with ammonia and dimethylamine, respectively.

Clusters containing up to four molecules of sulfuric acid with up to three molecules of ammonia or diemthylamine together with up to five water molecules were modelled using a RICC2/aug-cc-pVTZ//B3LYP /CBSB7 level of theory. Based on these results the realtive populations of the repsective hydrates were simulated for different relative humidities.

Clusters consisting only of sulfuric acid form in general stable hydrates with an increasing energy of hydration with increasing number of sulfuric acid molecules. Only in case of the cluster containing four molecules of sulfuric acid one hydrate was found to be considerably more stable than would be expected from the trend in energies. Consequently this hydrate is also predominantly populated over a wide range of relative humidities.

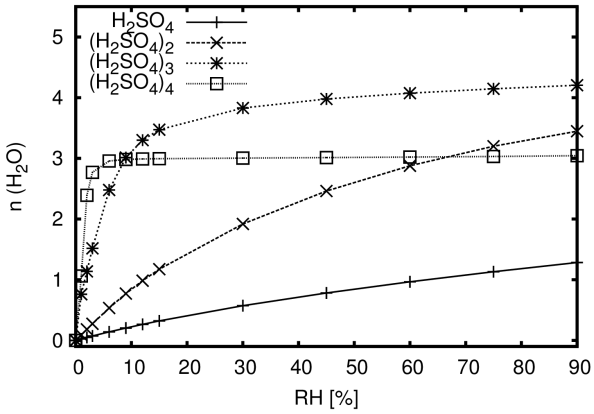

Figure 1. Hydration profiles for sulfuric acid clusters.

The resulting average hydration of clusters containing no base can be found in Fig. 1.
For systems containing both sulfuric acid and ammonia in general smaller hydration energies were found as compared to the base free system. Also, these systems do not exhibit broad distribution of hydration energies as the systems containing only acid, and show average hydration umbers between approximately 1.5 and 2.5 for relative humidity approaching 100 %.

Clusters containing both sulfuric acid and dimethylamine show an even lower affinity for water. For all clusters studied, the energy for at least one hydration step has been found to be positive. In case of the cluster consisting of two molecules of sulfuric acid and dimethylamine, all hydration energies were positive. Consequently, the average hydration of the dimethylamine-containing clusters is lower than for the other systems (cf. Fig. 2).

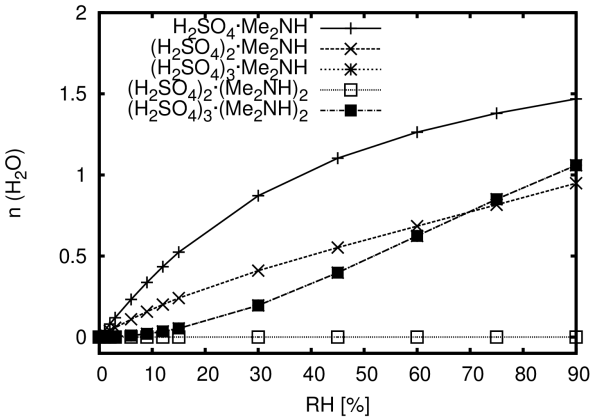

Figure 2. Hydration profiles for clusters containing sulfuric acid and dimethylamine.

At the same time, the profiles of the average hydrations of these clusters are not as uniform as for the other systems studied.

The observed differences in the hydration profiles will clearly have consequences on new-particle formation. Due to the differences in stability of certain hydrates, pathways towards particle formation can both become more and less likely, potentially altering the importance of different factors for the overall process significantly.

We thank the CSC–IT Center for Science in Espoo, Finland, for computing time, and ERC StG 257360 MOCAPAF, and the Academy of Finland (Center of Excellence program project #1118615, LASTU program project #135054) for funding.

Mäkelä, J. M., Yli-Koivisto, S., Hiltunen, V., Seidl, W., Swietlicki, E., Teinilä, K., Sillanpää, M., Koponen, I. K., Paatero, J., Rosman, K., and Hämeri, K. (2001) *Tellus B* **53**, 380–393.