Hydration of Sulfuric Acid-Methylamine Clusters in the Troposphere

Bobby Cao, Berhane Temelso, George C. Shields
Department of Chemistry, College of Arts & Sciences, Bucknell University, Lewisburg, PA 17837

Sulfate aerosols in the atmosphere have a cooling effects on the earth's climate. Sulfuric acid (H_2SO_4) is the main driver of these aerosols and the presence of bases like ammonia and methylamine (CH_3NH_2) stabilize molecular clusters and enhance aerosol formation through a process called ternary nucleation. We are studying the formation of particles that include sulfuric acid dimer $(H_2SO_4)_2$, methylamine and up to three water (H_2O) molecules. Thousands of clusters of the form $(H_2SO_4)_2(CH_3NH_2)(H_2O)_n$, n=0-3, were initially generated by using genetic algorithm (GA) search on semi-empirical (PM7 and SCC-DFTB) potential energy surfaces. Then the most stable clusters were studied more rigorously at the PW91/6-311++G** level of theory.

Comparing the results from the current system $[(H_2SO_4)_2(CH_3NH_2)(H_2O)_n$, n=0-3] with that of a binary sulfuric acid-water system $[(H_2SO_4)_2(H_2O)_n$ n = 0-3] and a ternary sulfuric acid-methylamine-water system $[(H_2SO_4)(CH_3NH_2)(H_2O)_n$ n = 0-3], we concluded that the addition of methylamine stabilizes the sulfuric acids substantially, but it does not affect the subsequent hydration thermodynamics significantly. The addition of methylamine to a two sulfuric acid system stabilizes the cluster by 20 kcal/mol compared to a system without methylamine. Also, acid dissociation of one or both sulfuric acids is accelerated in the presence of methylamine compared to binary (H_2SO_4-H_2O) systems.

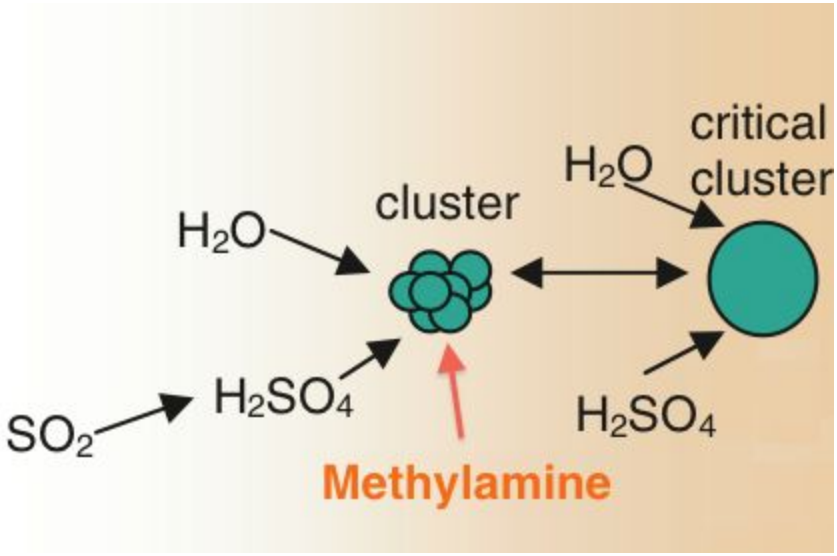

Figure 1: The role of bases like methylamine in the early stages of atmospheric aerosol formation Figure adapted from Curtius, J. *EPJ Web of Conferences* **2009**, 1, 199-209.