Hydration and mobility of bisulfate ion-sulfuric acid-ammonia/dimethylamine clusters from computational studies

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Secondary atmospheric aerosol particles are known to form almost everywhere around the world. A high proportion of these particles are formed from sulfuric acid vapor, which binds strongly to some base molecules (ammonia or dimethylamine) to form stable small clusters susceptible of further growth. The stability of these clusters can be affected by their charging state, thus modifying both the collision and evaporation rate constants and hence their dynamics (Ortega et al., 2014).

We performed calculations on a set of bisulfate ion-sulfuric acid-ammonia and bisulfate ion-sulfuric acid-dimethylamine clusters (HSO₄⁻(H₂SO₄)ₙ(NH₃/(CH₃)₂NH)₂, with s = 0-3, b = 0-2) using ab initio methods. Up to five water molecules were involved in the calculations. The clusters equilibrium structures and the energies of stepwise hydration were determined. The equilibrium hydrate distributions of the investigated clusters were further predicted at 298.15 K and various relative humidities between 1 and 100%.

As opposed to the traditional approach used to derive cluster structures from ion mobility measurements, we used a particle dynamics model (Larriba et al., 2013) to predict the mobilities in air of the cluster ions investigated in this study, under standard conditions. The cartesian coordinates of the lowest energy configurations were taken as inputs.

We found that the hydration of the HSO₄⁻(H₂SO₄)ₙ(NH₃/(CH₃)₂NH)₂ clusters is weaker than that of their corresponding protonated counterparts (Henschel et al., 2014). Furthermore, we find that the hydration of clusters containing base molecules is more energetically favourable than that of base-free clusters, while the hydration of ammonia-containing clusters is more favourable than that of dimethylamine-containing clusters. As a consequence, the hydrate distribution of ammonia-containing clusters is wider than that of dimethylamine-containing clusters.

We predicted ion mobilities falling in the range of 1.05-3.42 cm²/Vs, corresponding to the mobility diameter range of 0.52-1.11 nm. The ion mobility decreases with hydration as can be seen from Figure 1, most likely due to the increase in the collision cross section with increasing hydration. It is also apparent from Figure 1 that the change in ion mobility is weakly sensitive with hydration in large clusters.

Figure 1. Variation of the electrical mobilities (at 1 atm and 298.15 K) in air of the HSO₄⁻(H₂SO₄)ₙ clusters (s=0,1,2,3) with hydration.

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