Water Evaporation From Tropospheric Aerosols

Grand Valley State University

Online MU3C Conference

A. Gilde
N. Siladke
C. Lawrence
Aerosols

- Minute particles in the atmosphere.
- Why tropospheric aerosols?
  - Facilitates chemical reactions
  - Role in radiation reflection and cloud formation
- Often contains impurities and covered with an organic surfactant
  - Our main focus is the short chain butanol
Sources of Impurities

- Continental – Soil derived dust, biomass (life), volcanic aerosol, man-made (pollution)
- Marine – Sea salt spray, DMS (sulfur), phytoplankton (sulfur)
Previous Work

• Experiments with aerosols and long chain surfactants (18 carbons) show that water evaporation is reduced by a factor of 10,000.

• Experiments with aerosols and short chain surfactants show the rate of evaporation is unaffected.*
  
  However, because Nathanson’s experiment requires a low vapor pressure, it is performed with sulfuric acid at low temperature. This questions the validity of its comparison to a true tropospheric aerosol.

Goals

- To understand water evaporation from a surfactant covered aerosol using simulations.
- Using molecular dynamics, we can trace the evaporating water trajectories.
Model

Water

- Bonds as springs.
- Partial charges were incorporated to model hydrogen bonding.
- Prevent atom overlap through dispersion forces. The repulsive sphere for water was its oxygen atom.
Butanol

- In addition to charges on the H, O, and alpha mythelene, the butanol molecule also had torsion forces.
- Individual hydrogen and carbon atoms were grouped as one unit, and this unit was the repulsive sphere in calculating the dispersion forces.
Simulation

- Due to the infrequent evaporation of water molecules, we measured the condensation of gas molecules contacting a liquid surface.
- Rate of Evaporation = Rate of Condensation
- Rate of Condensation = Number of Collisions x Fraction that Condense
Preparation of Interface

500 water molecule system equilibrated for 250 ps at 300 K.

After the box was extended in the z direction, butanols were placed on to the surface.

System was again equilibrated for 250 ps.
A water molecule was introduced into the vapor phase at 20 Å away from the surface.
These graphs were used to track the z-position of the vapor molecule over the time the simulation was run. These four represent a typical condensation. In the case of pure water, 100% condensation was observed.
In the case of butanol, the condensation percentage varied. In addition to condensations, the vapor molecule would also reflect off the surface, or have several interactions with the surface and then leave.
Our original definition of a condensation only required that the water molecule stay in contact for the duration of the simulation. However, this resulted in counterintuitive results as the condensation percentage increased at higher surface coverage.
The definition of a condensation was then redefined to include only those molecules that stayed in contact during the duration of the simulation and contacted the water in the bulk of the system. Much more logical results were observed.
In order to determine if the vapor molecule reached the bulk we tracked the hydrogen bonds formed.

Hydrogen bonds were determined by meeting geometric criteria.
Graph of z-position (similar to previous), and the number of H-bonds observed over the course of the simulation.
Water Position and Hyd Bonds

Distance from Surface (Å) vs. Time (ps)

# of Hyd Bonds
Importance of Hydrogen Bonds

• It has consistently been observed that molecules that condense have shown long sustained hydrogen bonds.
• It has also been noted that those molecules that do not condense lack bonds of this nature as indicated by the previous slide.
In order to better understand the condensation mechanism, we repeated our simulations without electrostatic interactions between the incoming water molecule and surfactant. This essentially inhibits hydrogen bonding between the molecule and surfactant without changing the surface of the system.

It was observed that the interactions with the surfactant do play a role in the mechanism, specifically at higher surface coverage.

Additionally, these results closely resembled those attained after a condensation was redefined.
Water-Butanol Simulation

- % Condensation vs. Number of Butanol Molecules
- Three conditions: No Hyd Bonds, All Condensations, Bulk only Condensations
- Estimated monolayer
The Switch to Sulfuric Acid

- In solution, sulfuric acid dissociates into either hydrogen sulfate or sulfate producing hydronium ions.
- The knowledge of temperature and concentration allows us to predict the amount of each species.
- Water, butanol, hydronium, and sulfate species have been modeled previously.
- Hydrogen sulfate spring and torsion constants were calculated using gaussian calculations.
- In the simulation, an equilibrium composition is used, but the species are not allowed to interchange (water is always water and hydronium is always hydronium).
The Switch to Sulfuric Acid

- Higher temperature (300 K) acid simulations have shown to closely resemble our butanol/water system despite the difference of species.
- Lower temperature (213 K) acid simulations are underway. Preliminary results show a significant increase in condensation percentage.
Changing the composition of the bulk does not account for the difference between our results and those of Nathanson et al. However, our preliminary results on low temperature solutions show much higher condensation percentages.
Acknowledgments

• Dr. Lawrence

• Grand Valley State University

• Petroleum Research Fund