

Chapter 5
Conclusions and Future Studies

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The results of the studies presented in this thesis confirm that ambient and laboratory-generated aerosols exhibit complex behaviors, and deserve further studies. In the study of SOA formation from cycloalkenes, it was found that the SOA yield can be predicted qualitatively from the parent hydrocarbon structure. Through a large number of experiments (at least seven individual runs per compound studied), the overall “yield curve” depicting the variation SOA yield with the absolute organic mass formed (ΔM_o), was constructed for each individual precursor compound. Interestingly, the recent work by Ng et al. (2006) (Appendix L of this thesis) showed that the contribution of first- vs. second-generation product of SOA formed in oxidation systems can be predicted by the number of double bonds in the parent hydrocarbon. Compounds with one and two double bond(s) will generate SOA that is mainly composed of first- and second-generation low-volatility oxidation products, respectively, due to the differences in the rate-limiting step in the oxidation kinetics of each type of compounds. This distinction brings forth an interesting property for precursor compounds with one double bond, in which the time-dependent yield curve of a single high-initial-concentration experiment matches well with the overall yield curve constructed from multiple final yield points derived from many experiments. Thus, in the future, it may be unnecessary to run a large number of experiments to obtain an overall yield curve. If the compound of interest contains only a single double bond, it is possible to construct an overall yield curve from a single experiment using a high initial precursor concentration. Furthermore, additional time saving is made possible in future studies through the ability to predict relative SOA yield according to the parent compound structure as discussed in Chapter 2.

In the hygroscopicity studies of aerosol, complex growth behaviors were again observed for both chamber-generated SOA and aerosols produced from atomization. In the study presented in Chapter 3, SOA was shown to be slightly hygroscopic, with the water uptake inversely correlating with the aerosol-forming potential of the precursor. It was also observed that SOA exhibits smooth water uptake throughout a wide range of RHs, which suggests that SOA can play an important role in extending the range of RHs over which particle-bound water influences aerosol properties, such as density, light scattering, or refractive index. It is hoped that the data presented in this work will be incorporated into atmospheric aerosol models to help better estimate the water content of aerosols in regions where the SOA fraction may be significant.

In the study presented in Chapter 4, we found that when particles composed of water-soluble organic compounds are atomized from a methanol solution, they still exhibit hygroscopic growth throughout a wide range of RHs, similar to the behavior found for deliquesced particles. For many compounds, our data compare well with literature data. We also report the hygroscopic growth of a few species that have never been studied. Due to the existing experimental setup, only “dry” particles could be investigated. In the future, it would be of interest to study the complete water cycles of these and other species by first atomizing the aerosol from an aqueous solution, bypassing the dryers, and classify the wet particles directly. By drying the deliquesced particles between the two DMAs, the water content of the originally wet particle could be studied, similar to what was performed for SOA from humid photooxidation experiments in Chapter 2. This would either confirm the growth behavior presented in Chapter 3 or introduce another branch of water uptake for the never-before-studied compounds such as

pinonic acid, 2-hydroxycaproic acid, and sinapic acid. Other more complex organic species could also be studied now that the experimental setup has been tested for a number of common organic acids.

In making these measurements, we found that the phase and morphology of the particle under study can impact the observations of hygroscopic growth. Presence of void volume, irregular particle shape, or retained solute could all complicate interpretation of experimental data. The latter issue could be solved by using another high-volatility, non-polar solvent for atomization, which is expected to be more readily removed from the aerosol phase and be less likely to form complexes or solvate with the organic acids being studied. Cyclohexane is one potential candidate for such a solvent.

HTDMA measurements are also inherently subject to uncertainties in the classified particle size, which are affected by evaporation, further drying, and possible particle restructuring after classification. There are also potential changes in the classified particle composition and morphology as the atomizer solution becomes concentrated over time (especially in the case when methanol is used and readily evaporates away). In light of these uncertainties in conducting hygroscopic growth measurements using the HTDMA, future studies should take advantage of the availability of a well-characterized and highly controlled electrodynamic balance system available in our laboratory (Olsen et al., 2006) to perform complementary growth measurements. The EDB could be used to verify HTDMA data for systems that exhibit unexpected behavior as well as to provide additional data at conditions that are unattainable in the HTDMA. For instance, the humidity in the TDMA could not be raised much above 92% due to the risk of high voltage arcing in the scanning DMA. In experiments that involve drying of

wet particles between the DMAs, the drying capability is also limited by the rate at which water could be removed from the system operating at a high flow rate. In addition, the aerosol-containing flow is not passed through the Nafion dryer itself in order to prevent possible loss of semivolatile species due to reactions with the Nafion membrane, and only the particle-free excess air is dried and then later mixed with the moist monodisperse flow. Thus, the lowest RH that could be achieved with this setup is approximately 8%, as reported in the SOA drying-mode experiments. In the EDB, however, because only a single particle is studied at a time and can be kept levitating for as long as the particle does not evaporate away, the possible artifacts arising from time variation of particle properties and size are significantly reduced. The flow rate that is circulated through the EDB chamber is also much lower (0.07 L/min compared to 2.5 L/min in the HTDMA), which allows for a more extreme degree of drying and humidification. The RH range achievable in the EDB described by Olsen et al. is 0–96% RH. The extremely low RH attainable can be especially useful when studying species that exhibit low efflorescence RH. In addition, uncertainties in the dry particle density can be circumvented as the supermicron particle used in an EDB study is generated from the bulk solid. Finally, the system provides opportunity to investigate species that may exhibit significant mass transfer limitation in water uptake or loss, as a single particle could be held at a constant RH over many hours, as long as evaporative losses are not significant.

While the EDB can potentially provide many advantages in measuring water uptake by a particle, the HTDMA still remains the most suitable way to measure aerosol hygroscopicity for a number of cases. This includes studies in which the effect of particle size may be important for hygroscopic growth or for any system that is only available as

submicron particles (for example, SOA generated in the smog chamber). Another condition that could be better suited to an HTDMA measurement is that of a mixed particle. High-quality data on water uptake of a mixed particle, whether of an inorganic mixture, organic mixture, or organic-inorganic mixture, can be very useful for providing a more stringent test for thermodynamic models.

One of the limitations in the predictive ability of equilibrium thermodynamic models is the lack of experimental data that can be used to provide chemical interaction parameters. Currently, interaction parameters derived from a small subset of systems in limited range are used when modeling complex mixtures. Also, these parameters in UNIFAC are binary and therefore do not inherently take into account third-body or higher-body interactions. In multicomponent mixtures, parameters derived from simple binary mixtures, such as those from growth data of a pure organic compound, may be inaccurate when other functional groups are present. While the original UNIFAC parameter matrix does contain parameters derived from a wide range of compositions and interactions between functional groups, these numbers were not necessarily derived from atmospherically relevant species, temperatures, or sufficiently high concentrations. Thus, the capability of thermodynamic models still depends on experimental data to provide interaction parameters as well as to serve as validation test case.

Thus, it would be important in the future to perform a well-controlled study of the hygroscopic growth of mixed particles. Such a study would require a careful setup and thorough verification of the composition of the aerosol produced. In many previous studies in the literature, mixed particles are generated by atomizing a bulk solution mixture containing the species being studied. However, recent tests in our laboratory

using the AMS to measure the size-dependent composition indicate that particles generated in this manner actually have highly variable composition. For example, a mixed organic-inorganic atomizer solution may generate two almost distinct particle populations, a smaller population consisting mostly of the organic species, and another consisting of mostly of the inorganics. Along the same line, the study presented in Chapter 4 shows that different organic species exhibited varying limitations in the ability to generate sufficient number of particles at different classified sizes, even at similar concentrations. These observations indicate that the size distribution of the aerosol generated by atomization is very much a function of chemical composition. Thus, particles atomized from a mixed solution cannot be expected to have constant mixing ratios across all sizes. It is hoped that these difficulties can be overcome in the future experiments, and that uncertainties associated with both the modeling and measurement of aerosol hygroscopic growth can be minimized.

References

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