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Atmospheric Chemistry and Physics
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Discussions

Interactive comment on "Hygroscopic behavior and chemical composition evolution of internally mixed aerosols composed of oxalic acid and ammonium sulfate" *by* Xiaowei Wang et al.

Anonymous Referee #1

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In this work, the authors measured the hygroscopic phase transitions of organic-sulfate particles. Specifically, pure oxalic acid, pure ammonium sulfate, and mixtures of both were studied using Raman microspectroscopy. Shifts in Raman spectral bands at specific relative humidities marked both deliquescence and efflorescence. The deliquescence relative humidity (DRH) and efflorescence relative humidity (ERH) of oxalic acid (OA) and ammonium (AS) sulfate agree with previous literature with one exception: the ERH of OA was higher (77%) than literature values (∼55%). Mixtures of OA with AS exhibited different hygroscopic behavior than pure substances, which depended on the molar ratio of OA to AS. Increasing the molar ratio of OA to AS increased the mixture's ERH. Furthermore, at the highest OA to AS molar ratio (3:1), aqueous chemical

reactions in the particle during drying formed nonhygroscopic products. These nonhygroscopic products, such as NH4HC2O2 and residual OA, did not deliquesce upon rehumidification.

While this paper uses sound techniques, cites relevant literature, and is well written, it ultimately fails to address relevant scientific questions within the scope of ACP. The reviewer admits this work presents two new pieces of novel data. First, the ERH of the studied mixtures was dependent on the molar ratio of oxalic acid to ammonium sulfate. Second, aqueous reactions in drying droplets of OA and AS can produce nonhygroscopic products. This novel data, however, is not discussed within the framework of our current knowledge in the literature. Thus, it is not clear to the reviewer how atmospherically relevant or important this work is.

This reviewer suggests two pathways to increase the efficacy of this work. In one pathway, the authors would expand this workâĂŤespecially the discussion section. Currently, the discussion section contains no effort to frame the results of this study into the existing literature. In the second pathway, the authors could to submit to a technical journal that does not emphasize "studies with general implications for atmospheric science." In addition to this very general comment, several general comments and specific comments are outlined below. Technical comments, however, are omitted in this initial review.

General Comments:

Page 5, line 15: In general, the reviewer feels that the authors did not take advantage of the microscope in their experiment. Do the authors know the contact angle of water on their Raman substrate? If so, the physical growth factor of a spherically equivalent drop could be determined; this measurement would greatly increase confidence in the spectroscopic growth factor measurement. A physical growth factor measurement could also help explain the low-RH results in Figure 4b, where it is unclear if OA shrinks when it transitions from its dihydrate form to it anhydrous form.

Page 7, Line 1: Do the authors have an image of the effloresced particle to affirm that the ν(SO42-) peak shift corresponds with a hygroscopic phase change?

Page 8, Line 2: Since multiple components are crystallizing, can the authors take advantage of the high spatial resolution of Raman microscopy to tell if there is a spatial distribution of chemicals? These results would explain if components are efflorescing in specific order and, consequently, if effloresced components are heterogeneously nucleating other components.

Specific Comments:

Page 3, Line 16: Is there a reference for the reactions of organic acids with mineral salts, chloride salts, nitrate salts, and ammonium and amines?

Page 4, Line 21: What was the dry diameter of these particles?

Page 5, Line 8: What is the numerical aperture of the 50x objective?

Page 5, Line 12: Why was 40 minutes chosen for the equilibration time? Do the authors have spectral evidence of this equilibration (perhaps from the area under the OH water peak?)

Page 7, Line 3: It is unclear from the text if 874 cm-1 corresponds to only HSO4- or both HSO4- and HC2O4-. The reviewer suggests this be clarified.

Page 9, Line 11: The statement “likely due to drop size, substrate, and experimental methods” is vague. Can the authors be more specific about the cause of OA’s high ERH in this study?

Page 9, Line 16: Do the authors believe that 77% is the true ERH of OA, or that heterogeneous nucleation is occurring? If the latter, the reviewer suggests that the authors refrain from using the phrase “ERH of OA” hereafter.

Page 12, Line 8: Do the “rapidly-dried” particles look physically different than the “regularly-dried” particles? Furthermore, do the rapidly-dried particles have a different ERH? This could help discern the underlying mechanism of efflorescence.

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