

Interactive comment on “Reactive processing of formaldehyde and acetaldehyde in aqueous aerosol mimics: surface tension depression and secondary organic products” by Z. Li et al.

Anonymous Referee #4

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Overall Comment and Recommendation:

This manuscript is very well-written, concise, and describes the research problem well (i.e., the role of the reactive uptake of carbonyl-containing VOCs [cVOCs] by wet aerosols in reducing surface tensions by SOA production). The combination of the aerosol surface tension and aerosol chemical ionization mass spectrometry (Aerosol-CIMS) measurements is well suited for this study. The major finding that was found was that mixed cVOCs in wet ammonium sulfate aerosols led to surface tension depressions that were in excess of additive models based on single-species isotherms. The results of this study are certainly important to the literature and to the research

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community that is currently examining the aqueous aerosol processes that lead to SOA.

Before publication, I kindly ask the authors to address two issues I found when reviewing this manuscript:

1.) Do you have any concerns with the high concentrations of these cVOCs (i.e., 0.018–0.54 M) that you used to examine this process? Maybe certain reactions are favored that are not representative of atmospheric aerosol processes due to these high concentrations employed in this study? Should any caution be made to the readers of your manuscript about this issue?

2.) With the volatilization step in your Aerosol-CIMS technique, do you fear that there could be the potential of chemical artifacts dominating your mass spectra? Thus, in these mass spectra are you observing what is actually present in the aqueous solutions?

Additionally, do you have any concerns about the ions you interpret as SOA products being artifacts of the ionization? One thing I worry about is these mass spectra are very complicated (without any upfront separation of the chemical mixture) to interpret, especially since ions produced by H_3O^+ reagent ion chemistry likely produces several fragment ions from the parent ion. How do you know some of the ions you suggest as products of these reactions are not just fragment ions of the H_3O^+ reagent ion chemistry?

These issues come up for me since: (1) you don't have high resolution MS data to know the true elemental compositions of these ions; and (2) since it was difficult for you to propose reasonable reaction routes. In the case of the latter, as an example, you found it difficult to explain the production of some of the tentatively identified organosulfates. As the authors indicated in the Discussion section, these could have formed due to the atomization process. I agree with this especially since you subsequently heat up the aerosol. Could this remove enough water to favor sulfate esterification? There is now some debate developing within the community that surfactants, such as organosul-

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fates, might help to remove water from the system to help enhance the organosulfate reactions (or other condensation reactions).

Let me just state, I don't think the authors were careless here at all. They were very cautious/careful in stating in several places throughout the text that these are tentative proposals for the structures in Tables 2-5. I think without accurate mass data (which confirms elemental compositions of the ions you propose), MS/MS data (which provides ideas on functionality of these compounds), and even authentic standards, it will be difficult to validate any sort of detailed reaction pathway that seems to be occurring based on the surface tension data. I think the surface tension data provide some credibility to the chemical characterization results. I think the authors might want to be clear on this by saying in the Discussion or Conclusions section that further work is needed to really know the detailed reaction pathways that explain these compounds they seem to be observed by Aerosol-CIMS. Even though the authors say "tentative structures" in the text, they might want to also consider adding the word "tentative" in their Table headings, especially since many readers these days don't carefully read all of the text and usually go right to figures and tables to understand the results of a study.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 19477, 2011.