

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 #2

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General Comments

This study tests if surface-active compounds can be produced directly from volatile organic compounds in water. Li and coauthors approach this problem using two of this class of compounds, formaldehyde and acetaldehyde, as well as their mixtures with methylglyoxal. Experiments were designed to study their possible condensation in pure water and in 3.1 M ammonium sulfate solutions. The range of concentrations studied was 18–540 mM for acetaldehyde. The total organic concentration of mixtures with methylglyoxal ranged from 200 to 2000 mM. The time scale of the experiments was 1 day and the initial pH was between 2.7 and 3.1. Surface tension decreases for

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higher total organic concentration following a Szyszkowski–Langmuir fitting with minimum and maximum discrepancy of 8 and 24%, respectively. The manuscript indicates the presence of oligomeric reaction products, in agreement with other publications studying aldehyde condensation reactions. Oligomers are thought to have originated via hemiacetal and aldol condensation reactions. The results suggest that these two highly volatile organic compounds produce surface-active oligomers. Possible chemical structures are proposed based on aerosol chemical ionization mass spectrometry analysis. Some data interpretation will need to be reconsidered to improve this already well written manuscript that provides interesting results to the audience of ACP. Some questions and minor comments to improve the manuscript should be addressed. Noteworthy, no surface tension change was observed in the case of formaldehyde in water and a better theoretical justification is needed for this observation. The experimental section does not currently show the concentration of formaldehyde used. A better assignment of some of the products reported is necessary. After all these observations are answered a general reassignment of some peaks will be possible. Discussion and conclusions sections could be affected and may need to be edited. The confirmation of assigned peaks should be the focus of future studies.

Specific Comments

Page 19478

Line 12 (Abstract): The statement about identifying a hemiacetal sulfate ester for the formate–ammonium sulfate system does not seem to belong to the abstract. Although the word “tentatively” is used, based on the results section of the manuscript that reports products that are not completely identified, this statement should be reserved only for the discussion section. Further input on this issue is given below.

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Line 13: The manuscript will benefit if an explanation for the concentrations used is given. This could be included in the introduction or in the discussion section. In addi-

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tion, there is no indication of the concentration of formaldehyde used in the experimental section.

Page 19481

Lines 10-15: A control experiment using freshly prepared solution should be included in the supplement and cited here. In addition, a calculation should prove the statement that < 3.5 s is a shorter time than required for reaction to occur at $135\text{ }^{\circ}\text{C}$. How long does it take for product formation to occur?

Lines 13-15: Unify the way of expressing surface tension changes. For example use the corresponding percentage change after the reported values for acetaldehyde "(20.6%)" and the measured change followed by "(9 %)" for formaldehyde.

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Results

Line 16: Why is the concentration of formaldehyde in Figure 1B studied up to $0.20\text{ mol C/kg H}_2\text{O}$ while acetaldehyde concentration was 5-times larger in Figure 1A? Would you expect to see any change in surface tension at larger formaldehyde concentration in water? A dashed line may be used to distinguish that formaldehyde-water is not a Szyskowski-Langmuir fitting in Figure 1B.

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Line 19-25: What is the concentration of formic acid (impurity) in the stock solution? What is the concentration of this impurity in the dilution of Figure 5? A typical 37% formaldehyde solution has $< 0.03\%$ formic acid. Peaks at m/z 81.7 and 208.7 amu appear to be too intense (Figure 5) to be due to a very small impurity of formic acid. It is mentioned in the next page that the most common stabilizer in 37% formaldehyde water solution from Sigma-Aldrich is Methanol ($\sim 15\%$). A better justification of the peaks and/or a clarification of the composition of the reagent are necessary. The assigned hemiacetals clusters (peaks at m/z 223.3, 291.1, 325.5 amu) are of very low intensity in

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the mass spectrum of Figure 5. Are they important to the composition of the mixture? Low intensity peaks at 273.8, 291.1, and 304.7 amu appear to be related to peaks at 176.7, 193.8, 208.7 amu. There is a difference of 97, 97, and 96 amu. How was the spectrometer calibrated? What masses were used for calibration? Is it possible to have a >0.5 Da amu error compared to previous work published by this group?

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Lines 9-12: It is not possible to distinguish if the peak at 193.8 uma was assigned correctly. A blow up is needed to distinguish if there is a satellite peak (+2 uma). Based on the spectrum shown in Figure 5 the species of 176.7 amu appears to be $\text{C}_6\text{H}_9\text{O}_6$ - instead of $\text{C}_2\text{H}_7\text{O}_6\text{S}-\text{H}_2\text{O}$ because there is no satellite peak. Otherwise a blow up of this peak will also be needed. This issue is critical to the discussion and the output will considerably affect the abstract by confirming or rejecting the assignment.

Lines 13-14 (also applies to for page 19486, lines 16-17, and page 19487, line 1): A short statement should be included in the conclusions to summarize that the chemical structures and formation mechanisms of several products are unknown and that this task will require mechanistic studies.

Page 19486

Line 6-8: Figure 7 does not have any label to indicate a peak at 98.4 amu. It is listed in table 4. In addition, Table 4 is too small and the font size should be larger. Preferably use the font size of Table 2 for all tables.

Line 26: Could other possible assignments for peak at 314.3 amu be two formic acid molecules, one sulfate, clustered with iodide?

Line 28: The peak at 194.6 uma listed in Table 5 is absent in Figure 8. The same satellite peak analysis would apply here to confirm or discard the formation of possible products. Consider rewording the beginning of the sentence. It is likely that the supplement will be unnecessary if this species is for example $\text{C}_6\text{H}_{10}\text{O}_6$ in its undissociated

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form.

Tables 2 and 3 and Figures 5 and 6: Why there is no peak for sulfate or sulfate-iodide cluster? What were the conditions of the mass spectrometer? Can they be included in the experimental section or in the supplement?

Figures 2A and 4A-D: Figures will look considerably better by removing the exponent and using a 10^2 multiplication factor in the respective concentration label. Fig. 2A is too small and it is very difficult to read it.

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