Aqueous phase behavior of glyoxal and methylglyoxal observed with carbon and oxygen K-edge X-ray absorption spectroscopy.

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We thank both reviewers for their work and constructive comments. Below we provide our responses to each comment in a point-by-point fashion. The reviewers' comments are reproduced in *italics*, our responses in **bold** and quotes from the revised manuscript in **red bold** font.

Anonymous reviewer #3

Line 7: The abstract suggests that the X-ray spectra of methylglyoxal imply the presence of the dihydrate form, but there is little evidence of this form according to Figure 5. Any dihydrate transitions appear to be buried in the ionization peak. I think the data does not imply the dihydrate's presence or absence.

Authors' reply:

Thank you very much. Indeed the statement that dihydrated form of methylglyoxal is present in the solution cannot be observed in Fig. 5 and is based on the weak C=O signal of our spectra and the results of previous studies. We therefore rephrase the sentence "This implies . . . monohydrates" (lines 7 and 8) to:

"The relatively low intensity of C=O transitions implies that the monohydrated form of methylglyoxal is not favored in the solutions. Instead, the spectral intensity is stronger in regions where products of aldol condensation and enol tautomers of the monohydrates contribute."

Line 10: Since organic - inorganic interactions have been observed for these species by other methods, a statement about a lack of method sensitivity would be more appropriate than one about the weakness of these interactions. They are evidently strong enough to greatly increase measured Henry's law coefficients. (Kampf, Waxman et al. 2013 [2])

Authors' reply:

Thank you very much for the suggestion. We rephrase the sentence: "indicating that the organic–inorganic interactions at the studied concentrations are not strong enough to affect the spectra in this work" (lines 9 and 10) to:

"indicating that the XAS in the near-edge region is not very sensitive to these intermolecular organic–inorganic interactions at the studied concentrations".

Figure 3: Are the decreases in the C-OH ionization peak sizes caused by salt addition evidence of a chemical change? If so, this would be the opposite of what was observed for Na_2SO_4 *by Yu et al. (Yu, Bayer et al. 2011 [12]). Could the authors address this?*

Authors' reply:

Thank you very much. As we explain in the paper, since we cannot precisely determine the thickness of the liquid layer, we cannot directly compare the intensities of the spectra between different solutions. The overall signal in C 1s region would actually be expected to increase upon addition of salt to the solutions due to ionization of close-lying L-shells of Cl and S. The cross-sections of these orbitals are significant compared to the C K-shell in this energy range [11]. However, a change in the hydration state would be seen as new spectral features as predicted by the calculations. The following text is added in line 165:

"According to the calculations, a change in hydration state upon addition of salts towards mono or dehydrated form of glyoxal would have shown up as new spectral features around 286–287 eV, which is not observed."

Figure 4: Are the decreases in the size of the A and B peaks caused by salt addition (especially for NaCl) evidence of a shift away from enol forms?

Authors' reply:

To clarify this, we modify the sentence "Here we observe a small change in the relative intensities between the peaks A and B in pure methylglyoxal solution compared to solution spiked with Na_2SO_4**, but the shape of the background also changed in the spectrum and thus these changes remain inconclusive" (lines 225–227) to:**

"Here we observe a small change in the relative intensities between the peaks A and B in pure methylglyoxal solutions, compared to solutions containing Na_2SO_4 and NaCl. In salt-containing solutions, the relative intensity of peak A ($CH_{2(enol)}$) becomes slightly smaller than for peak B or the absorption edge ($\sim$ 291 eV). Considering that other hydrated forms of methylglyoxal contribute to the spectra in the energy range of peak B, this can indicate smaller abundance of the enol form compared to other hydrated forms in salt solutions. However, the addition of salts changes the shape of the background due to close-lying ionization continua of the Cl and S L-shells [11], and thus these changes remain inconclusive."

Line 274: This sentence states that C=O and C-H functional groups are found in the dihydrate form of methylglyoxal. For C=O this statement is false.

Authors' reply:

We agree that this should be corrected and we modify the sentence "They are found in the monohydrated and dihydrated forms of the compound and also from products of keto–enol tautomerism followed by aldol condensation reactions" (lines 274–275) to:

"They are found in the unhydrated and monohydrated forms of the compound and also in products of keto–enol tautomerism followed by aldol condensation reactions."

Technical Corrections:

Table 3: Why are excitation energies not listed for dehydrated methylglyoxal? The text states that they were calculated in line 136.

Authors' reply:

We agree that the calculated energies of dihydrated methylglyoxal should be discussed. We add in the caption of Table 3 the following sentence:

"For dihydrated methylglyoxal, our calculations did not identify any C 1s-π* excitations in the energy range of the recorded spectra and only the calculated IP are presented below."

Line 159: Are these differences of 0.1 – 0.2 eV significant, given that they are "within the photon energy resolution"? Or are they just random variation? If random, Table 4 should be moved to the SI section or eliminated from discussion.

Authors' reply:

We agree that Table 4 could be placed in the SI. While the values are close to experimental accuracy, they show a systematic shift of 0.1 eV when salts are added. We move Table 4 to the SI along with the text "The absorption edges . . . concentration" (lines 158–161). We replace the above sentences with the following text:

"The location of the absorption edge of aqueous solutions of pure glyoxal was at 289.6±0.1 eV (0.5 M) and 289.5±0.1 eV (1 and 2 M) and upon addition of inorganic salts, the absorption edge energy systematically increased by 0.1 eV in all cases. All values are however close to the experimental accuracy. All absorption edge energies can be found in the Supporting Information (Table S1)."

In Table 5, the functional group entry for peak B should also be labelled "enol", if I understand Figure 5 correctly. Also, no oscillator appears to line up with the C3 peak, so the origin of its assignment in Table 5 is unclear.

Authors' reply:

Thank you for your suggestion. To be consistent with the notations in Figure 5, we change the labels of the peaks A and B in Table 5 to "$CH_{2(enol)}$" and "C-OH$(CH_2)_{(enol)}$", respectively.

Figures 6-8 have two deep pink lines in the legend that look identical, but not in the figure itself.

Authors' reply:

Thank you for bringing this to our attention. We replace the purple dotted line of the legends in Figures 6, 7 and 8 that concern solutions with Na_2SO_4 with a purple dashed line which is more readily distinguished.

Line 276: This sentence calls 1 – 2 M "low solute concentrations," which is somewhat misleading. It seems like the issue is rather the large signals of water.

Authors' reply:

We agree that this should be modified. We rephrase the text "The oxygen K-edge spectra were similar to water, due to low solute concentrations and we only observed small changes in the case of mixtures with Na_2SO_4" (lines 276–277) to:

"The oxygen K-edge spectra for aqueous solutions were similar to

those of pure water. Organic and inorganic solutes did not remarkably modify the water network at the studied concentrations, except in the case of Na_2SO_4 . . . ."

Anonymous reviewer #4

In the introduction, there is no mention of relevant literature with regards to characterizing molecular structure and electrolyte-nonelectrolyte interactions in relevant systems. This is actually partially covered later in the discussion, but the work should be placed in context of prior art up front.

Authors' reply:

Thank you very much for your suggestion. We add in line 46 of the Introduction:

Recently, XAS has been used to study both solute–solute and solute–solvent interactions, including e.g. investigation of structure of methanol–water mixtures based on C and O K-edge XAS [6], quantification of sulfuric acid–water interaction using O K-shell and S L-edge XAS [8], and studies of ion-water interactions [10, 7].

These ionic strengths are quite low by atmospheric standards so there should be a caveat regarding the limitations of this study.

Authors' reply:

Thank you very much, we agree that this should be discussed. We add the following text in section "Atmospheric implications" and line 258:

The studied concentrations of glyoxal, methylglyoxal and inorganic salts are higher than their typical concentrations in cloud water, which have been estimated to be about five or more orders of magnitude lower [1, 5, 4, 9, 3]. Droplet evaporation, however, can lead to highly concentrated and supersaturated solutions, altering the chemical and optical properties of aerosol particles [3].

The authors introduce the "NEXAFS" later in the manuscript as if it were a different technique, but it's not clear that this is actually different from the technique used by the authors referred under broader term, "XAS".

Authors' reply:

Thank you very much for pointing that out. To avoid any confusion, we modify the sentence "applying near-edge X-ray absorption fine structure (NEXAFS)" in line 198, to:

"applying XAS in near-edge region"

and we replace the term NEXAFS in line 200 with the more general term "XAS".

Apart from studying water (as cited by the authors), the O K-edge has generally not been found to be useful for characterizing specific structures of organic compounds (apart from indicating total oxygen content) in past work, and also seems to be the case here. The O K-edge does not really make a contribution to the main findings of the manuscript and should probably be summarized in a few sentence and removed otherwise (or placed in supplemental).

Authors' reply:

Thank you very much for the comment, we agree that the importance of the O 1s edge measurements in general was not clear. We believe that the results for O 1s are important from the perspective of both the solute and solvent. This aspect is now emphasized also in the introduction where we include recent studies utilising also O 1s XAS (cf. response to the first comment of reviewer #4). To clarify the significance of O 1s XAS results in our work, we replace the text "We do not observe any relative changes in spectral features as a function of concentration of the organic compound" in lines 237–238, by:

"This is most likely due to oxygen from solute molecules contributing mainly to the absorption above 536 eV, but for 2 M solutions of glyoxal and glycerol, there is also a small increase in the intensity after the pre-peak".

We also replace the first paragraph on page 14 "In conclusion, O K-edge spectra were found to be sensitive neither to the organic component at studied concentrations nor to addition of NaCl. However, addition of Na_2SO_4 affected the spectra as they started to resemble more pure Na_2SO_4 solution without any organics. Thus, no Na_2SO_4–organic interaction can be confirmed using this method" (lines 250–252) by:

"In conclusion, addition of organics and NaCl do not modify the overall structure of the measured O 1s XAS spectra. However, the presence of strongly hydrated SO_4^{2-} anions leads to an observable effect on both the pre-peak and main peak regions. The effect on the shape was the same regardless of the identity of the organic compound in the solution, and we were not able to confirm any Na_2SO_4–organic interaction in the present study."

and we add in line 278 the sentence:

"The change in the shape of the spectra does not depend on the organic component. Thus, based on our study, the salting effects in water solutions of glyoxal and methylglyoxal upon addition of Na_2SO_4 would originate from changes in the structure of water by SO_4^{2-} anions, rather than interactions with the organic."

Table 4 also seems superfluous and can be moved to the supplemental since it can be summed up concisely in the text. **Authors' reply**:

Thank you for the suggestion. We move the table 4 to the Supplementary Information along with the text "The absorption edges . . . concentration" (lines 158–161). We replace the above sentences with the following text in the main manuscript:

"The location of the absorption edge of aqueous solutions of pure glyoxal was at 289.6±0.1 eV (0.5 M) and 289.5±0.1 eV (1 and 2 M) and upon addition of inorganic salts, the absorption edge energy systematically increased by 0.1 eV in all cases. All values are however close to the experimental accuracy. All absorption edge energies can be found in the Supporting Information (Table S1)."

Can the authors elaborate on how the measured absolute intensity or optical density calibration is used in the experiments?

Authors' reply:

Thank you for the comment, we agree that text related to spectral intensity and calibration was not sufficiently clear. We therefore add the symbol I_0 in line 74:

"During each measurement the incident radiation I_0 was monitored with a gold mesh placed before the liquid cell, so that the flux variations (<1%) due to the top-up mode were removed".

We also modify the text "The thickness of the liquid layer (x) was not precisely estimated. In order to avoid additional uncertainty on our results, the intensities of the XA spectra are given in arbitrary units." (lines 78–79) to:

"The thickness of the liquid layer (x) was not precisely determined, and thus we give the intensities of the XA spectra in arbitrary units (arb. units)."

In addition, we change the word "calibration" in line 93 to "energy calibration" and we rephrase the "ionization edge" in line 97 to "absorption edge".

The way the units is presented is not entirely clear since the authors talk about measured beam intensity and absorption intensity (abs. = absorbance units?). Can authors clarify in one of the Figure captions?

Authors' reply:

Thank you for bringing that to our attention. As explained in our response to the previous comment, the intensities of XAS are given in arbitrary units. We correct the typo in all the figures and relabel the y-axis from "abs.units" to "arb. units".

The inline equation at the top of pg. 5 should be the Lambert formula since Beer's contribution comes from introducing the molar or number concentration to the linear attenuation coefficient of the material.

Authors' reply:

Thank you. We change "Beer-Lambert formula" in line 72, to "Lambert formula".

The authors seem to use the term "salting in/out" to generally refer to non-ideal electrolyte-nonelectrolyte interactions instead of the consequence of their interactions, unless they are expecting a specific type of change in the spectra that was not made explicit in the manuscript.

Authors' reply:

We agree that we should define the salting in and out phenomena and describe how these could affect our spectra. We therefore add in line 23 of the Introduction section the sentence:

"Salting in and out effects refer here to the increase or decrease in the solubility of the organic solute (glyoxal and methylglyoxal) in water due to the presence of a co-solute, in this case an inorganic salt (NaCl, Na_2SO_4), in the solution."

And we modify the text "in both carbon and oxygen K-edge spectra, we did not observe any effects . . . demonstrated by Kurtén et al. (2014)", in lines 279–281, to:

"In the carbon K-edge spectra we did not observe significant changes with addition of salts. Our observation excludes any significant organic-

inorganic interactions that would change the abundances of different hydrated forms and does not reveal appearance of new species from such interactions. However, XAS might not be sufficiently sensitive to see additional changes to the hydrate formation equilibrium, as e.g. demonstrated computationally by Kurtén et al. (2014)."

Fig. 3: One of the vertical lines appear red while the other appears purple. It should be specified that it's these vertical lines that are scaled according to oscillator strengths and not the spectra (which are also drawn as lines).

Authors' reply:

We change the sentence "The lines have been scaled according to the calculated oscillator strengths" in captions of Fig. 3 and Fig. 5 to:

"The vertical lines have been scaled according to the calculated oscillator strengths."

Fig. 5. Since the overall fit is shown, can the authors display all the curves that are fitted (not just the Gaussian peaks)?

Authors' reply:

Thank you for the suggestion. We add in Fig. 5 the three curves that we fit in our spectrum at energies above 290 eV.

The authors talk about "IP of the C=O sites" (and for other groups) but would maybe more naturally be referred to as the "IP of the C=O moiety" in this context?

Authors' reply:

We change the word "sites" to "moieties" in lines 134, 135, 144, 145, 146, 147, 204 and in Table 3.

"SCF" is not defined.

Authors' reply:

Thank you, we agree that SCF should be defined. We add the definition in line 109:

"The core ionization and excitation energies were evaluated within the ΔSCF (Self-Consistent Field) method . . . ".

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