Reviewer #1

We kindly thank this reviewer for his or her helpful insights. We address specific points below:

In some places, the argumentation or inferences are however somewhat ambiguous and the authors may want to clarify their points. Some examples of this are:

1) page 553, line 17 "The surface tension depression of an aqueous mixture containing methylglyoxal and glyoxal, which undergo similar aqueous-phase chemistry, was successfully modeled using a sum of the individual organic contributions to surface tension, even though cross-reactions were found to be responsible for a large portion of the organic mass present (Schwier et al., 2010)."

To me this sounds like the good performance of the model is purely coincidental, since it is not taking products of a major reaction into account?

Based on the structure of the oligomers formed in this system (e.g. Sareen et al., 2010; Schwier et al., 2010) it seems reasonable that in a population of oligomers formed by methylglyoxal and glyoxal self- and cross-reactions, the surface tension depression is roughly proportional to the hydrophobic surface area, which is contributed solely by the methylglyoxal free methyl groups. We have added this commentary to the manuscript.

2) page 555, line 17 "These concentrations were used to determine the mass wt% of each component, and by assuming an average molecular weight of the organics, the relative amount of each species at a specified total organic concentration was calculated."

This sounds fairly straight forward, but from this description I have trouble reproducing the exact compositions of the mixtures studied. This would be critical in case one would be interested in using the data for exploring different functional relations than the ones presented here by the authors. For example, it is not clear to me why it was necessary to assume an average molecular weight? Maybe an example of calculations could be given in the supporting material.

We have rewritten this section to make it clearer to the reader: "Ambient in-particle concentrations of methylglyoxal, glyoxal, oxalic and succinic acids were taken from Kawamura and Yasui (2005), and acetaldehyde and formaldehyde in-particle concentrations were used from Grosjean (1982); all concentrations (ng m^{-3}) are shown in Table 2. These concentrations were used to determine the in-particle mass wt% of each component. Assuming a specified total organic concentration (i.e., 1 M) and an average molecular weight of all the organic species, the relative mass amount (or volume amount) of each species was then calculated based on the mass wt%."

3) page 561, line 17 "The Schwier2010 model assumes that each organic is entirely present at the droplet surface and will depress the surface tension to its maximum capability, while in actuality, the surface composition will be a mixture of the different organics with the excess organic in the bulk phase. Each organic has a different surface activity, so the actual surface tension of the

mixture is higher than the idealized Schwier2010 model. However, at lower total organic concentrations, this issue should not be important."

I'm not sure what is meant by the statement regarding the Schwier2010 model assumptions. That the surface is fully saturated with the organic, or that the organic is only in the surface and not at all in the bulk? How can this assumption be inferred from the model? Do the authors have any suggestion for the concentrations where this situation would be the case, that is, what is the validity of this assumption for the studied systems?

We have changed the wording of this statement to be clearer. Put simply, the Schwier2010 model did not take surface competition into account. The Henning model scales the possible surface tension depression of each species in terms of the total organic content present. In the data shown here, the complex organic mixture (Figure 7) is the most striking representation of the overestimation of the Schwier2010 surface tension model.

4) page 563, line 15 "Future work must be performed to determine how best to model cross-reactions between structurally dissimilar molecules. Thermodynamic models could also be used to describe complex organic-inorganic systems; however, new methodologies must be developed to better describe organic-inorganic interactions, and additionally, many thermodynamic parameters for atmospherically relevant organic species are unknown and must be determined."

I do not doubt that the authors know what is behind this statement, but the presentation is wavering. I suggest the authors clarify this section and specify their points, or simply leave it out.

We thank the reviewer for this point. This passage has been cut from the revised manuscript.

Specific comments:

1) I appreciate the effort taken to make surface tension measurements for a comprehensive number of solutions. However, there are not always that many measurements presented for different concentrations of each of the mixtures, in particular not enough to give a clear impression of the surface adsorption isotherms. Could the authors elaborate on what has determined the investigated concentration ranges?

In Sect. 2.1, we state "Most solutions were tested at atmospherically relevant concentrations and beyond (≤ 1 M total organic) in order to elucidate the behavior of the mixture as a function of organic concentration; however, Zhang and Anastasio (2003) was used as a basis for atmospherically relevant amino acid in-particle concentrations." Of course, solubility limits were also a factor for amino acid concentrations for mixtures. For the ternary mixtures, we used available data from Li et al. (2011). We have added this information.

I also think the value of the presented data set would greatly increase if the solution compositions could be clearly, readily, and unambiguously assessed. For example, in Table 1 – when the concentration of a component is variable, what is the range? And looking at Table 2 - how does one get the aqueous concentrations, what is the water content?

We have added the variable concentrations into Table 1 when applicable, and added the following text to the caption of Table 1: "Experimental mixtures studied in this work. All concentrations are given in molarity (M). The symbol "v" indicates that the concentration of the organic was variable throughout the experiment. In Mixtures #14-16, the total organic concentration was either 0.5 or 0.05 M; in Mixture #17, the total organic concentration ranged from 0-1 M. The k parameter was calculated using Eq. (6), as described in Sect. 3.5. See text for more details." We also have specified the concentration range of the variable component within the text, in the appropriate sections of the results. For the ternary mixtures of acetaldehyde/formaldehyde/methylglyoxal, we refer the reviewer to Li et al. (2011) for more specific information about the concentrations.

In Table 2, the intention was not to replicate the aerosol composition of the previous studies, but rather to use these in-particle concentrations to determine the mass ratio of each organic. The mass ratio was used to keep the relative amounts of the organics at atmospherically relevant proportions. We have clarified this point in the text.

It would also be most useful if the density data would be available for the solutions, perhaps in the supporting information? How accurately was it determined?

In Sect. 2.2, we state, "The density of each solution was determined in triplicate using an analytical balance (Denver Instruments)." Densities were determined to the 4th decimal point. Since solution density is not necessary for modeling surface tension depression (but rather for interpreting the raw PDT data) we choose not to include this very large amount of data in the manuscript. Solution density ranged from 1.1858 g cm^{-3} to 1.2078 g cm^{-3} for ionic solutions and 0.9862 g cm^{-3} to 1.0118 g cm^{-3} for aqueous solutions.

2) On pg. 563, line 7, the authors state "It appears that separately accounting for cross-reaction species in surface tension models is unnecessary for reactive systems consisting of structurally similar organic molecules."

This is as such an important result, but I do not see any evidence presented to show that these cross-reaction products are actually present in the solutions investigated, although it is certainly possible. Was this tested for the solutions in question in the present work? If not, why? Could a simple test be made for just a few of the present solutions? This is a central issue to the work, with regard to the title stating that the mixtures are reactive. I also cannot see from the data and argumentation at hand, why the observations on pg. 563, line 7 could not just as well be due to organic-organic interactions in solution?

We have previously studied similar bulk organic mixtures of methylglyoxal and glyoxal, and acetaldehyde, formaldehyde, and methylglyoxal with Aerosol-CIMS (see Li et al., 2011; Schwier et al., 2010) and found that cross-reaction products between carbonyl species were prevalent. De Haan and coworkers investigated SOA formation of glyoxal and methylglyoxal with amino acids and amine functional groups and detected the presence of high molecular weight oligomers and nitrogen-containing compounds (De Haan et al., 2009a,b,2010) showing that most of the systems studied in this work involved reactive species.

In line 14, also pg. 563, the authors state “because intermolecular reactions between the carbonyls and amino acids are not well represented within the model”. I wonder how does the model represent any chemical reactions? In my understanding, all models used are equilibrium models. Maybe this could be clarified?

We thank the author for raising this point. Both the Henning and Schwier2010 models are based on the S-L equation, which is a semi-empirical model based on a Langmuir isotherm. Chemical reactions between different organic species are not taken into consideration. We have adjusted the text to read, “Model performance is generally better for reactive systems consisting of structurally similar organic molecules with moderate surface tension depression. For carbonyl-containing species, cross-reaction products appear to have similar average surface-activity behavior to the reactants (possibly due to similar hydrophobic surface areas of the reactants and products), which leads to systems that can be well described by the S-L equation and parameters solely based on the reactants (Schwier et al., 2010). However, if cross-reaction products have very different properties from the reactants, additional terms may be needed to describe surface tension depression in the reactive mixture. Neither the Henning model nor the Schwier2010 model characterizes the mixtures of methylglyoxal or glyoxal with amino acids well. This may be because the Mannich reaction products may have significantly different surface-bulk partitioning and surface-activity behavior than the reactants due to a large change in hydrophobic surface area, or because intermolecular reactions between the carbonyls and amino acids are not well represented within models based on the S-L equation.”

3) I also do not see how the models presented show that it is not necessary to account for these potential cross-reaction products and their surface tension effects, if they are present. The models investigated do not perform all that well against the data, except in a few selected cases. This is an important result in itself. I am fully aware of the challenges involved in obtaining this with almost any model, and that the ones presented in the present work may do as well as any, but I do not think from the data presented that the case is closed. Also, since the authors do not present any actual attempts to explicitly include effects of cross-reaction products, how can the reader be convinced that this would not improve the performance of the model?

Please see our response to the previous comment. We have changed the wording in this passage.

Based on what criteria can the authors say that it performs adequately (pg. 562, line 24)? And for what purposes? What are the implications for the fundamentals of surface active aqueous aerosols from the findings regarding the model performances for the presented data? On pg. 562, line 26, the authors state that “The Henning model accounts for the finite number of surface sites at the gas-liquid interface that the surface active organics can occupy through the weighting term”. In my opinion, this would require an additional assumption that the molecules are oriented parallel to the surface, rather than standing up on the surface, which may not at all be the case. Maybe this could be clarified.

These models are able to describe the experimental data well for most mixtures containing structurally similar molecules, using the goodness-of-fit (χ^2) term as an indicator for model performance. We have changed the language here slightly to say that they perform “similarly” and allowing the reader to decide if model performance is adequate for a given application.

The Henning model accounts for surface competition by scaling the possible surface tension depression of each species in terms of the total organic content present by using the weighting term (updated as ψ in the manuscript); we have changed the text in the manuscript to be clearer.

On pg. 559, the authors state "The over-estimation using salt parameters by both models indicates that any reaction products forming between acetaldehyde and leucine must be less surface active than the contributions of the individual organics." Couldn't this also be explained by competition for surface sites?

The Henning model already takes surface competition into account via the weighting term (updated as ψ in the manuscript).

One wonders what would be the response of the model performance to changes in concentration, or to moderate changes in relative organic composition? Do the authors believe these models are sufficient for atmospheric process level modeling? Why/not? Are there any alternatives? What would be the effect of using the recommended parameterizations for Köhler calculations? On pg. 563, line 22 the authors give a recommendation of the Schwier2010 model, but do not specify for what purposes? I am not convinced of its general applicability to atmospheric conditions, which may also not be intended by the statement, and a recommendation could benefit from being accompanied by a specified set of conditions or concentration ranges.

This study focuses on aerosol conditions (high salt content, low pH and complex organic mixtures) and provides experimental surface tension data at these conditions. While these conditions are not appropriate for Köhler Theory (which describes the condition of particle activation), this study does provide insight into the presence of organics at the gas-aerosol interface, important for both heterogeneous chemistry and ice nucleation (McNeill et al., 2013).

We have added emphasis throughout the manuscript to the importance of surfactant films on aerosols for heterogeneous chemistry and ice nucleation. We have adjusted the discussion to be clearer and better describe our recommendations for modeling aerosol surface tension and modeling aerosols at particle activation conditions. It now reads, "The compositions of the experimental systems described within this work mimic aerosol conditions near 100% RH (near-saturation salt concentrations). For aerosol systems at higher relative humidity (> 100% RH), i.e. those at the condition of particle activation, the use of salt parameters may be inappropriate due to the higher water content at this point. Based on our results for organics in aqueous systems (Fig. 1, S1-3), to describe particle activation, if the dilute salt concentration is known, the Tuckermann approach (Eq. 5 or 6) is preferred; if the ionic concentration is unknown, we recommend the use of the Henning model with water fit parameters.

For aerosol conditions (up to 100% RH), we recommend the use of salt fit parameters in the Henning model (Eq. 3) over the Tuckermann approach, which uses water fit parameters (known more readily than salt fit parameters) but also requires an additional empirically determined parameter, k. The Henning (with salt parameters) and Tuckermann models provide similar modeling fits and goodness of fit (χ^2) values, yet the Henning model is overall a simpler and more physical approach. We recommend that the Henning model, with experimentally *determined salt parameters, be used to incorporate implicit salt effects on complex mixtures in future aerosol surface tension studies and predictions of surfactant film formation in aerosols."*

4) On pg. 563, line 24: I'm surprised the authors do not consider the parameter k from Eq. 5 to carry any physical significance, and I would tend to disagree, but maybe this could be clarified?

We have changed this text to read "For aerosol conditions (up to 100% RH), we recommend the use of salt fit parameters in the Henning model (Eq. 3) over the Tuckermann approach, which uses water fit parameters (known more readily than salt fit parameters) but also requires an additional empirically determined parameter, k."

5) As a minor comment, it can be confusing that the authors use the same character for the goodness of fit and for the compound weighting factor in the Henning model.

We chose χ *and* χ^2 *for these two parameters based on the original work in each case, but we agree with the reviewer that this leads to some ambiguity. We now use* χ^2 *to indicate the goodness of fit and* ψ *to describe the weighting term of the Szyszkowski-Langmuir equation for clarity.*