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Atmospheric
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Interactive comment on "Modeling the surface tension of complex, reactive organic-inorganic mixtures" *by* A. N. Schwier et al.

Anonymous Referee #1

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General comments:

In the manuscript "Modeling the surface tension of complex, reactive organic-inorganic mixtures", Schwier et al. present surface tension data for a number of multicomponent organic aqueous mixtures in the presence high inorganic salt concentrations and investigate the performance of several surface tension models in describing the observed behavior. I am very happy to see more and diverse surface tension data for atmospherically relevant aqueous mixtures presented to the scientific community, and to see an exploration of models for parameterizing the surface tension variation with aerosol composition. Both aspects are certainly greatly needed to enhance our understanding of atmospheric aerosol properties. The manuscript is really well-written and the work and methods are generally clearly presented.

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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?

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.

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.”

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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?

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.

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?

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? 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?

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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?

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?

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?

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

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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.

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?

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.

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?

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 549, 2013.