Editor comment concerning the final published version of the manuscript entitled “Modeling the surface tension of complex, reactive organic inorganic mixtures” by Schwier et al.

This comment, prepared by the handling editor of the manuscript, contains excerpts from the discussion that took place between the authors and the handling editor during the last iteration of the manuscript before final publication.

1) Discussion about mathematical/physical (in)consistency of different surface tension mixing models

Comment made by the editor:

Testing the performance mixing models describing the surface tension depression in mixed solutions based on the behavior of single component solutions is a key part of this manuscript. The Schwier2010 and Henning mixing models are extensions of the S-L equation for single component solutions to multi-component solutions. Such an extension should be physically reasonable and mathematically consistent with the single component S-L equation. However, an external expert in statistics pointed out that the Schwier2010 mixing model is unreasonable. Specifically, an extension of a model for a single-component solution to a model for multi-component solutions should for example provide the correct result if a single component solution is treated as a mixed solution of two components. Formally, this translates to the condition that the following equation must be fulfilled for any *x*:

$$\Delta^{\sigma}_{\mathrm{mix}}(x, C-x) = \Delta^{\sigma}_{\mathrm{S\text{-}L}}(x) + \Delta^{\sigma}_{\mathrm{S\text{-}L}}(C-x) \qquad \forall\, x \in [0, C] \tag{I}$$

where $\Delta^{\sigma}_{\mathrm{S\text{-}L}}(C)$ is the surface tension depression as a function of organic carbon concentration (*C*) in the solution according to the Szyszkowski-Langmuir (S-L) equation and $\Delta^{\sigma}_{\mathrm{mix}}(C_1, C_2)$ is the surface tension depression predicted by the mixing model for a mixed two-component solution.

Eq. I is indeed fulfilled by the Henning mixing model, while it is not fulfilled by the Schwier2010 mixing model (except if $bC \ll 1$; note: *b* is the second coefficient of the S-L equation for the organic solute under consideration). As a consequence, the Schwier2010 mixing model cannot be expected to provide reliable results for mixtures, or if it does, then most likely due to compensating errors. You could argue that there is no need to describe a single component model with a mixing model. However, I would hold against this argument with considering a mixture of two virtually equal solutes …

A second theoretical test for a surface tension mixing model is considering a mixture of a surface active compound (concentration C_1) with a surface inactive (but water-soluble; concentration $C_2 = C_1$) compound (under the additional assumption that these two compounds don’t interact in the mixture). For the Henning and Schwier2010 models follows:

$$\Delta^{\sigma}_{\text{mix,Henning}}(C_1, C_2) = 0.5\Delta^{\sigma}_{\text{S-L},1}(C_1 + C_2) \tag{II}$$

$$\Delta^{\sigma}_{\text{mix,Schwier2010}}(C_1, C_2) = \Delta^{\sigma}_{\text{S-L},1}(C_1) \tag{III}$$

No mathematical arguments can be brought up here for/against one or the other model. However, which result, Eq. II or Eq. III, would one naturally expect to be true from a physical point of view? One of the original referees (I contacted him again on this specific point) voted for Eq. II. What about your opinion?
Whatever your opinion may be, voting for one or the other equation (Eq. II or III) gets back to the physical processes behind the surface tension depression, in particular whether surface competition is expected or not.

Author reply:
You make an interesting point. However, we never claimed that the Schwier et al. (2010) model was a mathematically rigorous extension of the single-species S-L equation. As stated, it's a semi-empirical model, inspired by our physical observations of surface tension depression in mixed methylglyoxal-glyoxal systems (Schwier et al. (2010)). If you read that paper, you would see that it does indeed reproduce the observed behavior for both of those species individually and together, for the range of concentrations used in that experiment.
We have added the following note to section 2.3 after the introduction of the model: "This model was found to describe surface tension depression in mixed aqueous ammonium sulfate/glyoxal/methylglyoxal solutions well (Schwier et al. 2010). Since it does not take into account competition between organic species at the gas-aqueous interface, its application is limited to relatively low total surfactant concentrations."

2) Discussion about a suitable approach to propagate the confidence bands from the fitted model curves for single-component solutions through the mixing model

Below suggestion for the error propagation has been implemented in the final manuscript. It is repeated here to provide details about the approach, which are only very briefly mentioned in the final manuscript.

Comment made by the editor:
Obtaining an estimate of the uncertainty associated with the model curves for mixed solutions essentially involves two steps. First, the uncertainty must be quantified for the model curves of single-component solutions. Second, the uncertainty of the single-component model curves must be propagated in an appropriate manner through the mixing model.
[…]
I do have the following suggestion (as I am not really an expert in statistics, you should possibly cross-check this suggestion with your experts in statistics):

- Starting point is the assumption that the surface tension depression, Δ^{σ}_{i}, of a single component solution of substance *i* with concentration C_i can be described with the S-

L-equation (Eq. 1 in the manuscript):

$$\Delta^{\sigma}_{\text{S-L},i}\left(C_i\right)= f_{\text{S-L},i}\left(a_i,b_i,C_i\right) \tag{IV}$$

Where $f_{\text{S-L},i}$ is a placeholder for the S-L-model-function and a_i and b_i are the model coefficients.

- In a first step, the confidence bands for the single component model curves are to be determined (e.g. using the Igor Pro Software or the “nonlinear least squares” (nls) functions in R). This will provide you the confidence band for a single component solution of substance *i*, i.e. the confidence interval, $\Delta^{\text{CI}}_i(C_i)$, as a function of the solute concentration, C_i.

  (Note, the confidence bands should also be determined for substances that are apparently not surface active. The confidence band will be of finite width also for surface inactive substances, unless you have a perfect measurement. This means nothing else than that the actual outcome of the measurement of a surface inactive substance is “not surface active within the experimental uncertainty” rather than “absolutely not surface active”.)
- In a second step, the confidence bands of the single component model curves have to be propagated through the mixing model in order to obtain the confidence band for the mixed model curve, $\Delta^{\sigma}_{\text{mix}}\left(C_1,C_2,...,C_n\right)$. The Schwier2010 mixing model (Eq. 4 in the main manuscript) is simply additive without any interaction effects of the different solutes, i.e. the surface tension depression, $\Delta^{\sigma}_{\text{mix}}$, is described as:

$$\Delta^{\sigma}_{\text{mix,Schwier2010}}\left(C_1,C_2,...,C_n\right)=\sum_{i=1}^{n} f_{\text{S-L},i}\left(a_i,b_i,C_i\right)=\sum_{i=1}^{n}\Delta^{\sigma}_{\text{S-L},i}\left(C_i\right) \tag{V}$$

Consequently, it should be appropriate to use the standard approach for error propagation to obtain a reasonable estimate of the confidence band for the model curve of the Schwier2010 mixing model:

$$\Delta^{\text{CI}}_{\text{mix,Schwier2010}}(C_1,C_2,...,C_n)=\sqrt{\sum_{i=1}^{n}\left(\Delta^{\text{CI}}_i(C_i)\right)^2} \tag{VI}$$

Eq. VI and of course $\Delta^{\text{CI}}_i(C_i)$ is all you need to obtain a reasonable estimate of the confidence band for the model curves of the Schwier2010 mixing model.

The Henning mixing model is not as simply additive as the Schwier2010 mixing model, because it considers surface competition between the solutes:

$$\Delta^{\sigma}_{\text{mix,Henning}}\left(C_1,C_2,...,C_n\right)=\sum_{i=1}^{n} g_i\left(a_i,b_i,C_1,C_2,...,C_n\right)\neq\sum_{i=1}^{n}\Delta^{\sigma}_{\text{S-L},i}\left(C_i\right) \tag{VII}$$

Where g_i is simply a placeholder for the "mixing functionality" in the Henning mixing model. Specifically, the individual summands in above equation only contain the S-L model coefficients of one solute at a time, but they contain the concentrations of all solutes. However, it is possible to write the Henning mixing model as follows:

$$\Delta^{\sigma}_{\text{mix,Henning}}(C_1, C_2, ..., C_n) = \sum_{i=1}^{n} \psi_i \Delta^{\sigma}_{\text{S-L},i}(C) \tag{VIII}$$

With the following definitions:

$$C = \sum_{i=1}^{n} C_i \tag{IX}$$

$$\psi_i = \frac{C_i}{C} \tag{X}$$

Eq. V shows that the Henning mixing model is also an additive approach, just with the additional prefactor ψ_i and using C instead of C_i in the summands describing the contribution to the surface tension depression by the individual solutes. Consequently, it should be appropriate to use the standard approach for error propagation to obtain a reasonable estimate of the confidence band for the model curve of the Henning mixing model:

$$\Delta^{\text{CI}}_{\text{mix,Henning}}(C_1, C_2, ..., C_n) = \sqrt{\sum_{i=1}^{n} \left(\psi_i \Delta^{\text{CI}}_i(C)\right)^2} \tag{XI}$$

Eq. XI and of course $\Delta^{\text{CI}}_i(C_i)$ is all you need to obtain a reasonable estimate of the confidence band for the model curves of the Henning mixing model.

Author reply:
We thank the editor for his concerns. We have adjusted all of the confidence intervals in the figures, based on the error propagation of the confidence bands determined from Igor Pro. You will note that the problems with Figures S7 and S8 have been resolved. We have added the following text to section 2.3, Surface tension modeling, "Using IGOR Pro, we determined the 95% confidence intervals accounting for the correlation between the fit parameters, a and b, for the isolated organic species in both aqueous and ionic solutions (for nonlinear equations, IGOR uses the linear term of a Taylor expansion). The confidence intervals of the complex mixtures were then found by propagating the confidence regions from the isolated species based on either the Henning model or the Schwier2010 model (see Supplemental Information for more details). Due to the non-linearity of the S-L equation, a Bayesian inference approach should be used for the most rigorous confidence interval treatment of correlated variables, (we refer the reader to Blau et al., 2008 for such a treatment).". We have also added the following statement to Section 3, Results, "In all figures, the black dots represent the experimental data, the black solid line is the semi-empirical model fit, and the gray dotted lines show the 95%

confidence interval of the semi-empirical model fit. For some complex mixtures, the confidence interval is truncated in one or more of the subplots; this is because experimental data to determine confidence intervals were not available for one or all of the organic species at high enough concentrations. Additionally, for some modeling methods, the confidence interval data were not available at all for some species at higher organic concentrations. For these instances, the confidence intervals used were constant values calculated as the average confidence interval over a range of lower concentrations where data were available for the necessary organic species. The relevant figures have this information listed in the captions." We have replotted all figures, recalculated all $\chi2$ values, all Tuckermann k values based on the updated a and b fit parameters, and adjusted all necessary language throughout the manuscript to update the standard deviation discussion of the models. The supplemental information has also been updated to include the details of the confidence interval calculations.