

Reviewer #2

We thank this reviewer for his or her useful suggestions. We address specific statements below.

The authors present experimental results and model calculations for a temperature of 25°C, only. As the surface tension is a function of temperature, it would be useful to see at least selected experimental data also for different conditions. The authors show state/discuss, whether the given fit parameters (which were derived for a temperature of 25°C) together with the applied model equations can be used to accurately reproduce the surface tension at different (lower) temperatures or not?

The surface tension of solutions may vary with temperature, and in this work, only data at 25°C is shown. The goal of this work was focused more on atmospherically relevant combinations of organics and salt, but more experiments at different (lower) temperatures is an excellent suggestion for future work.

In the conclusions, the authors recommend to use the salt fit parameters together with the Henning model (Eq. 3) for saturated solutions (with respect to (NH₄)₂SO₄). However, in many cases the solutions are more diluted (e.g., particle activation). The authors should give suggestions how to proceed with such solutions. Or in other words, up to which (NH₄)₂SO₄ concentration is it suitable to apply the water fit parameters? It seems that for diluted solutions the modified Tuckermann approach (Eq. 6) gives better results and should be preferred.

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.”

In the discussion/conclusion part the authors should explain in more detail, why it can be stated that the reaction products of two structurally different organic species have a surface tension behavior, which is different from those of the reactants, while this is not the case for two structurally similar species. The whole paragraph is not very conclusive in its current version.

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. For reactions between structurally different organic species, it is probable that these reactions cause larger changes in the hydrophobic surface area, leading to a different surface tension depression than expected from the S-L equation and subsequent models. We have added this commentary to the manuscript and changed the text in the discussion 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.”

p. 554, l. 12 and also p. 555, l. 10: It might be not necessary, but I missed the conditions (temperature), at which the samples were stored for equilibration?

We have added the following line in Section 2.1, “The solutions were stored in 100 mL Pyrex volumetric flasks at ambient temperature, without further protection from ambient light.”

p. 554, l. 21: "...known presence in atmospheric aerosols and ice nuclei..." -I guess, the authors mean "atmospheric (cloud) condensation nuclei (CCN) and ice nuclei (IN)..." because IN are part of the aerosols.

We have changed this sentence to read, “The amino acids were chosen for this study due to their known presence in atmospheric aerosols and ice nucleation activity”.

p. 555, l. 21: "Our approach for surface tension measurements has previously been described (Li et al., 2011; Schwier et al., 2012)" – The given reference is a bit misleading because the method

is not explain therein (at least not in more detail than in the current manuscript). Therefore, I would suggest to refer the older paper of Shapiro et al., 2009 (ACP).

We thank the reviewer for this suggestion; we have updated the citation as recommended.

p. 555, l. 24: "measurements... at room temperature (approximately 25_C)." - What does this statement mean? What is the uncertainty of the given temperature value? The surface tension is largely influenced by the temperature, and with respect to the number of significant digits given in Tab. S1, the exact temperature has to be given. Even small temperature fluctuations of only 0.1K do not allow to determine the surface tension with such a high precision (given are 5 digits).

The surface tension of solutions may vary with temperature, and in this work, only data at 25±1°C is shown. We calibrate our PDT using Millipore DI water and our experiments are consistent with the published surface tension of water over this temperature range. We have decreased the number of significant digits given in Table S1.

p. 557, l. 3: "although most aerosols are saturated with respect to the inorganic" - This statement holds for low relative humidities. At high rHs (e.g. at the point of CCN activation) this is not the case. At high rH, the solution is (usually) highly diluted. Furthermore, at low rH (and consequently saturated solution) solution effects, characterized by activity coefficients, are more crucial parameters for modeling than the surface tension. Thus, the authors should put their statement into the perspective that the considered (almost) saturated solutions represent somehow the upper limit of the conditions relevant for the atmosphere.

We refer the reviewer to an earlier comment to show how we have changed our discussion in terms of different RH scenarios.

p. 556-557: Is it necessary to use two different variables describing the same term σ_0 and σ_{H_2O} ? σ_{H_2O} can be also applied for Eq. 3 and Eq. 4.

Both of the symbols are used to indicate the surface tension of the mixture without the presence of organics. However, as we show in this work for Eq. (3) and (4), in the presence of salt, it is more appropriate to use the surface tension of the ionic solution (in this case, the surface tension of an aqueous $(NH_4)_2SO_4$ solution) than the surface tension of water. For the Tuckermann approach in Eq. (5) and (6), explicit terms describe the presence of salt, so the surface tension of water is always used. We prefer to use both symbols to indicate these differences.

I recommend to use the same x-axis for all diagrams. There is no need to vary the scales for each diagram. For a better readability of the labels on the x-axis it would be also helpful to slightly increase the blank space between the diagrams, respectively.

We use different x-axis scales for different figures in order to best show the modeling approach for the data; the maximum value on the x-axis ranges from 0.13 to 2 mol C (kg H₂O)⁻¹, so we do not feel it is appropriate for all the figures to have the same scale. We have increased the blank space between the diagrams for readability.

What was the reason to do the model calculations only at a very small number of data points? I suppose, the calculations are not very computationally expensive. Due to the few data points, the black and gray lines have very sharp edges. The lines could be much smoother for smaller calculation steps.

We thank the reviewer for this comment. We have performed model calculations using smaller calculation steps where possible and replotted the data.

p. 558, l. 3: I would add a comma after "(W)"

p. 558, l. 20: this sentence should be rewritten.

p. 562, l. 4-5: "Washburn, 2003" - I recommend to refer to the corresponding page or number of the table.

p. 563, l. 14: "Mannich reaction products may have significantly different surface-bulk partitioning and surface-activity behavior from the reactants..." - than the reactants?

p. 563, l. 27-29: "determined salt parameters be used..." - a word is missing here

Fixed.

The authors are not consistent using "Figure" and "Fig.", e.g.: p. 559, l. 19 and p. 561, l. 10

We have changed the manuscript so "Figure" is used at the beginning of a sentence, but otherwise "Fig." is used in all other locations.

I recommend to show Tab. S1 in the manuscript and not in the supplemental part. The given experimental fit parameters are, at least for my point of view, essential results of the manuscript, although some of these data have been already published elsewhere (Li et al., 2011; Sareen et al., 2010). The authors also should add the reference to these data (the data, which have been already published). It should be also explained why several values given in Tab. S1 differ from the older ones (e.g., Acetaldehyde). Are these data newly fitted values? The authors should state more precisely the origin of the fit parameters given in Tab. S1. Applying fit parameters, derived from measurements of the same binary solutions, which were also used to prepare the more complex mixtures, would increase the confidence of the conclusions given in manuscript.

We feel that the modeling approach to complex surface tension is the main focus of this work, rather than the experimental fit parameter values, so we have chosen to keep Table S1 in the supplement. We have added references to the data already published as a note for Table S1. The fit parameters for acetaldehyde shown in this work have recently been published as a corrigenda to Li et al. (2011). We have also added the following text to the title of Table S1. "Table S1. Fit parameters for all species in Millipore H₂O and in 3.1 M (NH₄)₂SO₄ at 25 °C. These values were found using Eq. (1)."

Tab. S1: The authors should comment the standard deviations given for the determined experimental fit parameters. The values are (partly) quite high. Would it be possible to reduce the standard deviations by fitting a larger number of experiments?

The reviewer is correct that in some cases the standard deviations for the experimental fit parameters are quite large. We have added the following text to the discussion, “The standard deviation in some figures is very large, due to the experimental uncertainty in the fit parameters, a and b. In some cases this standard deviation could be reduced by performing additional experiments; however, in some cases (e.g., glycine in 3.1 M (NH₄)₂SO₄) the S-L equation does not adequately describe the surface tension depression data for the isolated organic species, leading to systematic uncertainty in the fit parameters.”

In Fig. S1-S5 the standard deviations of the model calculations (gray lines) seem to be wrong.

We agree that the standard deviations of the model sometimes appear strange. Depending on the error associated with the fit parameters (a and b), the standard deviation of the model fit drastically changes (i.e. there can be sign changes for certain terms within the Szyszkowski-Langmuir equation). We have checked and the standard deviations shown are, indeed, correct based on our calculations.

Several entries in Tab. S1 are missing but are necessary for the model calculations (Glyoxal). The authors should add these fit parameters.

The species which have no fit parameters in Table S1 were shown to be surface inactive in either aqueous or ionic solutions. We have indicated this as a note to the table, “This organic was not found to be surface active; fit parameters are equal to 0.”, and in the appropriate subsections of the results, Sect. 3.

Tab. S2: Results of the Tuckermann (2007) approach (Eq. 5 in the manuscript) are not shown in the manuscript. Tab. S2 can be therefore omitted or calculation results should be added to Tab. 3.

The results shown in Table S2 are strictly for one organic in an (NH₄)₂SO₄ solution and are provided for completeness to show the Tuckermann approach as originally intended. These results should not be combined with Table 3, which shows the results from the modified Tuckermann approach of more atmospherically relevant solutions containing two to six organic species in an (NH₄)₂SO₄ solution.

Concerning the inorganic term (γ / c_{salt}) in the (modified) Tuckermann approach (Eq. 5 and Eq. 6): Was the value for this term taken from literature or was it determined numerically? The applied values should be given in the manuscript.

Section 3.5 states, “... $\gamma / c_{\text{salt}} = 2.1701 \text{ dyn cm}^{-1} \text{ M}^{-1}$ (determined from the International Critical Tables, p.464, (Washburn, 2003))...” and can be directly calculated from the concentration and surface tension values of (NH₄)₂SO₄ supplied.

References:

Several doi-numbers are missing. The authors should complete the list. (e.g., Booth et al. - doi: 10.1039/B906849J)

Hyvarinen et al.: "Journal of Chemical and Engineering Data" ! J. Chem. Eng. Data

Washburn et al.: "1926-1930;2003" ! a blank is missing

Setschenow, J.Z.: The correct titel is "Ueber die Constitution der Salzlösungen auf Grund ihres Verhaltens zur Kohlensäure"

Fixed.