**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Surface tensions of multi-component mixed inorganic/organic aqueous systems of atmospheric significance: measurements, model predictions and importance for cloud activation predictions" *by* D. O. Topping et al.

D. O. Topping et al.

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Response to anonymous referee #2

Thank you for your general comments and support of the work which has been presented in the paper. The remarks made are addressed below.

'Since the results presented in the study have potentially a large range of applications, the authors should make the work more accessible to a reader lacking strong background in thermodynamics. To this end, several improvements to the manuscript

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should be made. First, the authors do not explicitly define several key terms in the text (such as competitive and non-competitive adsorption, "coupled inorganic/organic approach" and "LiLu full model") nor explicitly state the corresponding equations....'

AC - The point is taken that some sections perhaps assume prior knowledge of certain processes. In the revised manuscript the concept of bulk to surface adsorption is first introduced in section 3.1 where the first models are presented. In the beginning paragraph of section 3.1 the line 'A common approach consists combining thermodynamic relations together with an adsorption model' has now been extended to read 'A common approach consists combining thermodynamic relations together with an adsorption model, thus accounting for transfer of material between the bulk and a surface phase thus altering molecular forces and the subsequent surface tension.' In the last paragraph of section 3.1 the notion of competitive and non-competitive adsorption has already been introduced but is now clarified in section 3.1 where it is first mentioned. The same new portion of text is placed in paragraph 2 of section 3.3 as a quick reminder. The new text reads: 'Thus it assumes that there is no interaction, nor competing adsorption, from the other solutes. In other words, it assumes that the relationship defining the surface excess for a component used in a binary system still holds in a mixture.' In section 4.2 the following sentence has been added to describe what is meant by a coupled inorganic/organic model as it is mentioned here for the first time

'... Also the authors should clarify the definitions of some other terms (e.g. ideality and semiideality) and, when discussing about the results, remind the reader about the meaning of the key terms. Appropriate revisions should be thus made to Sections 3.3 and 4.'

AC - Elucidating more on the 'activity' of a compound, a new sentence has been added to the last paragraph of section 3. 1 where it is mentioned for the first time. 'The reader is reminded that activity represents an 'effective' concentration which relies on calculations of activity coefficients. Activity coefficients are related to the molecular forces taking place in a solution. The thermodynamics of a solution mixture however

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depend on the intermolecular forces that operate between molecules that are dependent on the nature of the solvent(s) and solutes. For more information the reader is referred to Topping et al (2005b) and references therein.' Given the lengthy discussion one can have regarding activity coefficients one of our previous papers is referenced. However the concept of ideality and semi-ideality is clarified in section 3.3. In the paragraph following equation 16 the text now reads 'One option is to assume semi ideality, using the total water content to derive appropriate concentrations for each binary system. Semi ideality assumes that there is no interaction between solutes in a mixture, only that between each solute and the solvent. For example, when calculating water contents one would simply add the water from each binary system. For calculating activity coefficients one would assume that each compound is present on its own at the concentration defined using the total water content. If one assumes ideality then the activity of each compound is simply represented by its concentration in the mixture using activity coefficients of unity.'

'....Second, the authors test several combinations of different modelling approaches (the authors call them "permutations", I would prefer term "combination") but do not give the corresponding sets of equations. Therefore the authors should make sure that the reader does not have to guess about applied equations.'

AC - In the new manuscript the term 'permutations' has been replaced with 'combinations'. To write out in full all of the model combinations would require quite complicated sets of equations which would most likely confuse the reader. Rather we have clarified certain terms such as 'semi-ideality' as mentioned in the last comment. Similarly there are terms such as the activity of each compound which cannot be simplified more than they have been presented in the manuscript. Combined with the response to the comments made above, the reader such be able to follow the different model combinations more clearly.

Specific comments: '1. Abstract. The sentence ending with phrase "...and this was composition dependent" is a little bit unclear (line 20, p. 12058)....'

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AC - This line has now been changed to read '...and this was dependent on the composition of the solutes present"

'......The abstract contains also nonscientific/qualitative terms: "realistic" (line 21, p. 12058) and "significant differences"'

AC - The term 'realistic' has been replaced with 'atmospherically representative'. Similarly the word 'significant' has been replaced with 'large'

'2. Introduction, p. 12059. The parameters R and T should be defined in connection with eq. 1.'

AC - The text has been updated to do so.

'3. Introduction, p. 12060, line 12. It should be made clear to which term in equation 1 the Raoult effect refers to.'

AC - An additional reference to the water activity has been added in the new text. Line 12 now reads 'The Raoult effect, encompassed in the water activity in equation 1, describes the influence of the solute on the equilibrium vapour pressure above solution....'

'4. Section 3.1., p. 12064-12065. The discussion about three groups of calculation(?) proposed by Hu and Lee (2004) is a little bit vague. Also, "ln" not "Ln" in eq. (2) and in subsequent equations as well. Finally, the reader is forced to guess what is meant by two different schemes of Li and Lu (2004). Does the difference lie in treating adsorption - competitive or non-competitive? If so, material in the last paragraph of the section should be presented earlier.'

AC - As noted in the text there have been 3 different groups of methods used for calculating the surface tension of inorganic mixtures according to Hu and Lee (2004), each varying in complexity and accuracy. It is felt that the initial sentence briefly describing two is enough to fit into this body of text. Any further description at this point would warrant a presentation of relationships describing basic thermodynamics which the reader can find from other sources such as the one referenced. However , in or-

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der to clarify the discussion somewhat in this paper some additional text has been added to line 22 in conjunction with the first general comment you made which was addressed above. Initially the two corresponding sentences read 'A common approach consists combining thermodynamic relations together with an adsorption model. In the model presented by Li and Lu (2001), the authors combined the Gibbs dividing surface, the Langmuir adsorption equation and an appropriate model for calculating activity coefficients in mixed solutions to arrive at two different schemes.' The new text is 'A common approach consists combining thermodynamic relations together with an adsorption model, thus accounting for transfer of material between the bulk and a surface phase thus altering molecular forces and the subsequent surface tension. With regards to the latter consideration, in the model presented by Li and Lu (2001), the authors combined the Gibbs dividing surface, the Langmuir adsorption equation and an appropriate model for calculating activity coefficients in mixed solutions to arrive at two different schemes. Briefly, the Gibbs dividing surface is a geometrical surface used to define the volumes of the bulk and surface phases.'

'5. Section 3.2, p. 12066. What does "linear dependence" (line 9) mean?'

AC - This is referring to the fact that one may form a relationship for the surface tension which depends linearly on the concentration of the solute.

'6. Section 3.2.1., p. 12066-12068. The term "N" is not defined in eq. 6. The parameter "A" is lacking indices (p. 12068, line 12). Also, the authors should give at least references discussing the validity of eq. 7 (p. 12068, lines 19-20).'

AC - As usual in such mathematical presentations the term N represents the number of components in question. The text has been updated to include this however. The parameter 'A' now has indices in the new text. Regarding the method of calculating surface areas, the validity of equation 7. as discussed by Suarez et al (1989) is presented in lines 1-11 page 12069.

'7. Section 3.2.1., p. 12069-12070. Equations 11 and 2 are identical. Are they derived

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in similar fashion? If so, why the derivation is not presented in connection with eq. 2 which would be the logical order?'

AC - Yes they are. Essentially it was the purpose in this paper not to focus too much on the effect of surface tension from solely inorganic solutes given the vastly superior understanding of this fraction. This is manifest in section 3.1 in the brief discussion of inorganic models available. In order to ease the concern raised, section 3.1 has been updated to refer the reader to a more indepth discussion later on in section (3.2.1). Line 25 page 12064 now reads 'The basic scheme for binary systems, derived and discussed in more detail in Sect. (3.2.1), is given as Eq. (2):'

'8. Section 3.2.2, p. 12072. The second paragraph is out of the context of the section (lines 5-20). It remains unclear if eq. 13 is used at all in the work. Moreover, why results are presented only for glutaric acid? Finally, can temperature dependence be incorporated into the "LiLu model" and if so, how?'

AC - Paragraph two here marked a brief discussion of alternative techniques for calculating pure component surface tensions, other than the Malceod-Sugden correlation. In order to remove confusion here this paragraph has been altered to highlight the temperature dependent fits for pure component surface tensions from the knovel database simply as an alternative to using the Macleod-Sugden correlation. Also, results are only given for glutaric acid as this is just one example which highlights the discrepancy between the knovel database and the computational method of the ACD labs software (another optional technique). Indeed, the paragraph now starts 'As an alternative to the Macleod-Sugden correlation, temperature dependent pure component surface tensions are recorded in texts such as the knovel DIPPR Project 801database (www.knovel.com). For example, using this database, the temperature dependence of the pure component surface tension for glutaric acid is given as:' Technically a temperature dependence could be incorporated into the LiLu model. To do this the effect of temperature on the surface tension of water, adsorption constants, saturated surface excess and activity coefficients would have to be included. The first effect is rather easy

and readily available. The second, third and fourth effects would warrant detailed studies of the measured binary surface tensions and activity coefficients at varying temperatures in order to derive temperature dependent parameters and correlate models with measured results (eg. Analyse the temperature dependence of UNIFAC predictions).

'9. Section 3.3., p. 12073-. Tables 3 and 4 seem to have changed places in the text - the authors should make sure that the contents of the tables are presented in the right order throughout the manuscript.'

AC - There is an error in the text, line 25 on page 12073 should refer to table 4. This has been corrected.

'10. Page 12074, line 6. What is "n"?'

AC - N represents the number of solutes, this has been updated in the new manuscript.

'11. Page 12075, lines 12-13. Two typos appearing here should be corrected ("von Szyszkowski" and "Laungmuir").'

AC - These typos have been corrected.

'12. Page 12075, line 19. Word "of" is missing between the words "coupling" and "intermolecular".'

AC - The sentence has been corrected in the new document.

'13. Page 12077, equation 22. Should the left-hand side of the equation contain omega with an overbar?'

AC - This equation is copied directly from the original source where there is no overbar present.

'14. Page 12078. Line 16: What is "full" LiLu model? Moreover, the step from (23) to (24) needs justification since the result does not follow simply by taking logarithms of both sides of (23). Also, index "sol" is missing from the left-hand side of (24).'

AC - The 'full' model is the LiLu model applicable to multicomponent systems. In other words, use of the binary lilu model within the Fainermann-Miller mixing rule leads to this here. This has been clarified in the text. An additional sentence reads. 'Note that the 'full' LiLu model refers to the LiLu model framework applicable to multicomponent systems (Eq. 15)' With regards to equations 23 and 24, two additional portions of text has been added to clarify the calculation. Line 20 now reads 'Substituting Eq. (18) and Eq. (19) into Eq.23 and taking the logarithm on the resulting expression, this further simplifies to:' Following this, after equation 4 a portion of text explains how the average molar surface area is used. 'Now replacing the individual molar surface areas with the average value calculated using Eq. 22 gives:' Also the relevant subscripts have been added to equation 24.

'15. Page 12079. Line 2: Here eq. 11 is used, not 13. Equation 27: one overbar seem to be missing.'

AC - This has been corrected in the new document. Also the symbols for the average molar surface area has been changed in accordance with point 13 addressed above.

'16. Section 4.1. Page 12080, lines 2-3. Actually many of the studied solutions do not display notable decrease in the surface tension compared to pure water over the studied mole fraction range (e.g. oxalic and malic acids, levoglucosan). Referring to my general comment (see above), the authors should make sure that the reader understands which model combinations and which equations are used when referring to e.g. "Tamura mixing rule" or "Suarez method". This applies to Section 4 in general.'

AC - Line 2 sentence two has been removed. The new document contains more references to the relevant equations in order to help the reader. In this instance, sentence 3 now reads 'For the two predictive models, labelled as 'Tamura' and 'Suarez', a range of values is given (Eq. 3 and Eq. 6 respectively).'

'17. Section 4.4., p. 12083-12084. The results for "Multi 1" are not explicitly discussed in contrast to other higher-order solutions.'

AC - Section 4.3 discusses the results for 'Multi 1'(a mixed organic system) whereas section 4.3 is reserved for the mixed inorganic/organic systems. Generally all systems are given equal weighting. However, there are significantly more model combinations to discuss for the latter which is likely to cause the observed bias.

'18. Page 12086, lines 1-2. "highly surface-active", not "highly surfactant".'

AC - The text has been corrected accordingly.

'19. Fifth and sixth paragraphs of Section 5 (p. 12086-12088). The differences should be indicated in percentages using reasonable accuracy.'

AC - The text has been updated to include percentages

'20. Sixth paragraph of Section 5 (p. 12087-12088). The result that methods based on utilizing binary data may yield unphysical predictions for more complex systems is important since it may limit the applicability of such methods. This point should be discussed in more detail and brought out in conclusions and in abstract.'

AC - Generally these paragraphs indicate that the use of theoretical frameworks which contain parameters derived from binary data may produce unphysical behaviour when taken beyond the concentration ranges used to fit such parameters. The new document has been updated such that the above is stated at the end of paragraph 6. Similarly, the abstract now contains the line 'However, results indicate that the use of theoretical frameworks which contain parameters derived from binary data may predict unphysical behaviour when taken beyond the concentration ranges used to fit such parameters.'

'21. Last paragraph of Section 5 (p. 12088). The paragraph contain some qualitative and vague sentences. These are the first sentence and sentence "Calculations carried out here...in a consistent theoretical framework". Also, critical supersaturations predicted by different models converge with increasing particle size and, on the other hand, only particles having dry diameters >50 nm (roughly) are able to activate under tropospheric conditions. Therefore it would be interesting to get a rough estimate on

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the relevance of these differences to the lower troposphere, i.e. how large differences in predicted CCN concentrations are induced by using different modeling schemes in the particle size range 50-100 nm?'

AC - The question posed is certainly an interesting one. As pointed out in another referees comments, cloud drop formation is a complex process, and dynamic factors as well as the particle size distribution have an effect on the activation. Thus in order to assess the impacts on actual CCN concentrations would require the use of other complex modelling tools. This could form the focus some very interesting future work!

'22. Tables. The authors should define all symbols appearing in the tables (e.g. for Table 3). Also, referring to the general comment given above, the authors should make sure that the reader understands what is meant by terms appearing in Tables 4, 6 and 7.'

AC - Table 3 has been update to include definitions of each symbol in the new document. The caption associated with table 4 has been updated in order to explain the terms used in the table as was done with table 6.

'23. Figures. The various red lines in Figures 5-8 should be introduced separately.'

AC - The figure captions have been changed to elucidate more on the red lines. The idea was to separate the use the LiLu model within the Fainerman mixing rule and the full lilu model (and all variations thereof) from all the other methods. Specifically, remove the last two approaches from use of entirely predictive frameworks and assuming the surface tension of pure water. To describe each red line in detail would be excessive, suffice to say that the use of a theoretical model fit to binary data may produce unrealistic physical behaviour when taken outside the range of experimental data. Following on from point 20 raised earlier, the main body of text and abstract has been updated.

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