

***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 #4

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

‘General comments: The manuscript is in some parts difficult to follow because 1) some slight structural inconsistencies and 2) all the relevant parameters and concepts are not explained / consistently referred to. These problems will be particularly pronounced, if

the reader does not have a sufficient background in thermodynamics of mixtures. The authors should carefully check that all the relevant variables and concepts as well as the used models are first explained comprehensively and referred to consistently later on in the text.'

AC - This has been highlighted by two other referees in some detail. There have been significant changes applied to the revised manuscript in order to make it more palatable for the general reader. For example, descriptions of certain processes relevant to surface tension and general aqueous thermodynamics are now given. Similarly, errors regarding lack of consistency regarding use of certain variables have been removed. For a more detailed description please refer to the response to referee#2. However the specific points raised by yourself are addressed below:

'Specific comments/technical corrections: Abstract, p. 12058, line 16; (also Sect. 3.2.2, p. 12073, line 19): The authors state that '...two predictive models found in the literature provided a range of values...' Can you speak of a range when you actually have two point results?'

AC - The range of values discussed here relate to the use of other predictive models for calculating pure component surface tensions. Generally there appears to be no specific pattern whereby one can draw general percentage deviations and it is likely to be highly case dependent. This may be down to the different basis sets used in such methods. Within the main body of text an example is given to highlight the possible discrepancies. Notably the largest difference was found for Suwanee River fulvic acid where huge surface tension ranges of 5-109 mN/m were found!! However this was based on a representative structure provided by HNMR analysis. This range may differ when another structure is used. However, it is clear that this highly sensitive dependence on pure component surface tensions is a drawback for both predictive methods analysed, specifically as measured data for many compounds is likely to be unavailable.

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'Introduction, p. 12060, line 22: R and T should be explained as well.'

AC - This has been included in the revised manuscript.

'Sect. 2.1: The authors explain how the binary and multi-component (number of constituents higher than 3) samples were chosen and prepared. Why do they skip the ternary systems in this context? In my opinion it would be logical to say a couple of words about those as well.'

AC - The new document has been updated to include a brief description of the ternary mixtures. This was a simple oversight on my behalf.

'Sect. 2.1, p. 12063, line 13: The reference Svenningsson et al. (2006) should be in parentheses, i.e. (Svenningsson et al., 2006).'

AC - This has been updated in the revised manuscript.

'Sect. 2.1, p. 12063, line 20: In the end of the section 2.1. the authors state 'The ability of models chosen in this study to reproduce the behaviour of such (multicomponent) systems aer discussed in Sects. 4.3 and 4.4' Why do the authors only refer to the comparisons made for the multicomponent systems, as the same kind of comparison was made for binary and ternary systems as well? I think it would be consistent to refer to these comparisons (Sects. 4.1 and 4.2) as well.'

AC - Following the update from your second comment, the new manuscript now refers to sections 4.1 and 4.2 after the introduction of the binary and ternary systems respectively.

'Sect. 3.1, p. 12064, lines 23-25: The concepts 'Gibbs dividing surface' and 'Langmuir adsorption isotherm' should either be shortly explained or comprehensive references should be given.'

AC - This was also raised by referee#2. The new manuscript now has the following body of text in section 3.1 : 'With regards to the latter consideration, in the model

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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. The langmuir adsorption isotherm is a relationship which describes the number of adsorbed molecules on a surface to the concentration above that surface. For more information on this model the reader is referred to Seinfeld and Pandis (1998) ' This reference was chosen due to its generalised introduction to concepts pertinent to atmospheric chemistry. The bibliography has been updated accordingly.

'Equations 2 (p. 12065, line 2), 6 (p. 12067, line 23), 9 (p. 12069, line 27), 11 (p. 12070, line 11), 15 (p. 12074, line 19), 16 (p. 12075, line 2), 27-30 (p. 12079, lines 2-5 and 7): The notation of the natural logarithm should be consistent in all the equations. Now varies between 'Ln' and 'ln'. I would suggest 'ln'.'

AC - The manuscript has been updated to removed this inconsistency, the notation of the natural logarithm is now 'ln'.

'Equations 2 (p. 12065, line 2), 10 (p. 12070, line 7), 15 (p. 12074, line 19), 16 (p. 12075, line 2), 27-30 (p. 12079, lines 2-5 and 7): The notation of the adsorption equilibrium constant should be consistent in all the equations. Now varies between 'K', 'k' and 'k'. I would suggest 'K'.'

AC - As above, the new manuscript follows your suggestion and the adsorption equilibrium constant notation is now 'K' throughout.

'Equation 2 is exactly the same as Eq. 11. Why do they both need to be presented?'

AC - In this paper the emphasis was very much on the combined effect of inorganic/organic solutes and also a detailed study on mixed organic aqueous systems. Firstly it was of course necessary to briefly discuss the influence of inorganics and the model used to treat them in this paper. As a result, equation 2 was presented without

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any derivations. However another focus of this study was an analysis of existing binary methods to reproduce measured behaviour for organic systems. It was clear that one could use equation 2 for organic systems but for the benefit of the reader, especially considering the detailed comparison with experimental data later on, it was considered beneficial to provide a full derivation here. Similarly, it is useful in the sense that concepts which might be unfamiliar to many are discussed in this paper.

‘Sect. 3.1, p. 12065, lines 19-22: The authors should explain what ‘competing adsorption’ means.’

AC - Following the comments provided by referee#2 this has been included in the new manuscript.

‘Equation 6, p. 12067, line 23: Should be denominator in the logarithm be ‘xigammai’? Also, the variable N should be explained.’

AC - Yes, that is correct. Also the variable N has now been explained.

‘Several places in the manuscript, for instance, p. 12068, line 24; p.12073 lines 7, 8, 10, 17; p. 12097, Table 2: The correct reference for ‘Yens-Woods/Yens-Wood/Yens and Woods’ method should be checked. In my opinion the correct way to cite this method would be ‘Yen-Woods’.’

AC - The new manuscript now consistently uses the references Yens-Wood.

‘Sect. 3.2.2, p. 12071, line 15: Should ‘sudgen’ be replaced by ‘Sudgen’?’

AC - Yes this has been corrected.

‘Sect. 3.2., second para: Why is the temperature dependence of glutaric acid surface tension presented here? Is it used in the work, and if it is, what about the other compounds? I find this para a little unconnected to the rest of the manuscript.’

AC - Referee#2 made a similar comment. In response, paragraph two here marked a brief discussion of alternative techniques for calculating pure component surface

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tenions, 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).

‘Sect. 3.2.2, p. 12073, line 20: Should you refer to Table 2 instead of Table 1?’

AC - Yes this has been updated.

‘Sect. 3.3, p. 12076, line 12: ‘von Szyszkovski’ should be replaced by ‘Szyszkovski’, and ‘Laungmuir’ by ‘Langmuir.’

AC - This has been corrected.

‘Sect. 3.3, p. 12078, line 16: Table 4 should be referred to before Table 5, or the order of the tables should be changed accordingly.’

AC - The tables are in the correct order according to the results and discussion section.

In order to address your comment the reference to table 5 has been removed from section 3.3, rather section 4 is referenced.

‘Sect. 4.1, Tables 1a, 2 and 3, Figs. 3: In Tables 1a, 2 and 3 citric acid is mentioned. Why is not the results related to it presented in Figs. 3/ mentioned at all in the text?’

AC - This was an oversight in the original manuscript. Figure 1 has been updated.

‘Sect. 4.2, p. 12081, lines 8 and 27: Should Table 5 be cited instead of Table 4?’

AC - Yes this has been corrected.

‘Sect. 4.3, p. 12082, lines 16 and 19: Should Table 6 be cited instead of Table 5?’

AC - Yes this has been corrected.

‘Sect. 4.4, p. 12083, line 18: Should Table 7 be cited instead of Table 6?’

AC - Yes this has been corrected.

‘Sect. 5: In several places the authors state that as the dry size increases, the aqueous solution in the droplets gets more dilute. The physical background of this should be explained. Sect 5, p. 12087, line 12: I assume that the authors mean Table 7 instead of Table 6.’

AC - In the new manuscript the reader is reminded of the influence of the kelvin effect. Page 12086 line 26 now reads ‘Despite increased convergence at larger dry sizes, thus more dilute droplets (reduced kelvin effect), there is still a noticeable difference between assuming the surface tension is that of pure water and explicitly taking into account the influence of solutes.’

‘Sect 5, p. 12088, line 6: ‘Figure 8’ should probably be replaced by ‘Figure 9’, and I assume that you mean ‘Figs 5-8’ instead of ‘Figs. 5.1-5.4’

AC - Yes these errors have been corrected.

‘Sect 5, p. 12088, line 15: A space should be entered between ‘40’ and ‘nm’.’

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AC - This has been updated.

'Table 2, p. 12097: The reference 'Marrero and Gani (2001)' is not in the reference list. In the text (Sect. 3.2.1, p. 12068, line 27) the authors cite Topping et al. 2005b in the corresponding context. Also the meaning of all the variables in the Table should be explained. The same applies for all the tables.'

AC - The tables have indeed been updated in the revised manuscript. Also the bibliography has been updated to include the Marrero and Gani reference and the Topping et al 2005b reference removed.

'Tables 3a-3d, p. 12098-12101, and Figures 1a-1c, p. 12106-12108: Why are the systems not presented in the same order in the tables and figures? It would be easier to follow the results if the order of the systems was the same. And: what happened to citric acid?'

AC - Citric acid has been included in figure 1 as this was a simple oversight. Similarly figure 1 has been reordered in line with table 2

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 12057, 2006.

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