

Interactive comment on “An analytical solution to calculate bulk mole fractions for any number of components in aerosol droplets after considering partitioning to a surface layer” by D. Topping

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I would like to thank referee2 for their constructive comments and suggestions. General and minor points are addressed in the following text with changes made in the original manuscript where required.

In general, it would be very useful to derive the equations for the any number of components-case. Currently it is not clear how the calculations are made in the case

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of multi-component mixtures.

Response: Apologies, as stated in the response to referee 1 who raises a similar concern, the revised manuscript now contains an example of how the partitioning of components between a bulk/surface layer changes as a function of wet droplet size for a 5 component system. Whilst the original manuscript did state that the equations presented are used in the same fashion for binary and multicomponent mixtures this has been made clear in section 3 which has now been split into 2 new subsections (3.1 Binary mixtures, 3.2 Ternary and higher order mixtures). Specifically after the sentence 'The equations presented in the previous section can be applied to mixtures of any number of components as dictated by the surface tension model employed.', a more detailed description of how the equations can be applied to a mixture of 5 components is given with figures illustrating how the bulk/surface concentrations vary as a function of droplet size. Section 3 is now much more detailed, with application to binary mixtures (as before), multicomponent mixtures and comparisons of cloud activation potentials for a mixture of sodium chloride and sodium dodecylsulphate (SDS) aimed at addressing further concerns stated below.

Also, some additional approximations, which are not justified in the current manuscript, are needed for the multi-component case. Optionally, predictions from the analytical equations could be compared with those from a numerical model, where approximations are not needed. This update is optional, because suitable numerical models may not be directly available for multi-component solutions. Of course, it is possible to develop such a model, but the numerical solution is not that simple.

Response: Apologies, this should have been made clearer in the original manuscript. The main ethos behind the equations presented here is based on the assessment of simple mixing rules for multicomponent surface tensions developed outside of the atmospheric community. The success of these mixing rules, which facilitate derivation of the equations presented here, forms the overarching assumption in this study. The

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most obvious assumption contained within this approach, and stated in the original manuscript, is that it is assumed the behaviour of the solute within a binary solute pertains in the mixed solution. This is re-iterated in a new subsection (3.2) which specifically describes the method for multicomponent mixtures. This of course can be considered the pivot assumption in this case and neglects phenomena briefly referred to in the original manuscript such as competing adsorption, which is included in alternate permutations of the Li and Lu models. Whilst reference is given to future developments with an aim to include this phenomena, the assumptions required for applicability to multicomponent solutions are re-iterated in the new manuscript in section (3) where comparisons are made with the data presented by Sorjamaa et al (2004). I would suggest, as the referee also suggests, that comparison with a numerical model which contains no assumptions beyond a ternary mixture is not worthwhile given the one of the main reasons for the equations presented here are for multicomponent solutions for which no benchmark model currently exists in the literature. Rather, a clearer discussion on the phenomena neglected within this approach are presented with an aim to satisfy the referees preceding and proceeding comments.

The derivation of the analytical solution (Sect. 2) begins with a rather lengthy (about three pages) review of surface tension models. I agree that it is important to show that the surface tension model (Eq. 6) is really working, but otherwise this part of the text could be condensed. It looks like Eqs 5 and 6 are needed in the derivation of the analytical solution, so what is the reason for showing Eqs 4 (single solute case of Eq. 6), 7 and 8 (the same as Eq. 6)? Is Eq. 5 valid for the multi-component case? If yes, what approximations are needed for this?

Response:Apologies, it was the aim of this original manuscript to provide the atmospheric reader, who may not be well versed in surface tension studies, with an adequate introduction to the range of 'bulk' surface tension models available before proceeding to derive a set of equations designed for multicomponent mixtures which are largely based on the applicability of said models. As stated in response to the comment made previously and as stated in the original manuscript, is that it is assumed the be-

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haviour of the solute within a binary solution pertains in the mixed solution. The single solute case (Equation 4) is shown to illustrate that the equations which enable calculation of bulk/surface partitioning in multicomponent mixtures are based on a simple mixing rule which assumes that the mixed surface tension can be expressed as a linear combination of the contributions from each solute at the total concentration of the mixture. Equations 7 and 8 have been removed in the revised manuscript for clarity, a more detailed discussion already provided by Topping et al (2007). It is assumed equation 5 is valid for the multicomponent case, as stated above, to enable derivation of the final equations. Following the referees comment above, the equations have been condensed for clarity.

There could be more discussion about validity and usability of Eq. 6. For example, what about the effect of common ions? Added sodium chloride increases surface tension of pure water, but it decreases surface tension of aqueous SDS solution (e.g. Li et al., 1998). Equation 6 is based on solute activities, but activity coefficients are rarely used in surface tension parametrization. In addition, concentration scales other than mole fractions are commonly used. Does this mean that most published surface tension parameters are not directly valid for the analytical equation?

Response:Apologies again, the drive to present equations which can be applied to multicomponent mixtures possibly neglected a brief discussion of phenomena which is studied using models capable of assessing detailed processes within ternary solutions. This concern was also raised by referee 1 who states the presence of inorganic solutes can change the critical micelle concentration. In the revised manuscript I have made reference to phenomena which is explicitly neglected in the theoretical considerations of the derivations in new section (3). The assumption that the success of mixing rules which facilitate derivation of the analytical expression is re-iterated within section (3). With regards to the common-ion effect, for example, following suggestions by referee 3, comparison is made with the predictions of Sorjamaa et al (2004) in the form of a table of critical saturation ratios for mixed sodium chloride-SDS solutions. With regards to the use of parameters derived using concentrations other than mole fractions, the

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surface excess parameter can be used directly. The second parameter can be derived by either 1) converting, for example molarity to molality based scales using the volume additivity assumption or 2) fitting directly to the experimental data. So whilst it is true that direct use of some published parameters may be limited, the steps required to obtain the parameters used in this study are not complex.

It is recommended that Eq. 9 (page 1095) is derived for the multi-component case. Then e.g. the effect of common ions should be explained. For example, Raatikainen and Laaksonen (2010) have derived different analytical equations for mixtures with and without common ions, and they have also shown that the common ion effect is important for surfactant partitioning.

Response: As in the response to referee 1 and stated above, an explicit multicomponent example is given in the revised manuscript with clear instructions as to the analytical expressions are employed. This is included in new section (3). In addition, the newly published paper of Raatikainen and Laaksonen (2010) is referenced in the new manuscript when discussing the comparisons with the data presented by Sorjamaa et al, as suggested by referee 3.

The justification for getting rid of the activity coefficients (page 1096) is not very clear. First of all, zero water surface excess and chemical equilibrium (line 2) does not mean that activity coefficients in Eq. 8 can be set to unity. The justification for Eq. 12 is either the ideal solution approximation or that the surface tension parametrization is based on concentrations instead of activities. However, the ideal solution approximation is needed for Eq. 17.

Response: Apologies, this should have been made clearer in the manuscript. First of all, the requirement of neglecting activity coefficients in the first instance is to facilitate derivation of the analytical expressions, as referee 3 recognises. The justification for eq. 12 is that the surface tension parameterisation is based on mole fractions, rather than activities, and that the two surface tension parameters adequately capture the variation of surface tension with concentration in the binary solution. Secondly, the

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same assumption is used within Eq (5). The statement which created this confusion has been removed, and a reference added to support the assumption of a surface excess of water of zero.

The usage and meaning of the dotted surface tension parameters (page 1097, line 2) is not clear. Concentration dependent activity coefficients can not be taken into account by these dots, so why these are used? What is the relation between parameters with and without dots (based on Eqs 19 and 20 they should be equal)? This should be explained at least in the example in the beginning of Sect. 3.

Response: The dotted surface tension parameters refer to that fact that these parameters have been fit to an idealised framework (i.e. the surface tension equation with only the mole fraction in the logarithmic expression), thus implicitly accounting for at least a consideration of solute activity within an optimised fit. This is now re-iterated within section 3 of the manuscript.

In general, paragraphs and sections are quite long. Readability of the manuscript could be improved by increasing the number of paragraphs and/or subsections. The other technical corrections are listed below.

Response: In line with the response from other referees, the initial sections have been condensed and reformulated with regards to formatting. Section 3 is split into 2 subsections for clarity. This makes the manuscript much easier to read.

Page 1090: Computational efficiency of the analytical solution is . . . less than a similar iterative approach?

Response: This has been corrected

Page 1090, line 23: RH is, vw is, σ ws is, rdrop is

Response: Apologies, I don't quite understand what is being requested here, all

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variables and units are already defined.

Page 1090, line 24: The unit of v_w should be $m^3 mol^{-1}$

Response: This has been corrected

Page 1091, line 2: Reference Topping et al. (2007) is missing

Response: This has been corrected

Page 1091, line 15: Maybe. . . and n_{bi} and n_{si} are the bulk . . .

Response: This has been corrected

Page 1091, line 24: Why there is reference to Eq. 2?

Response: This was to illustrate the fact that it is possible to solve the concentrations in a bulk and surface layer, as displayed by Eq.2 . This is made clearer in the revised manuscript by introducing the term in brackets '(and calculate concentrations in the bulk and surface layer)'.

Page 1091, line 24: Something missing from 'systems two solutes'

Response: Apologies this originally had brackets around said phrase which was somehow lost in the conversion. This has been corrected.

Page 1091, line 26: Reference Sorjamaa and Laaksonen (2006) is missing

Response: This has been corrected. The original reference was erroneously included in the document.

Page 1092, line 1: If there is just one organic component, 'binař y organic systems in water' could be 'binař y organic/water systems'. Also, 'ternary mixed inorganic/organic systems in water' could be 'ternary inorganic/organic/water systems'

Response: This has been changed

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Page 1093, line 8: Reference Topping et al. (2005b) is missing or it should be referenced as Topping et al. (2005)

Response: This has been corrected

Page 1093, line 10: Maybe 'surface area' instead of 'cross sectional area'?

Response: This has been changed

Page 1093, line 14: Eq. 2 is not the Gibbs adsorption equation (equation instead of Eq.). Also, it looks like Eq. 5 is not based on Eq. 4, so the origin of Eq. 5 should be clarified. I assume that Eq. 5 is based on Eq. 3; then chemical potentials (μ_i) should be defined.

Response: This was also raised by referee1 and is made clearer in the revised manuscript. Eq. 4 is simply the binary formulation of the Li and Lu 2001 model. The referee is correct, Eq.5 is based on Eq.3, This has been corrected in the revised manuscript and referencing was wrong, apologies. Also, the definition of the chemical potentials is given in the discussion of equation 3..

Page 1093, line 18: "Sorjamaa" should be "Sorjamaa"

Response: This has been changed

Page 1094, line 11: Check the style of references Fainerman and Miller (2001) and Fainerman et al. (2001)

Response: This has been corrected and should have read Fainerman et al. (2001a,b)

Page 1095, line 12: Eq. 2 does not describe surface tensions

Response: Apologies, this should be referring to Eq. 4, which has been corrected.

Page 1095, line 16: Something missing from "it would in a binary"

Response: This perhaps wasn't clear and has been updated to read 'can now be used to describe the behaviour of each component as it would pertain in a binary system'.

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Page 1095, Eq. 9: There are different notations (super and subscripts; capital and lower case letters) in the manuscript, e.g. n_{si} and n_{is} . Consistent notations should be used through the manuscript.

Response: Apologies, this is indeed inconsistent with equations 2 and 3, which have been correctly notated now.

Page 1097, Eq. 20: Wrong sign, and different notation for the dotted K_i

Response: Apologies, these equations have been condensed at the request of an alternative reviewer and the signs have been corrected.

Page 1098, line 5: $(1-x_iB)$ missing from the first term

Response: Yes apologies. At the request of an alternative referee, the equations have been condensed to provide the reader with the end quadratic, which is a simple manipulation of the preceding equation

Page 1098, Eq. 27: $-4ac$ should be in the square root term

Response: Yes, this managed to convert wrong from latex and has been corrected.

Page 1099, Eq. 29: Wrong value and unit

Response: Yes, this was raised by the other 2 referees and has been corrected.

Page 1099, line 13: Unit of Γ_i (should it be $\Gamma_i^{w'}$ or are these equal?) is missing

Response: These refer to the dotted parameters expressed earlier within the document. Thus the text has been updated to make this clear.

Page 1099, line 18: The latter bulk mole fraction is not correct

Response: Yes this was raised by another referee and has been corrected in the new manuscript.

Page 1103, line 23: "Inluence" should be "Influence"

Response: Apologies, this has been changed.