

Interactive comment on “A simplified treatment of surfactant effects on cloud drop activation” by T. Raatikainen and A. Laaksonen

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We would like to thank Referee #1 for constructive comments. In general, several parts of the text will be clarified by adding more details and improving notations. Responses to the specific and minor comments are below.

Page 1142, line 12 replace, ‘Here, so called Raoult’ with ‘The Raoult term..’

Will be replaced

Page 1143, line 14 the sentence ‘the total number concentrations of droplet species can be calculated from input parameters’ is a little vague. Input parameters into what?

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It will be clarified that the ‘input parameters’ are dry particle size and composition and droplet size

Page 1143, line 24. ‘The effect that the partitioning to surface’ should read ‘to a surface layer’

Will be corrected

Page 1144, line 1-2. Shouldn’t this read ‘it wouldn’t have a noticeable effect on the bulk concentration’

The sentence will be clarified

Page 1144. What units are the concentration in equation 3. Presumably this is molality since the normal symbol for molality based activity coefficients is used?

Actually any unit is possible as our purpose is to derive equations which are independent of the concentration scale. This will be clarified here and also in other parts of the text.

Page 1145, line 7. Presumably this should read ‘no other species other than the’

The sentence will be clarified

Page 1145. lines 15-20. Here the authors present the need for assuming no concentration dependence of activity coefficients in order to derive analytical equations. This is true, as is the mention that generally activity coefficient models are not validated for surfactant like compounds. Setting unit activity coefficients should indeed be a fair approximation if the correct reference state is assumed in the point raised earlier. This

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should be clarified. Again, I understand the detail given the context of the paper, but some may not.

We will justify our approximation based on the definition of the infinite dilution reference state. In addition, this approximation is tested in the model comparison section by comparing predictions with and without activity coefficients.

Page 1145, line 21. What does 'co' represent? Is this kilogram of solvent (water)? This should be explained here and not later.

c^0 is mass of water (kilograms), volume of liquid phase (liters), total liquid phase number concentration (moles) or any corresponding number used in expressing concentrations. As mentioned above, our purpose is to derive equations which are independent of the concentration scale. We will explain this and the symbol c^0 in the text.

Page 1146, line 7 should read 'the surface tension gradient.'

Will be corrected

Page 1146, line 14. Please list the equations which have been combined to derive the following expression. Presumably this comes directly from equation 3. Also it is tricky for a reader to make their own presumptions as to why additional, previously unexplained variable such as the dissociation factor has been introduced. Whilst a portion of the readers may understand it, some may not. This presents too large a jump in expression derivation. It is presented later on, but introduction of any new variable should be made clear at that specific point in the manuscript.

The equation comes from Eqs 3 and 5 when assuming constant or unit activity coefficients ($d\ln(\gamma_i^B)=0$) and that concentration (in any scale) is linearly dependent on the number of moles ($c^B = n^B/c^0$). If the surfactant dissociates, ion concentrations

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depend on the dissociation factor ν_i . Dissociation factor ν_i and the origin of Eq. 6 will be explained in the text.

Page 1146, lines 16-22. Removal of a subscript 'i' from variable expressions dealing with non-dissociating surfactants suggest the expressions are not considering any complexity beyond 3 compounds. However, upto this point the paper is presented as a generalized derivation without any mention of limitations with regard to complexity of the system (with regards to number). Limitations should be made clear from the beginning, which the authors do complete with regards to some detail at the bulk/surface interface. Do the terms represent behaviour of surfactants in binary mixtures which are then propagated to higher order systems? For example, would then reader apply different sets of equations for a multicomponent mixture?

Removal of a subscript 'i' means that we are not accounting for surfactant–surfactant interactions. However, following the approach of Topping (2010), the single surfactant equations can be applied to surfactant mixtures as well. The number of non-surfactant solutes is unlimited, but there are two sets of equations; mixtures with and without common ions. We will clarify our usage of subscripts and model limitations, and also mention possible extensions.

Page 1147. Line 7. What happens when the negative solution is used? Presumably the positive solution always leads to realistic values for a wide range of parameters in the surface tension equation?

Negative concentration values are obviously unphysical. The solution is physically realistic for all reasonable Szyskowski equation parameters. Of course, it is possible to find such parameters that, for example, n^B will be much greater than n^T , but then the surface tension will be unphysical. We will add a comment about reliability of the equation to the text.

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Page 1147. Further up the manuscript the authors state how assuming unit values for activity coefficients, or any set values, facilitate derivation of the required equations. Given the equations presented in this page one would presume the assumption of ideality is always used. How does this connect with the use of the 'inverse activity coefficient' within the surface tension equation? Are both separate entities?

The 'inverse activity coefficient' is just an adjustable parameter in the semi-theoretical Szyskowski surface tension equation. To avoid the confusion, we will remove the term 'inverse activity coefficient'.

Page 1148. The authors present a cubic expression stating difficulties in finding the correct real root analytically. Reading the abstract one is presented with 'The purpose of this paper is to present analytical equations for surfactant partitioning equilibrium'. Is it therefore only possible to derive analytical expressions for a certain type of surfactant system. A statement should be made with regard to this as it is slightly misleading. Also whilst it is stated that the correct root can be found efficiently, no statistics are given. How does the reader know, for example, that the solution to the simplified cubic expression is much more efficient than solving the 'full' partitioning model? Some example statistics should be given.

There are well known analytical solutions for the cubic and quadratic equations, but only the solution for the quadratic equation is presented. The reason is that there is no single equation that would give the correct root of the cubic equation in all reasonable cases. In addition, numerical methods are very reliable and quite efficient in finding the correct root of the cubic equation. We will clarify our terminology and explain why the solution for the cubic equation is not shown even if it does exist.

We will add a simple example of computing times with (1) iteratively solving the adsorption equation, (2) analytical solution for the quadratic equation, (3) analytical

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solution for the cubic equation and (4) iteratively solving the cubic equation.

Page 1148, line 15. Again, there is reference to 'our analytical partitioning equations' which does not correlate with the previous discussion.

As mentioned above, we will clarify our terminology.

Page 1149. The authors use the SDS-NaCl system for comparison 'full' and reduced complexity expressions. I do appreciate the availability of laboratory data for this system, but how does one prescribe confidence, therefore, in equation 9? Can the authors state what would be required to make this comparison? It is useful to have recommendations for further validation such that the community at large may be able to contribute.

The SDS-NaCl mixture was chosen partly because largest differences are expected for mixtures with common ions. When common ions are properly accounted for, predictions from the simplified and full model are very similar. If common ions are just ignored and Eq. 9 is used as is, differences will be very clear, but this is of course unfair as the difference comes from model considerations, not from accuracy. If there are no common ions (e.g. pure SDS particles), predictions from the 'full' model and Eq. 9 will be practically equal. We will clarify this point. Recommendations for the future validation will be given in conclusions-section.

Page 1152. Conclusions. Again, 'analytical expressions' is slightly misleading. The paper presents a mixture of analytical expressions and reduced complexity formulations. If the authors wish to present the cubic analytical expressions, this should be made clear. Also, the conclusions should reflect the fact that only comparison with one system is made and further validation is required, theoretically and from laboratory studies.

We do not wish to present analytical solution for the cubic equations for the reasons

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mentioned above. We will clarify our point of view and terminology.

We will emphasize the fact that 'analytical' and 'iterative' approaches lead to very similar predictions for a wide range of single surfactant systems with and without additional solutes. The SDS-NaCl system is more like an example of that. Of course, there are some cases such as mixed surfactant solutions which need further validation.

The reader is told that the use of the new equations (all of them or just the quadratic?) reduces the computer time needed for droplet concentration roughly by an order of magnitude but no absolute statistics are given. A brief comparison of time or iterations required for the full model and reduced complexity models would be useful if possible. I leave this up to the preference of the authors.

We will add a comparison of computing times to the manuscript. It will show that the both new equations are significantly faster than the iterative solution.

References

Topping, D.: An analytical solution to calculate bulk mole fractions for any number of components in aerosol droplets after considering partitioning to a surface layer, Geosci. Model Dev., 3, 635-642, 2010.

Interactive comment on Geosci. Model Dev. Discuss., 3, 1139, 2010.