



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

### **Anonymous Referee #1**

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The authors present reduced complexity expressions aimed at treating bulk/surface partitioning. The paper is very interesting, relevant and certainly worthy of being published. The question addressed is complex and the authors have extensive knowledge and background in the area.

Before this, however, I do have some slight concerns regarding what I would call ‘rushed’ derivations which should be clarified for the benefit of the wide readership. The text is sometimes difficult to piece together in places and the reader is told there is a compilation of analytical expressions whilst, in specific cases, a cubic expression is presented with vague reference to difficulties in finding analytical expressions requiring ‘a suitable numerical method’. Similarly, there are vague references to increased computational efficiency, without any statistics presented. The authors should also

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make comment as to what level of complexity (with regard to number of compounds) the equations presented are applicable, comparisons made with the 'full' model for an SDS-NaCl system.

Specific and minor comments are listed below:

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

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?

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

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

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?

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

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

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

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

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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.

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?

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?

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?

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

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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.

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

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.

Page 1152. Conclusions. Again, 'analytical expressions' is slightly misleading. The paper presents a mixture of analytical expressions and reduced complexity formulism's. 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.

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 upto the preference of the authors.

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