**Atmospheric
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Comment

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

'I believe that the work done on measuring multicomponent surface tensions and evaluating different models against the measurements is very valuable and should definitely be published in ACP, and I believe that referees 2-4 have commented adequately regarding the surface tension work. However, I am not entirely happy with the critical

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supersaturation calculations. First of all, the title of section 5 (Activation predictions) is misleading. That a particle exhibits a Köhler maximum at a given supersaturation does not necessarily mean that it is able to activate to a cloud droplet at that SS. Cloud drop formation is a complex process, and dynamic factors as well as the particle size distribution have an effect on the activation. I suggest that the title of section 5 is changed to "Critical supersaturations" (activation is mentioned in several other places, a similarchange should be made where appropriate.)'

Yes the title for section 5 is perhaps misleading considering all of the complicated factors which are actually involved in cloud activation. Thus, the title has been changed to 'Critical Supersaturations'. Similarly, references to cloud activation has now been changed to critical saturation ratios within the abstract, main body of text and conclusions.

'A more important concern, however, is the neglect of bulk-to-surface partitioning of the organics. The authors state on p. 12086 that "Whilst some theroretical studies suggest the effect of highly surfactant compounds may alter the water activity by decreasing the effective number of molecules in the Raoult term, experimental studies for atmospherically relevant species have not been carried out nor has the effect of non-ideality been explored, and as such is not considered here (Sorjamaa et al., 2004)." First, not only is the Raoult term affected: the depletion of surfactants from the bulk of the droplet decreases the bulk concentration used in determining the surface tension, which is therefore increased. Secondly, the bulk-to-surface partitioning is calculated using well established Gibbs surface thermodynamics, which is not dependent on whether the surface tension depressing organic is an atmospherically relevant compound or not, and therefore experimental support of the theory for sodium dodecyl sulfate (Sorjamaa et al., 2004) certainly suggests that it is better to account for surfactant partitioning than not in Kohler calculations, regardless of the type of the surfactant. Thirdly, we have recently shown that the partitioning affects Köhler maxima (and cloud drop activation) also with clearly less surface active compounds than SDS (Sorjamaa and Laaksonen,

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2006, Kokkola et al., 2006). Finally, concerning the non-ideality: it is true that the activity coefficient terms in the Gibbs adsorption equation have been approximated as unity in the partitioning calculations. However, the same approximation is done also in evaluation of the Raoult term in any case, so I do not think that the fact that "non-ideality has not been explored" is a good argument for completely ignoring the partitioning, especially as the available experimental support for the partitioning theory (Sorjamaa 2004) suggests that the non-ideality is a minor issue. I would also like to point out that as the bulk-to-surface partitioning depends on the gradient of the surface tension, the relative differences of Köhler maxima (and not just their absolute values) obtained using the different surface tension models may change somewhat when the partitioning is accounted for.In conclusion, I do not find good reasons for ignoring the partitioning in the Köhler calculations, and recommend that the authors should repeat the calculations before the paper is accepted to ACP.'

The authors are aware of the consideration of bulk to surface partitioning when calculating critical saturation ratios. This indeed was neglected in the last manuscript whereby a 'traditional' approach was used in that total solute concentrations were used within the fundamental Kohler equation. Firstly, in order to explore possible effects of this process highlighted by recent publications a new section has been added to this paper (5.1 Bulk to surface partitioning). In this section a brief summary is given before two examples are given based on one binary system (Suwanee River fulvic acid) and one mixed organic system (Multi 1). For the binary system a solution to the Gibbs adsorption equation is found by assuming the surface excess of water is zero following Li et al (1998). The gradient of surface tension is found by employing the Szykowski equation and activity gradients were calculated using the original UNIFAC framework and the parameters of Hansen et al (1991). Including the effects of partitioning on calculations of surface tension and water activity leads to an increase in the critical super-saturation of 91.19, 37.28, 15.97 and 3.88% at 40, 100, 200 and 500nm dry diameter respectively. The figure also shows predicted critical points if one does not treat bulk to surface partitioning for calculations of both water activity and surface ten-

sion, the latter assumed equal to that of pure water. Interestingly, these predictions are closer to the 'full' partitioning calculations than those where one accurately captures the variation of surface tension with concentration alone. For example, increases in the critical super-saturation of 13.55, 9.88, 4.08 and 0.33 % at 40, 100, 200 and 500nm dry diameter respectively were found when assuming the surface tension of pure water compared to the 'full' partitioning calculations. For ternary systems Sorjamaa and Laaksonen (2006) introduced the constraint that the ratio of water and salt molecules is practically constant as a function of radius in order to solve the appropriate set of equations. Since we are dealing with a multi-component surfactant mixture in this instance we have not used this approach. Instead we have assumed that the behaviour of each organic behaves as it would in a binary mixture. The consequences of using such an assumption will form the focus of future work, as will the influence of including inorganic compounds in systems more complex than ternary mixtures. As before, a solution to the Gibbs adsorption equation is found by assuming the surface excess of water is zero following Li et al (1998). The gradient of surface tension is found by employing the Szykowski equation and activity gradients were calculated using the original UNIFAC and the parameters of Hansen et al (1991). In this instance an increase in the critical super-saturation of 63.98, 31.77, 16.62 and 5.85% is found for 40, 100, 200 and 500nm dry diameter respectively. Interestingly the difference between 'full' partitioning calculations and using the total concentrations combined with the surface tension of pure water is very small with differences of only 2.38, 2.54, 2.15 and 1.21% at 40, 100, 200 and 500nm dry diameter respectively. Thus results clearly show that consideration of bulk to surface partitioning can significantly increase the predicted critical saturation ratio for both the binary and multicomponent systerm. Further analysis will form the focus of future work, where we reference a more detailed analysis of choice of surface tension methods for example. The abstract and conclusions have been updated to highlight the new calculations.

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