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Atmospheric
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Discussions

Interactive comment on "Surfactants in cloud droplet activation: mixed organic-inorganic particles" *by* N. L. Prisle et al.

Anonymous Referee #2

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This manuscript presents new measurements of cloud condensation nucleation activity for internal mixtures of sodium chloride and fatty acid sodium salts. The authors interpret these data in the framework of multicomponent Köhler theory that includes surface/bulk partitioning of surfactants. The data suggest that surface/bulk partitioning is a real effect occurring in internal mixtures, adding to a growing body of evidence that surface tension depression measured in bulk solutions should not be applied in Köhler theory calculations.

I find that the manuscript contains valuable new data and analysis that merits publication in the peer-reviewed literature and that it is well within the scope of the journal Atmospheric Chemistry and Physics. Despite this endorsement, I find that the manuscript requires major revisions before I can recommend it for publication. The reasons for my

assessment are given in detail below and can be summarized as

(1) The manuscript is difficult to read and is hard to digest even for people that work in the same subject area.

(2) The analysis and discussion of the experimental data are insufficient to demonstrate convincingly the adequacy of the theory and its predictive power.

General comments

Personally, I struggled with following the arguments throughout the paper. Certainly this is in part due to the complicated nature of the theory. However, I also fault the authors for adopting a particularly awkward notation. Perhaps a brief look at pg. 24690 demonstrates this best. At least my brain has difficulty with sentences that almost entirely consist of ratios of simultaneously sub and superscripted quantities. There has to be a better way to present this type of information verbally and in a physically intuitive way. One possibility would be to assign names to these ratios and to spell them out in the text. In general the use of inline equations in the text should be eliminated. I would also discourage the cluttering use of sub and superscripts in the same symbol.

The description of the thermodynamic model is difficult to follow. A number of quantities are described in the text, but it seems to me that as presented the theory is incomplete (i.e. one could not repeat the calculations from the equations given in the text). It would be clearer if the authors simply point to the previous paper, and maybe in form of a table or bulleted list, give the assumptions that are made. Alternatively an appendix or supplement with the complete equations could be constructed.

The authors present a new phenomenon, namely that surface-bulk partitioning effectively raises the surface tension above the value of pure water. What I consider the key analysis in this paper is shown in Figure 4, where the authors present observed and theoretical mixing lines for critical supersaturation for surfactant/inorganic particles. This type of plot convincingly demonstrates how badly bulk surface tensions predicts the behavior in internally mixed particles. However, I have a number of comments regarding this analysis:

1) It would be useful and trivial to include the data for the endpoints of the mixing lines, i.e. pure NaCl (available from the calibrations) and pure surfactant (which the authors published previously).

2) I recommend presenting the same type of plot for all of the mixtures. The reason for this is as follows: here for the first time partitioning is shown to effectively raise the surface tension above the value of pure water (I understand that surface tension is still lowered and that it is an overall effect). From Figure 3 it seems that this universally true for the data presented in this manuscript. However, this was not observed previously, either for pure compounds, including C12, or SDS (see Fig. 11 in Sorjamaa et al.). It is therefore crucial to especially analyze the SDS data and show where the 'blue' and 'purple' lines cross, and how the data behave with respect to the theory, including data for the pure compounds. Or is this just because different assumptions were made about SDS in the theory? Or was the theory modified somewhat from the original version? Regardless of the reason, all the data must be shown in this context.

On pg. 24679 the authors state 'In most cases, droplets are sufficiently dilute at the point of activation that ideality of all droplet components must be a reasonable assumption'. I find that this statement conveys a bit of wishful thinking. To my mind asserting that a hydrocarbon molecule with 11 aliphatic functional groups behaves ideally in water seems questionable and is not supported by UNFIAC and similar theories. In fact, it is my opinion that the observations indicate a tradeoff between solution non-ideality, surfactant presence, and partitioning. In the theory presented here it is assumed the number of soluble ions is 2. If one were to assume a lesser value, e.g. 1.5 or 1 to account for the excess free energy of mixing by the hydrocarbon, how would the picture change? What about the unresolved question on why the technically insoluble (for CCN purposes) surfactants behave as effectively soluble? (This should be addressed more clearly in the text since the reference Prisle et al. is rather vague). What

about Na+ organic interactions, making the underlying assumption of ZSR mixing invalid? What about the possibility that droplet composition varied with particle size? While partitioning is undoubtedly important to the problem, the discussion and conclusion should include a disclaimer that the theory used here is incomplete and thus may falsely attribute experimental non-ideality, aqueous solution-non-ideality, non-ZSR mixing or organic-ion interactions, etc. to partitioning effects.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24669, 2009.