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

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## Authors' General Comments

The authors would first like to thank the Referees for their careful revision of our manuscript and many valuable comments. Below we address these comments in a point by point fashion. The manuscript has been revised accordingly, and special attention has been made to avoid repetition and enhance clarity of text and figures. Major changes to the manuscript involve:

- Section 4 concerning the thermodynamic model has been rewritten. It now provides the detailed model equations and furthermore lists the assumptions and

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approximations involved in the model calculations.

- Parts of Section 5, concerning the analysis and discussion of our model calculations, have been revised. Specifically, the following major changes were made:
    1. Figures 3 and 5 in our original manuscript have been removed and instead replaced by more intuitive and easily digestable plots. Figures 2 and 4 appear as parts of these new figures and have therefore been removed as separate figures. In the new plots, previously published experimental data for pure surfactants (Sorjamaa et al., 2004; Prisle et al., 2008), NaCl calibraton data, as well as data from Rood and Williams (2001), are also included for comparison.
    2. Focus is now maintained on the performance of the different model approaches to surfactant properties in representing experimental results. We have therefore chosen to exclude some of the discussion concerning model dynamics, including Figures 6 and 7.
- Model calculation sensitivities were revisited and new discussion and figures are included in relation to this. The sensitivity analysis now addresses more specifically the issues of:
    1. surfactant bulk mass-density
    2. dry particle composition
    3. surfactant dissociation
    4. droplet component activities
    5. surfactant water solubility and micelle formation

  In addition, we briefly discuss possible mechanisms leading to size-dependent deviation of experimental results from equlibrium theory predictions, including size-dependent kinetic effects on droplet activation.

## Response to Anonymous Referee # 1

General Comments

- "Although such CCN experiments have been fairly commonly conducted over the past decade, the influence of surface activity on CCN activity is still poorly constrained, and to my knowledge the specific compositions described here have not been previously reported."

  Similar experiments were reported by Rood and Williams (2001) for mixed particles of SDS and NaCl. However, to our knowledge, the details of these experiments have never been published. The new aspects of the the present study are that we here present results concerning both

  1. experimental CCN activities and
  2. model calculations taking detailed thermodynamic properties of the mixed organic-inorganic aerosol systems into account

  for mixed organic-inorganic particles with highly atmospherically relevant organic surfactants (fatty acid sodium salts).

- "I believe this manuscript is too long and repetitive, particularly in the Results/Discussion section."

  We agree to some extent with the Referee on this point, and have revised our manuscript significantly.

- "I suggest the authors rewrite section 5, making it both shorter and more clearly organized. First, present the results, then discuss the contributions of the individual Kelvin and Raoult terms. Section 5.4 seemed unnecessary to me, as it did not contribute significantly to the conclusions already reached in earlier sections. Even the title of this section - "Activation properties of mixed surfactant-salt particles" - suggest that this is true. Is this not the subject of the entire manuscript?"

We present new results regarding *both* laboratory experiments *and* thermodynamic model calculations. Therefore, comparisons are made between experimental results and model predicitions, as well as between predictions using different thermodynamic representations of surfactant properties. Section 5.4 was then intended as an overall statement of the combined results for the effects of organic surfactant and inorganic salt properties and their interaction for droplet activation. This final synthesis emerges from the preceeding discussion and is not immediately deducible from any of the individual sections.

We however agree with the Referee and, for clarity, we have rewritten Section 5 with focus on the performance of Köhler model calculations using the different surfactant representations, with respect to our experimental observations. The discussion of detailed model calculation dynamics of the individual Kelvin and Raoult terms have therefore largely been removed from the revised manuscript.

- "It might be that, once the repetition is eliminated, the manuscript will be too short to stand on its own. The authors might want to consider combining these results with the surface tension measurements in the Prisle et al. manuscript in preparation and resubmitting."

  The Prisle et al. (2010) manuscript has a different aim from the present study and is more related to fundamental thermodynamics; only the ternary solution surface tension parameterizations are of interest here. Therefore, we prefer to keep the two manuscripts separately.

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We present here measured CCN activities for 15 different particle compositions, each covering a significant and well-resolved range of dry particle sizes and corresponding critical supersaturations. Of these particle compositions, 12 have to our knowledge not previously been reported in the literature, and furthermore represent highly relevant model systems of atmospheric aerosols. In addition, all experimental results are here compared to comprehensive state-of-the-art thermodynamic model calculations, which have not previously been made for mixed organic-inorganic particles of either of the studied compositions. We therefore find that the results presented are fully capable of standing on their own.

- "{...} I suggest that section 5.5.1 ("Micelle Formation in Droplets") be removed."

  We included Section 5.5.1 in our original manuscript to address recurring comments from the audience upon presenting this work in meetings and conferences. The issue of possible micelle formation in droplets is addressed in order to argue why we believe micelle formation does *not* need to be included to ensure thermodynamic consistent *model calculations*. In the revised manuscript, Section 5.5.1 has been removed, as suggested, and the discussion pertaining to the necessity of accounting for micelle formation has been moved to the new section concerning model sensitivities. We believe this clarifies our point.

  We fully agree with this Referee that:

  1. No conclusions can be made from the *experiments* in question, regarding the presence of micelles within the activating droplets.
  2. Very likely, due to surface partitioning, surfactant concentrations in the droplet bulk are well below the respective cmc values at the point of activation, in the *experimental* systems studied here.

3. A significant surface tension reduction in a bulk aqueous solution does not rely on the formation of micelles. In fact, micelle formation would be expected to constrain any further surface tension reduction with increasing surfactant concentration.

We do not believe the statements made in Section 5.5.1 are saying anything to such effects.

Specific Comments

- "L52: Li et al. (1998) did not study the CCN activity of single-component particles; rather, they presented results of calculations of the CCN activity of mixed NaCl-SDS particles."

  The order of the references given was wrong and has been corrected.

- "L64: I don't think "to comply with" is the right phrase to use here - something more like "to distinguish from" or "as opposed to" makes more sense to me."

  The section has been rewritten and the phrase has been changed in the appropriate place.

- "L67: I think a citation of Seidl and Hanel (1983) would be appropriate somewhere in this paragraph - they pointed out the importance of the high surface:volume ratio of activating cloud droplets with respect to surface-active compounds."

  The section has been rewritten and the suggested reference has been included in the appropriate place.

- "L84: I suggest that the main conclusions of the manuscript be removed from the introduction."

  We agree and have done so in the revised manuscript.

- "L115: I am a little troubled by the claim that the mass fractions in Table 1 are "exact", given the author's previous point that "(i)t is an underlying assumption that the relative mass fractions of organic-to-inorganic components in the dry particles reflect the solute composition in the atomizer solution." While I agree that this assumption is reasonable, I still suggest that the authors refer to the "exact mass fractions" of the solutes in the atomized solution, not the dried particles."

  We agree that this notion is misleading and it has been changed in the revised manuscript. Furthermore, the significance of potential differences in atomizer solution and dry particle compositions for model predicted activation properties is now discussed in more detail in the added model sensitivity section.

- "L228: It is somewhat misleading to refer to an ideal solution when accounting for the salting-out effect. I suggest the authors mention that salting-out behavior is explicitly included in some of the theoretical calculations."

  The statement in L228 refers to the assumption of ideal droplet bulk-phase solutions in our model calculations, by assuming all droplet bulk-phase component activity coeffecients are unity

  1. upon iterating the partitioning equilibrium from the Gibbs adsorption equation and
  2. when droplet bulk-phase concentrations are subsequently applied to evaluate the Kelvin and Raoult effects in the Köhler equation.

The inorganic salt may affect surfactant properties by enhancing surface partitioning due to decreased organic solubility in an aqueous salt solution. In the macroscopic ternary surfactant-NaCl solutions, from which the surface tension parameterizations are here made, this leads to increased surface tension reduction at a given surfactant concentration (increased surfactant strength). In our model calculations, non-ideal solution effects, in terms of surfactant-NaCl interactions leading to enhanced surfactant surface partitioning, are taken into account when

1. the ternary solution surface tension parameterizations are used to evaluate droplet surface tension (using $\sigma, \mathrm{p}$ and $\sigma, \mathrm{b}$) and when
2. the partitioning equilibrium is iterated from the Gibbs adsorption equation using the mean-ionic surfactant anion and sodium cation concentrations - where the latter is determined by the presence of both surfactant and NaCl salts - together with the ternary solution surface tension parameterizations (using $\sigma, \mathrm{p}$).

We have revised the description of the thermodynamic model calculations and believe that the accounts of droplet solution ideality and the effects of enhanced surfactant surface partitioning are now more clearly stated.

- "L328: This paragraph seems like it belongs in the introduction."

  We believe these statements are too detailed for the introduction and therefore belong in the discussion. The formulation has been improved in the revised manuscript.

- "L341: I think it would be better to say that enhanced surface partitioning may decrease surface tension, rather than "increase surfactant strength" which is more ambiguous. Alternatively, the authors could define "surfactant strength.""

"Surfactant strength" has been defined for the purposes of this manuscript in Section 4.2 L280-L281. With this definition, the meaning of the statement should be unambiguous, that the surface tension reduction attained at a given surfactant bulk-phase concentration is increased when surface partitioning is enhanced.

- "L358: It should be mentioned that the conclusions of this section are very similar to those of Li et al. (1998)."

  We agree in this point and have included a reference to Li et al. (1998) in the revised manuscript. It must however be noted, that the conclusions made in L356-L358 of our manuscript pertain strictly to the presented experimental results, whereas Li et al. (1998) make their conclusion for thermodynamic model predictions of droplet activation. In addition, the model of Li et al. (1998) does not consider the effects of surfactant surface partitioning on the Raoult effect/term. Their conclusions therefore only with regards to the relative magnitudes of the effects of increasing solute molecular mass vs. decreased droplet surface tension. Therefore, even if the conclusions made here and by Li et al. (1998) are very similar, the arguments involved are not identical.

- "L386: I think it would be better to say something like "either the equilibrium Köhler or the surface partitioning models.""

  The partitioning model iterates the equilibrium distribution of surfactant and other droplet components between bulk surface phases. These are then implemented in the Köhler equation for evaluation of the equilibrium droplet saturation ratio. All model calculations therefore assume equilibrium conditions for the droplets.

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In L385, we refer to the potential existence in our experiments of a particle size-dependent effect, which is unaccounted for in our model calculations. We address possible mechanisms leading to such size-dependent effects in more detail in the revised manuscript. These may arise from either

1. size-dependent conditions during particle production, or
2. size-dependent kinetic effects acting during droplet activation.

The first mechanism is not considered in the general model calculations, but the effect is addressed in the sensitivity study of the revised manuscript. The latter mechanism is the reason we emphasize that our model calculations are in all cases based on equilibrium Köhler theory, which will inherently not account for such kinetic effects. We believe this has now been clarified in the revised manuscript.

- "L390-391: Why are the words "smaller" and "larger" in quotes?"

  We felt it was a somewhat ambiguous distinction of particle sizes, which was made here mainly for sake of illustration.

- "L525: I think it would be better to say "due to the limited amount of SFT relative to the large surface area" than "due to surfactant partitioning" - it is confusing because it is, in fact, surfactant partitioning that causes sigma to be reduced in the first place."

  We agree that this formulation may be somewhat ambiguous and have changed it in the revised manuscript. The subtle point was that surface partitioning in macroscopic solutions causes surface tension to be reduced more than would be the case for an isotropic aqueous solution of dissolved surfactant. In microscopic droplets, however, the large surface-area-to-bulk-volume ratios

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can lead to significant bulk-phase depletion and, with a given concentration gradient, diminished surface excess, of the surfactant. The surface tension reduction may therefore be smaller than in macroscopic solutions of the same total composition.

- "L551: Capitalize "CCN"."

  OK

- "L593-594: I am not sure what is meant by "NaCl by mass fraction" here."

  We mean that, when a component comprises a given mass-fraction of the dry particle, NaCl will yield a larger Raoult effect in a given size droplet than any of the surfactants, solely due to the smaller molecular mass of NaCl (and in case of surfactant bulk-phase depletion, the difference will be even greater).

- "I found Fig. 5 difficult to read - too many data points on top of one another. I would recommend splitting it into four panels, one for each SFT, as was done in Fig. 3. Also, both Figs. 3 and 5 might benefit from use of a variety of symbol shapes (squares, diamonds, etc.) - hard to say without seeing it done, but it seems like it would be worth a try to see if it improves clarity. Also, regarding Fig. 5, there are some blue $(\sigma, \mathrm{p})$ points depicting large errors $(\sim 0.6\%/\%)$ between theoretical and experimental SS. I found this confusing, as the general conclusion of the paper is that the $\sigma, \mathrm{p}$ formulation matches the experimental data well. The authors should comment on these anomalous data. Also, I only see one point in Fig. 3 above $0.4\%/\%$ for the $\sigma, \mathrm{p}$ formulation, which makes me wonder if one of the figures has incorrectly plotted data."

  We have changed Figs. 3 and 5 in the revised manuscript, as explained above. As suggested, results are split into separate panels for the different surfactants. The presentation of our results in the revised figures should now be more intuitive and easy to read.

The error bars in Fig. 5 are reduced by the experimental critical supersaturations ($\pm 2\tau / SS_c^{\mathrm{exp}}$) and large error bars may therefore partly reflect low absolute experimental values for the particles. The $\sigma, \mathrm{p}$ representation is however also seen to overpredict $SS_c^{\mathrm{exp}}$ for the smaller particles with the larger mass-fractions of FAS. This is seen more clearly in the revised figures, and the reasons are discussed in the text.

We have not been able to find any discrepancy between the data plottet in Fig. 3 and the subset shown in Fig. 5. Specifically, we do not see more points above $0.4\%/\%$ for the $\sigma, \mathrm{p}$ representation in Fig. 5 than in Fig. 3.

Technical Comments

- "L207: The variables for mass fraction should be italicized."

  We had in our original manuscript adopted the notation that experimental quantities were not italicized, whereas model quantities were italicized. This notation has however been changed according to journal typesetting standards and we have adopted a slightly different notation in the revised manuscript to convey the same meaning. We emphasize that, in our original manuscript, the italicized mass fractions are the droplet bulk-phase relative mass-fractions of surfactant and NaCl, evaluated in the model calculations. The non-italicized mass fractions are the atomizer solution relative mass-fractions of surfactant and NaCl, determined in the experiments. Even if the total droplet solute compositions are assumed to reflect the solute composition of the atomizer solution, due to droplet bulk phase depletion, these quantities are not identical when surfactant surface partitioning is accounted for in the calculations.

- "L318, and elsewhere: Correct "Fig.s" (either "Figs." or "Fig.")

  OK

- "L318: Variables should be italicized here and later in the manuscript."

  See comment to L207 above.

- "L371: The word "respectively" is unnecessary."

  OK

## Response to Anonymous Referee # 2

- "The manuscript is difficult to read and is hard to digest even for people that work in the same subject area {...} 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 {...} In general the use of inline equations in the text should be eliminated."

  We do not disagree with the Referee on these issues, which have been discussed extensively upon the preparation of our original manuscript. Nevertheless, in order to keep notation shorthand while maintaining a precise formulation, we find that spelling out the names of the different quantities would be too long and introduce additonal difficulty in digesting the material presented. As an example, a central quantity is $SS_c^{\sigma,\mathrm{p}}$, the "particle critical supersaturations predicted from equilibrium Köhler theory, using concentration-dependent droplet surface tension reduction given by the ternary solution parameterizations and accounting for surfactant surface partitioning in both Kelvin and Raoult terms", as described in Section 4. For the three surfactant property representations employed, we believe to present an unambigous, yet still condensed, notation, which we find is crucial for precision, clarity and readability. We therefore opt to preserve the notation as it is.

  We do agree that the inline equations could indeed have been presented in a more reader-friendly way. As we have chosen to exclude the discussion concerning details of the different model representation dynamics, we believe this largely takes care of the problem for the present purposes. We will however keep this point in mind for future work.

- "The analysis and discussion of the experimental data are insufficient to demon-

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strate convincingly the adequacy of the theory and its predictive power."

The main conclusions drawn from results presented in our manuscript are

1. Using the surfactant bulk solution representation $(\sigma, \mathrm{b})$ in Köhler model calculations greatly underestimates experimental critical supersaturations.
2. The comprehensive thermodynamic representation accounting for reduced surface tension and surfactant surface partitioning $(\sigma, \mathrm{p})$ is capable of predicting experimental data well.
3. Contrary to what was observed for pure surfactant particles (Prisle et al., 2008), $\sigma, \mathrm{p}$ can yield significantly different predictions of critical supersaturations than simply ignoring surfactant properties altogether and assuming the constant surface tension of pure water throughout droplet activation $(\sigma_{\mathrm{w}})$. For the mixed particles, the latter can lead to underestimations of experimental critical supersaturations, but on the other hand appears to be applicable for particles with less than 50% by mass of surfactant.

We find that our main result (1) is firmly supported in all cases studied by the presented experimental data and model predictions. We also believe that the superiority of $\sigma, \mathrm{p}$ in comparison to $\sigma, \mathrm{b}$ (2) is clearly demonstrated in all cases, especially considering that both of these representations constitute state-of-the-art thermodynamic modeling of the systems at hand. We believe this is more clearly presented in the new figures of the revised manuscript.

The results regarding $\sigma, \mathrm{p}$ and $\sigma_{\mathrm{w}}$ (3) are less conclusive in terms of specific gauges for the applicability of either approach, as we point out. These new results concerning the potential inadequacy of the simple solute model are however of great significance to the representation of organic surfactant properties in future model calculations accounting for droplet activation. We therfore find it important to report our contributions.

- "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)."

  We agree with this point and have revised the description of our model calculations thoroughly, as explained above. We believe that the information and level of detail now supplied is sufficient for reproduction of both our Köhler and partitioning model calculations by others.

- "What I consider the key analysis in this paper is shown in Figure 4 {...} 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."

  In the revised manuscript, we have expanded Figure 5 into 4 individual figures, showing the comparison between measured and model calculated critical supersaturations for each of the studied surfactants separately. Previously published data has been included for comparison, as mentioned above.

- "The authors present a new phenomenon, namely that surface-bulk partitioning effectively raises the surface tension above the value of pure water {...} 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."

We appreciate that this Referee does indeed understand the details concerning the interrelated effects of surface partitioning on droplet activation via both Kelvin and Raoult terms. However, we object to the notion of an effectively raised surface tension above the value for pure water. Avoiding any ambiguity arising from such a notion was partly the motivation for the detailed discussion of model dynamics presented in our original manuscript. We emphasize that the droplet surface tension is *not* raised above that of pure water, which would be counter-intuitive regarding aqueous droplets comprising water-soluble surfactant solutes with the macroscopic bulk-solution properties presented here. Rather, surface partitioning decreases the amount of surfactant solute in the droplet bulk-phase, and this raises the Raoult term to higher values, for a given droplet size and corresponding total solute concentration. The critical point of droplet activation is then reached for smaller droplet sizes, where the Kelvin term is larger, due to greater surface curvature, despite the droplet surface tension still being reduced, compared to pure water.

The Referee makes an important point in emphasising that $SS_c^{\mathrm{exp}} > SS_c^{\sigma_\mathrm{w}}$ was not observed for any of the pure component particles previously reported and this has been further highlighted in our revised manuscript.

Model predicted $SS_c^{\sigma,\mathrm{p}} > SS_c^{\sigma_\mathrm{w}}$ was observed for pure C8Na and C10Na in our previous study, but not for pure C12Na and SDS (Sorjamaa et al., 2004; Prisle et al., 2008). Careful inspection of the new figures analogous to Figure 4 show that a cross-over of predicted $SS_c^{\sigma,\mathrm{p}}$ (blue) and $SS_c^{\sigma_\mathrm{w}}$ (pink) curves occur at high mass-fractions (close to 100%), for mixed particles with SDS, but not for any of the FAS. It is not generally expected from theory that such a cross-over of model predictions will occur, but sometimes it is seen. Future work must clarify which model representation of surfactant properties describes observed activation best, for other surfactants and particle compositions.

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- "{...} Or is this just because different assumptions were made about SDS in the theory? Or was the theory modified somewhat from the original version?"

  Minor changes have been made to the calculations in the present study, from the model versions used in Sorjamaa et al. (2004) and Prisle et al. (2008). For particles with SDS, these were seen in validation calculations to have only correspondingly minor effects on predictions. The main differences, between model results for pure FAS in Prisle et al. (2008) and mixed particle calculations with nearly 100% FAS in the present study, are due to the different binary and ternary solution surface tension parameterizations employed.

- "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 {...} What about the unresolved question on why the technically insoluble (for CCN purposes) surfactants behave as effectively soluble? {...} What about Na+ organic interactions, making the underlying assumption of ZSR mixing invalid? What about the possibility that droplet composition varied with particle size?"

  The Referee has a good point, that it would be desirable if droplets were indeed sufficiently dilute at the point of activation for the ideal-dilute solution approximation to apply, and that this may not be exactly the case within the actual experimental systems. Since the relevant concentration-dependent component activity coefficients and other solution properties are currently in most cases not available in the literature, this is however a necessary approximation in our model calculations.

As explained above, we have tested the sensitivity of our model predictions to solution effects in terms of

1. surfactant dissociation,
2. droplet component activities, and
3. limited dissolved surfactant concentration

for the droplets, as well as dry particle composition, in terms of

1. FAS bulk mass-density and
2. deviations from the atomizer solute composition.

The influences of these mechanisms for the predictive efficiency of the different surfactant representations in our Köhler model calculations are discussed in the revised manuscript.

It must be noted that UNIFAC theory is not valid for electrolytes, but we have used droplet component concentration-dependent bulk-phase activities predicted from Debye-Hückel theory (Debye and Hückel, 1923; Clegg et al., 1992). In addition, predicted surfactant bulk concentrations at activation differ greatly with the different representations, depending on whether surface partitioning is accounted for, or not. This affects the sensitivity of calculations to concentration-dependent solution effects.

ZSR mixing can in this context be regarded as an expression of droplet solution ideality and is thus an underlying assumption for the droplet solution bulk-phase components, in the Köhler calculations. As explained above - in relation to the similar non-ideality issue raised by Anonymous Referee #1 - effects of Na+/organic interactions are partially accounted for by

1. using ternary SFT-NaCl solution surface tensions ($\sigma$, p and $\sigma$, b) and
2. using mean-ionic concentrations for Na+ and SFT- ions in the partitioning calculations ($\sigma$, p).

The potentially insufficient representation of solution component non-ideal mixing interactions is tested by using the Debye-Hückel activities for all droplet components in both Köhler calculations and possible partitioning calculations. It is not the most significant source of model sensitivity, especially not when applying the $\sigma$, p representation.

- "{...} 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."

  We find that the results presented in this work, together with the model sensitivity analysis, generally support the notion that surfactant properties significantly influence droplet activation, and that this occurs via both surface tension reduction and surface partitioning. Nevertheless, we do indeed agree with this Referee that we cannot unambigously conclude from the present results, that activation properties of surface active organics in the mixed particles are in fact caused by these mechanisms, as opposed to other potential explanations. We do not wish to state, that our results prove conclusively that surfactant partitioning is the cause of the activation behavior observed in our experiments, but rather that the experimental observations can be explained in a thermodynamically consistent way from surface partitioning. We believe this is clarified in the revised manuscript.

Specifically, the sensitivity calculations show that the large underpredictions of experimental critical supersaturations by the bulk solution surfactant representation cannot be resolved by any of the investigated mechanisms, even for perturbations beyond what we find realistic for dilute droplets. The relative performances of the partitioning and simple solute surfactant representations are more ambiguous, and $\sigma_\mathrm{w}$ can in some cases be favored by plausible perturbations to the model parameters and assumptions applied. Likely, a combination of effects such as mentioned are present in the actual experimental systems and it is certainly possible that some degree of trade-off between these mechanisms and the specific surfactant properties investigated may determine droplet activation. Granted, we cannot from the experimental and modeled results at hand discriminate between the relative significances such trade-offs.

It is nevertheless remarkable and very reassuring that, in particular for SDS, where well-known ternary surface tensions and bulk density information are available, the partitioning representation is able to closely reproduce our experimental observations in a thermodynamically consistent manner, without invoking additional solution phenomena, such as dissolution, dissociation, and solute or water non-ideality. We believe this points to the adequacy of $\sigma, \mathrm{p}$ for describing activation properties of the experimental systems at hand. Naturally, in order to be gererally established, this must be investigated for many other types of mixed organic-inorganic particle systems, which will be the focus of future work.

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