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Discussions

Interactive comment on "Modeling CCN activity of chemically unresolved model HULIS, including surface tension, non-ideality, and surface partitioning" *by* Nonne L. Prisle and Bjarke Molgaard

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We thank both reviewers for their careful revision of our manuscript and constructive comments. To address related points made by both reviewers, we here first present a summary of the aim and context of the present work. We have aimed to clarify these points in the introduction, results and discussions sections in the revised manuscript. Below we respond to the specific comments from each reviewer in a point-wise fashion.

The overall aim of this work is to present a thermodynamically consistent frame-

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work that enables self-contained, predictive calculations of droplet growth and activation with considerations of both surface adsorption and surface tension equation for chemically unresolved, surface active complex organic mixtures representative of real atmospheric aerosols. Similar to our previous work (e.g. Prisle et al. 2010), the model is based on coupling Köhler theory with the Gibbs adsorption and Szyszkowski surface tension equations. However, the present model is formulated on a mass-basis, to allow for a quantitative description of chemically unresolved organic mixtures with immediate atmospheric relevance. We show that, with this formulation, it is possible to obtain composition-dependent descriptions of non-ideal solute interactions governing both bulk and surface properties necessary to predict droplet growth and activation. The model is used to calculate a suite of properties for growing and activating droplets, to illustrate the intricate ways in which organic surface activity affects this process. Results of the presented framework are compared to those of several other predictive Köhler frameworks, where the effects of surface active components in droplet solutions are considered in different ways.

The common presence of surface active organic material in atmospheric aerosols is now well-established (e.g. Petters and Petters, 2016; Gérard et al. 2016; Kroflič et al. 2018), whereas the influence of surface activity on aerosol hygroscopic growth and cloud droplet activation is still under debate. Because specific characterization of key properties, such as water activity and surface tension, are still very challenging to obtain directly for activating droplets (e.g. Bzdek et al. 2020), a robust model framework is needed to gain further insight into the droplet equilibrium growth process. This specifically requires the ability to predict the droplet water activity and surface tension as functions of composition, as the droplets grow by condensation of water.

By definition, surface active (surfactant) material adsorb at the solution surface, leading to enhanced surface concentrations (activity), compared to the bulk phase, and an ensuing concentration gradient between the bulk and surface of the solution.

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Due to this enhanced surface activity, surfactants can have a large impact on reducing surface tension of aqueous solutions at a given concentration. At equilibrium, the surface equation of state can be given in terms of either the bulk or surface composition, as these quantities are related via the equilibrium bulk-to-surface concentration gradient for a given surface active substance.

Several techniques exist to experimentally determine the surface tension–composition relations for surfactant solutions, which predominantly require macroscopic (e.g. millimeter-scale or larger) sample sizes. In these macroscopic solutions, surface adsorption and enhanced activity of surfactants involve only a small fraction of the total surface active solute and therefore have negligible effect on the bulk composition. Surface tension–composition relations are therefore typically reported in terms of total solution composition, which closely corresponds to the bulk composition and is relatively easily quantified for macroscopic solutions.

For microscopic and sub-micron activating cloud droplets, however, a range of studies, including our own previous work (e.g. Prisle et al. 2008; 2010; 2019; Kristensen et al. 2014; Lin et al. 2018; 2020 and references therein), have consistently demonstrated that treating the droplet as a macroscopic solution, by using solution property relations based on total composition without explicit consideration of the impact of surface adsorption on bulk composition, can lead to gross over-predictions of cloud condensation nuclei (CCN) activity. The reason for this is the depletion of the droplet bulk-phase concentration of surface active solute from surface adsorption, due to the large surface area (A)-to-bulk volume (V) ratio of small droplets. In micron-sized droplets, A/V is increased by several orders of magnitude, compared to macroscopic solutions, which can significantly change the partitioning of surface active species between the bulk and surface phases (Prisle et al. 2010). This size-dependent shift in both surface and bulk composition at adsorption equilibrium in turn affects composition-dependent solution properties, including droplet water activity (a bulk

property) and surface tension (a surface property). Until recently, the experimental evidence for this effect has been indirect, from the reported inability of macroscopic surface tension–composition relations to reproduce observed droplet activation properties. Bzdek et al. (2020) recently provided the first direct experimental demonstration of this surface partitioning bulk depletion effect on droplet surface tension.

In Köhler calculations, experimentally determined macroscopic solution property–composition relations are connected to those of a growing droplet with changing A/V via a partitioning model, which is based on an adsorption isotherm and surface tension equation of state for the surface active components. Several such partitioning models have been presented in recent years and deployed with varying degrees of success to reproduce measured CCN activity for different surfactant containing particle systems. An overview of the most commonly used models is given by Malila and Prisle (2018). Common for all these partitioning models is that composition-dependent droplet properties are required in some form. It is our assessment, that uncertainties related to these properties and their variation across relevant droplet compositions and conditions are likely to be responsible for most of the open questions related to the description and impact of surface activity and partitioning in Köhler theory. Even when the molecular identities and mixing state of droplet components are well known, as is assumed to be the case in laboratory studies of simple binary and ternary proxy systems, the variation of solution properties across the full range of compositions and conditions spanned by growing and activating droplets are typically unconstrained by measurements. A common and often necessary assumption is therefore to assume some form of ideal mixing properties in growing droplets, typically with simple volume additivity of pure components or unity activity coefficients in all mixing states. Both these assumptions miss any solute–solute and solute–solvent interactions which can affect both water bulk activity and surfactant surface activity.

Previous studies involving predictive modeling of cloud droplet activation have

been carried out for model binary and ternary droplets comprising simple surfactants of assumed well-known composition and composition-dependent impact on surface tension and water activity. However, real atmospheric organic aerosols, as well as more elaborate laboratory experiments, typically involve complex chemical mixtures which are either partially or entirely unresolved. Even in the hypothetical case where all components of the aerosol mixture and their quantities would be known, it is still not realistic to obtain a well-constrained description of their variation in all solution states corresponding to growing droplets. For such mixtures, several approaches can been taken to construct a prescriptive model for droplet growth. A common approach is to assume a well-known single compound or mixed proxy system to represent the properties of the unresolved mixture. The key challenge of this approach concerns how representative the chosen proxy is of the actual complex aerosol and in particular how well it represents the response to varying conditions. Furthermore, for all but a relatively small group of atmospherically relevant compounds, interaction parameters even for binary, as well as higher order, aqueous solutions are typically not constrained by measurements. For specific compounds, measurements of for example composition-dependent surface and bulk activity can be made and used to construct continuous parametrizations for predictive modeling. However, capturing the full range of a multi-dimensional composition space for higher order mixtures requires extensive work. This approach is therefore only feasible for specific mixtures.

In the present work, we take the approach of producing continuous parametrizations constrained from macroscopic measurements for bulk water activity and organic surface activity in aqueous mixtures comprising unresolved organics. Application of such parametrizations to a partitioning model involves two key steps. First, we describe composition dependency of aqueous solutions in terms of only three conceptual components – water, inorganic salt, and organic – on a mass basis, which is a quantity readily determined in experiments without specific knowledge of the molecular identity of all solution components. Second, we develop our framework to

predict bulk/surface partitioning of the surface active organic in our droplets in terms of mass units. This is the overall aim of this work. We show that with continuous mass-based parametrizations of surface tension and water activity, we can predict bulk/surface partitioning and droplet growth to reproduce measured CCN activity in the form of critical supersaturations for complex, unresolved Nordic Aquatic Fulvic Acid (NAFA) mixtures. In such mixtures, the units of partitioning mass in reality vary according to the distribution across unknown molecular sizes. Here, we show that in most conditions studied, predictions of droplet activation are not very sensitive to the assumption of a single size of partitioning mass.

Thermodynamically consistent, predictive modeling allows us to investigate details about how droplet properties change as they grow and activate. For our organic aerosol model system NAFA, including experimentally constrained accounts of non-ideal interactions in both water and organic surface activity leads to predictions of droplet behavior which closely resembles that previously seen for systems comprising simple, strong surfactants, such as sodium dodecyl sulfate (SDS) and fatty acid salts. The "missing Raoult effect" from bulk-phase depletion due to surface adsorption overpowers any enhancement of droplet growth and activation from decreased surface tension. The result is that the surface active component have nearly vanishing overall impact on droplet growth and activation, corresponding to an insoluble surfactant, or a hygroscopicity parameter of $\kappa = 0$. Recent work by Ovadnevaite et al. (2017), as well as some of our own work (e.g. Hansen et al. 2015; Lin et al. 2018; Prisle et al. 2019), on the other hand provide evidence for significantly reduced surface tension in activating droplets comprising complex organic mixtures. These differing results highlight that most likely none of the existing Köhler frameworks fully capture the breadth of interactions governing effect of organic surface activity in cloud droplet activation.

The advantage of the present model is that it is fully predictive and take all non-ideal

interactions into account via continuous parametrizations independently constrained by measurements. No additional parameters are introduced in the framework. A remaining disadvantage is that while water activity and surface tension can be accurately measured with standard instrumentation, these experiments and the multivariate fitting are still both non-trivial and labor intensive and require significant amounts of sample material to obtain a sufficient number of data points for robust fits. Here, we used the comprehensive data set of water activity, surface tension and CCN activity for the aqueous NAFA–NaCl system published by Kristensen et al. (2014) and Lin et al. (2020). We are currently unaware of any other data sets that would allow for a similar analysis. Our hope is, however, that the framework presented here will motivate more of these measurements, to allow thermodynamically consistent characterization for a broad range of surface active organic aerosol systems. This will contribute significantly to clarify the compositions and conditions where each of the effects of surface activity is dominating.

Referee #1

Issues:

1. The modeling results are interesting and informative. However, the major issue with this work is that the novelty is limited to the application of the models to the NAFA + NaCl data. I hesitate to recommend publication without extending the model framework and discussion to other mixtures. This would tend to better highlight, and shift the focus to, the context of this work with regard to atmospheric aerosols.

   The overall aim of this work is to present a model framework that enables thermodynamically consistent, independent and fully predictive Köhler calculations for unresolved complex chemical organic aerosol mixtures with consideration of non-ideal solution effects. We apply the model to illustrate

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   the impact of surface activity on cloud droplet activation for the unresolved organic model system NAFA. To our knowledge, this is the first time such consistent and comprehensive modeling with a full account of non-ideal solute interactions on both water activity and surface tension in a Gibbsian bulk/surface partitioning framework have been presented for complex aerosol mixtures. We are not aware of any other framework that currently allows to perform similar predictive, independent calculations for unresolved mixtures. The present results add to those of other recent works (e.g. Nozière et al. 2014; Ruehl et al. 2016; Ovadnevaite et al. 2017; Forestieri et al. 2018; Prisle et al. 2019; Lin et al. 2020) in highlighting the complex mechanisms of surface activity impacts on droplet growth and activation, which remain to be fully constrained.

   We fully agree with the reviewer that investigating other aerosol mixtures comprising unresolved surface active organics will be needed to shed further light onto the general nature of the present as well as previous results. However, conducting the full suite of surface tension, water activity, and cloud condensation nuclei activity measurements needed for the presented analysis represents a large amount of work, just as constructing suitable continuous, ternary parametrizations from this data to facilitate the Köhler modeling is non-trivial. Kristensen et al. (2014) present only 2-dimensional parametrizations (with linear composition domain) from their data, which do not enable full calculations of surface/bulk partitioning. Currently, we are not aware of any other system for which a similar data set exists to perform these calculations. Prisle et al. (2019) use the presented mass-based framework for pollenkitt model organic aerosol mixtures, but fully constrained continuous ternary parametrizations could not be obtained with the limited amount of sample available and resulting spread of data points. We therefore find that obtaining additional comprehensive data sets, constructing full ternary parameterizations and performing Köhler model simulations for additional systems should be the focus of future work. It is our

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hope that the presented framework and addition of the modeling results for NAFA droplet mixtures to the general discussion regarding the role of surface activity in cloud formation will motivate future comprehensive studies to deliver the necessary detailed data sets.

2. How do the models of the present study compare to the model used by Kristensen et al., 2014? The original model was simple and should be discussed.

Kristensen et al. (2014) use two different Köhler models to predict measured CCN activity of NAFA–NaCl particle mixtures (their Fig. 7). These models do not consider bulk/surface partitioning and therefore correspond to the models B (bulk solution, concentration-dependent surface tension and water activity) and K (bulk solution, constant surface tension equal to that of water and concentration-dependent water activity) of the present work, with some differences in the actual model implementation. In this work, models B and K are used for reference to predictions with the full and simple partitioning models and therefore for consistency run with the full ternary surface tension and water activity parametrizations presented here, even if these are not needed in absence of partitioning calculations. Kristensen et al. (2014) used simpler, 2-dimensional fits to the surface tension and water activity data, which are not continuous with respect to variation in the NAFA–NaCl mixing ratio and therefore have slightly different forms than the full ternary fits used here, even at the lines of intersection. It should also be noted that the surface tension parametrizations used by Kristensen et al. (2014) are made for data points corresponding to measurement times $t = 0$ s, whereas here we have used data corresponding to measurement times $t = 600$ s. A detailed investigation of the effect of surface tension time-dependence has recently been made by Lin et al. (2020).

Kristensen et al. (2014) find, as also seen in the present work and a num-

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ber of other studies (see point 3 immediately below), that using bulk surface tension (our model B) greatly exaggerates the CCN activity of surface active NAFA mixtures. Similar to the present work, Kristensen et al. (2014) also find that the basic Köhler model (our model K) where NAFA activity is completely ignored gives good agreement with measured CCN activity for NAFA–NaCl mixtures with up to 50% NAFA, as well as for pure NAFA particles (but not for mixtures with 80% NAFA). This counter-intuitive result has previously been seen also for simple, strong surfactants, such as SDS and C8-C12 fatty acid salts (e.g. Prisle et al. 2008; 2010; 2011). Comprehensive modeling with a full account of NAFA bulk/surface partitioning and solution non-ideal effects (our presented model P) show that the good agreement of model K with measured CCN activity and close resemblance of model K to predictions with the full partitioning model P are in large part due to cancellation effects between the impact of surface activity on the individual Kelvin and Raoult terms of the Köhler curves. In addition to Figures 2 and 3 in the original manuscript illustrating these effects, we have in the revised manuscript added plots showing the full Köhler growth curves, as well as surface tension, water activity, and partitioning factor along these curves, for selected NAFA solution droplets. These plots replace Figure 5 in the original manuscript. This nearly full cancellation effect may not be present for all surfactant-containing droplet mixtures, as evidenced by the findings of recent studies (e.g. Ruehl et al. 2016; Ovadnevaite et al. 2017; Prisle et al. 2019), which further strongly suggests that the basic Köhler model K is too simple to fully capture CCN activity of surface active material across all atmospherically relevant particle compositions and conditions and that, in the general case, a full partitioning model is needed for robust predictions.

We have emphasized these points in the discussion of the revised manuscript.

3. Page 10. It should be noted here that experiments by other groups have also

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found that using bulk surface tension exaggerates the CCN activity of surfactants, some of whom are already cited here (e.g., Rood and Williams, 2001; Alshawa et al, 2009; Ruehl et al 2010; Harmon et al., 2010; Zamora et al., 2013; Petters and Petters 2016; Forestieri et al. 2018).

This result is now emphasized more in the discussion and additional references have been added in the revised manuscript.

4. Page 18 line 15, 16: "This may prove to be a signature feature of surface activity impact on CCN activity for relatively strong surfactants." This statement and the statements before could be better developed and discussed in context of past (and future) findings for simple and complex mixtures. See past comment [3].

In continuation of the response to point 2 above, mutual agreement between experimental critical supersaturations and Köhler model predictions with both the full partitioning model and basic Köhler theory has been observed for strong, simple surfactant mixtures in several previous studies, including our own work (e.g. Prisle et al. 2008; 2010; 2011). The good agreement can be explained by cancellation effects between the perturbations in predicted Kelvin (surface tension depression) and Raoult (water activity depression) terms for growing droplets, compared to the basic Köhler model, introduced by surface activity. Several recent studies (e.g. Ruehl et al. 2016; Ovadnevaite et al. 2017; Prisle et al. 2019) find evidence that surface tension is significantly reduced in activating droplets and therefore suggesting that similar cancellation effects are likely not always present. These studies involve both simple and complex surfactants, at least some of which are less strong than those where near-full cancellation has been predicted. This led us to speculate that cancellation effects of surface activity seen for both NAFA and simple surfactants could be a feature of CCN activation in the presence of strong surfactants. Future work

involving thermodynamically consistent, independent, full partitioning modeling will contribute to verifying this speculation. The model of Ruehl et al. (2016) involves fitting to droplet growth curve measurements and is therefore analytical rather than predictive. The model of Ovadnevaite et al. (2017) is predictive for a selected proxy composition. Prisle et al. (2019) did not use a fully ternary parametrization of surface tension and did not account for potential non-ideal water activity. These results can therefore not be conclusively commpared to predictions for NAFA with the present model.

Differences between the Köhler models used in the present work and the models of Ruehl et al. (2016) and Ovadnevaite et al. (2017) are discussed in more detail in response to Reviewer #2 below.

We have emphasized these points in the discussion of the revised manuscript.

Other comments:

1. Page 20 line 20-27. This paragraph makes an important point about equilibration timescales that could be featured more prominently at the beginning of the paragraph. The paragraph states that the surface tensions measured after 10 minutes using the macroscopic pendant drop method should be applicable to the microscopic droplets, based on their much smaller diameters (and therefore smaller equilibration times). It has been said elsewhere that CCN experiments with surfactants are invalid due to long partitioning times (measured for macroscopic droplets). The present work makes a good explanation why this is not the case. This is informative and could be highlighted.

We trust the reviewer refers to Page 7 line 20-27. Measurements of surface tension at different times after formation of the (macroscopic) droplet

surface for a wide range of NAFA–NaCl aqueous mixtures were reported by Kristensen et al. (2014) and Lin et al. (2020). Kristensen et al. (2014) used separate 2-dimensional parametrizations based on the highest surface tensions, corresponding to the first measurements after surface formation (t= 0 s), in their bulk solution model. Presumably, these values provided the best representation of measured CCN activity without including bulk/surface partitioning effects. The use of surface tension data corresponding to measurement times t= 600 s in the present work is based on a simple, intuitive argument, which was also presented in previous work (Prisle et al. 2008). Lin et al. (2020) recently presented a detailed analysis of the effects of using of surface tension parametrizations corresponding to different measurement times in Köhler calculations. They observe complex relations between the influence of droplet size and composition, surface adsorption, and measurement time. A clear progression of predicted surface adsorption is seen when using surface tension parametrizations corresponding to longer measurement times, but the Kelvin and Raoult effects of surface adsorption on predicted CCN activity nearly cancel at every time step. Because we are not aware of any experiment that would currently allow verification of these predictions, and because we are only aware of this single existing data set to enable these calculations with considerations of time dependence in connection with bulk/surface partitioning, we cannot at this point say how general this feature is.

We have chosen to keep the arguments for choosing surface tension data corresponding to measurement times t= 600 s in the present place in the revised manuscript. We have added the points about the findings of Lin et al. (2020) in connection with the discussion of cancellation of effects on Kelvin and Raoult terms from bulk/surface partitioning.

2. Figure 1 is difficult to read. Could SS be plotted on a log scale as in the earlier

papers (Prisle et al., 2010 and Kristensen et al. 2014), or could 0%, 20% 50% 80% and 100% each get their own panel with four models? Please clarify.

Results in Figure 1 are now shown on a log-log scale. We still prefer to emphasize in each panel the performance of a given model across the full CCN data set.

3. Page 9, line 20-22: other studies have also reported this trend for strong surfactants mixed with NaCl and for marine biopolymer mixed with NaCl (Petters and Petters 2016; Dawson et al. 2016). Similar to Kristensen et al. 2014, marine organic aerosols were the motivation of Dawson et al., thus it would be relevant to point out that the trend holds for more complex aquatic molecules.

Indeed, this trend has been commonly observed. Additional references and contrast to the work of Dawson et al. (2016) have been added to the discussion in the revised manuscript to clarify.

4. Should figure S1 be called, model P at different temperatures? Please clarify. Also, some mention and explanation of the data points would be appreciated in the caption.

Both aspects have been clarified in the revised figure caption.

5. P5 line 15-16: "the NAFA bulk–to–surface partitioning equilibrium is iterated to determine the droplet bulk phase composition" – this means it was solved iteratively, no? Please rephrase.

This is correct, the sentence has been rephrased.

6. Page 7, equation 4: Please provide a reference for eq. 4 and for the surface tension parameterization of pure water.

Eq. 4 is adopted from Meissner and Michaels (1949) and the surface tension parameterization of pure water is used as given by Vanhanen et al. (2008). Both references have been added.

7. Page 7, equation 4: Is there a need to define so many q's (qst1, qst2, qa1, qa2) in the manuscript? If they are not mentioned more than once in the paper, could they have local names c1, c2, . . .?

Use of designated fitting parameter variables is not strictly needed for Eq. 7, but we chose to keep them as is, to emphasize the nature of the fit. Surface tension parameters are plotted in Figure 4 and discussed in the connected Section 3.4. To avoid conflicts with any other variable names of the model, we chose to keep the letter "q" notation for fitting parameters as is.

8. Page 9, line 18: what is meant here by "non-ideality" ? is this non-unity activity coefficient?

This is correct. With "increasing droplet non-ideality" we mean mole-fraction based activity coefficients, here specifically for water ($\gamma_w > 1$), deviating increasingly from 1. We have clarified this point in the revised manuscript.

9. Page 9, line 30: does "the latter" refer to models (S) and (K)? Please clarify.

Here, we meant to refer specifically to model K. We have clarified the sentence in the revised manuscript.

10. Figure 2a and 2b: The traces in 2b are the contributions of Kelvin and Raoult effects to the traces in 2a, no? Please clarify.

Yes, that is correct. We have clarified this point in the revised manuscript in the Figure 2 caption and related discussion in Section 3.2.

11. Figure 2b. Please clarify why there is an inflection in the Raoult term.

Figures 2 and 3 show droplet properties at the critical point of activation as functions of dry particle NAFA mass fraction. These properties are mutually interconnected and therefore do not produce intuitively simple functional dependencies with respect to the linearly changing dry particle composition. Specifically, the variation in critical droplet Raoult term in Figure 2b depends on the corresponding variation in critical droplet size and overall dilution state (critical growth factor, Figure 2c), bulk/surface partitioning (Figure 3c) and resulting concentrations of NAFA (Figure 3a) and NaCl (Figure 3b). The position of the critical point itself depends on the balance of the Kelvin and Raoult terms for each dry particle size and composition, and therefore on the droplet surface tension.

This is perhaps most clearly illustrated in terms of the concentration of NaCl in Figure 3b. As the dry particle mass fractions of NAFA grows, droplets activate for smaller growth factors (Figure 2c), leading to increased overall critical droplet concentrations, and in particularly of the non-partitioning species NaCl. This effect is sufficiently strong to lead to increasing NaCl concentrations in critical droplets, even as the dry particle NAFA mass fractions increase, and the overall amount of NaCl in the particles decreases. For very high NAFA mass fractions, eventually the trend reverses and even if the overall dilution state of the critical droplets continues to decrease with growing NAFA mass fraction, eventually the total amount of NaCl in the droplets is so small that critical droplet concentrations decrease. Due to the low hygroscopicity of NAFA (see Eq. 7 in the present work and Figs. 3 and 4 of Kristensen et al. 2014),

NaCl is responsible for the majority of the Raoult effect in growing droplets, and the strongly decreasing critical NaCl concentrations predicted with the full (P) and simple (S) partitioning models (Figure 3b) lead to increasing critical water activities for droplets comprising the very smallest total amounts of NaCl.

We have clarified this point in the revised manuscript, and as mentioned above included additional plots showing individual Köhler growth curves for selected dry particles representing the properties shown in Figures 2 and 3.

12. Page 11, line 17: The (P) and (S) models are indeed similar for supersaturation calculations, but they do not trace each other. As stated later, the (P) and (K) models are more similar, particularly for growth factor at activation.

This is correct and we have rephrased this point in the revised manuscript.

Referee #2

Issues:

1. The parameterization of surface tension of NAFA/salt solutions is taken from previous pendant drop experiments. It has however been pointed out in many studies to date, that macroscopic measurements of concentration vs. surface tension in macroscopic solutions may not be relevant to the CCN size range considered here. This disconnect between droplet and macroscopic measures of surface tension is made even more stark by the arguments presented here that in CCN droplets surface partitioning depletes the bulk concentration which is not the case for macroscopic surfactant solutions. This would then indicate that relying on Szyskowski type equations for surface tension parameterizations

of complex mixtures are of no use for CCN studies (see Harmon et al., Physical Chemistry Chemical Physics 15 (24), 9679-9693). The authors need to address this deficiency more clearly in their manuscript. In fact the authors should comment on whether an "insoluble" surfactant model is more appropriate for CCN studies of organic partitioning. To clarify an insoluble surfactant entirely resides at the interface, reduces surface tension and has negligible bulk concentration. Therefore there is no relationship between bulk concentration and surface tension but rather the key relationship is surface coverage vs. surface tension. This point connects to point #2. So as I see it model (S) describes as presented describes an unphysical situation where the organic is at the interface and neither reduces water activity or surface tension.

Several previous works, including our own, have shown that surface tension–composition relations obtained for macroscopic solutions of surface active material with finite water solubility can be applied in Köhler calculations, when the bulk solute concentration of growing droplets is properly corrected for the potentially significant depletion due to bulk/surface partitioning from adsorption of surface active material onto the large droplet surfaces (e.g. Prisle et. al. 2008; 2010; 2011; Petters and Petters 2016; Forestieri et al. 2018; Lin et. al. 2018; 2020). Indeed, a range of studies have demonstrated that application of macroscopic relations without this correction fail to reproduce experimentally observed CCN activity for a variety of surface active organic aerosol. The key to connecting macroscopic composition-dependent relations for surface tension, as well as other solution properties, to microscopic droplets with much larger A/V is a bulk/surface partitioning model, based on a suitable adsorption isotherm. Gibbsian adsorption with Szyszkowski-type surface tension equations have been most widely used, but other types of adsorption behavior have also been considered (see e.g. overview in Malila and Prisle, 2018).

Previous thermodynamically consistent calculations of bulk/surface partitioning in cloud droplet activation were made for droplet mixtures of simple, chemically well-defined surfactants. For example, although Ovadnevaite et al. (2017) apply their results to chemically unresolved atmospheric aerosol, thermodynamic calculations are made for well-defined proxy systems. The overall aim of the present work is to present a framework that enables similar thermodynamically consistent, independent, and preditive evaluations of bulk/surface partitioning for complex, unresolved organic aerosol mixtures.

Following previous work, the present model is based on the Gibbsian adsorption and Szyszkowski surface tension equations. Our present surface active organic model mixture is NAFA, which has significant surface activity and finite water solubility. Kristensen et al. (2014) show how the impact of NAFA on water activity is modest, mainly explained by the large average molecular mass of the mixture. Both Lin et al. (2020) and Kristensen et al. (2014) show that different forms of Szyszkowski-type surface tension equations describe macroscopic surface tension composition-variation well for aqueous NAFA-NaCl mixtures. We therefore chose to analogously describe the surface tension (and bulk water activity) composition relations in growing and activating droplets with similarly bulk-composition based relations. In principle, a surface-composition based surface tension equation could equally well be used, with an appropriate description of the surface concentration for the chemically unresolved mixture. However, the mass-based bulk-composition relations are directly constrained by the measurements for macroscopic solutions (where the bulk-phase mass is closely approximated by the total dissolved mass), as opposed to a potential relation based on surface mass composition. We therefore consider the use of bulk-phase composition dependent properties to be more useful here.

The effect of NAFA bulk/surface partitioning in droplets is to move the solution

mixing state to a different point in the 2-dimensional NAFA–NaCl composition domain. This is illustrated in Figures 2 and 3 for activation droplets of different composition. To further illustrate this point, we have included in the revised manuscript full Köhler curves for selected particles, together with individual surface tension, water activity, and partitioning factors in the droplets along the growth curves.

We have clarified these points in the revised manuscript. Considerations for insoluble surfactants are discussed in connection to the reviewer's point (2) immediately below.

2. In model (S), the surfactant resides entirely at the interface but does not reduce surface tension or water activity at the point of activation. This model indeed provides the best predictions of the data in Fig. 1, despite being quite physically unrealistic (see comment #1 about insoluble surfactants). The authors should show and discuss, if this is indeed the case, that although surface tension is not reduced below pure water at the point of activation, the computed Kohler curves do in fact exhibit the correct perturbations due to surface tension reduction prior to activation as was observed in Ruehl, Davies and Wilson, Science (2016). The authors should also compare and contrast their model (S) with the delta representation described in this paper. Finally, Ovadnevaite, et al. (Nature 2017) presents compelling evidence that surface tension can be reduced at the point of activation in their liquid-liquid phase separation model. It seem reasonable to me to provide some further context about how models P, S, B, and K might be related to the LLPS model. For example, if that authors relax the assumption in (S) that the surface tension at the point of activation is that of pure water, but rather something smaller how does this change the overall conclusions of the paper?

The simple partitioning model (S) was developed to represent the properties of activating droplets predicted with the thermodynamically consistent full partitioning model (P) for simple surface active organic mixtures (Prisle et al. 2008; 2010; 2011). The predictions of the full model P provide the thermodynamic basis for the empirical simple model S. In the thermodynamically consistent partitioning model P, the vast majority of surface active organic material is predicted to be partitioned to the droplet surface at the point of activation, while the surface tension is only very moderately reduced. The reason for this seemingly counter-intuitive state is the comparatively very large surfaces of activating cloud droplets, with A/V typically enhanced by several orders of magnitude, compared to a macroscopic solution (Prisle et al. 2010; Bzdek et al. 2020). Even if essentially all the organic material is adsorbed at the droplet surface, the finite-sized droplets do not comprise enough surface active material altogether to generate sufficient surface concentrations to significantly reduce droplet surface tension. As seen for predictions with the full partitioning model P, both in the present and our previous work, adsorption to the large droplet surfaces depletes the bulk of surface active solute, leaving the resulting amount of surfactant dissolved in the bulk phase at a given total concentration in the droplet essentially vanishing. This leads to the surfactant effectively behaving in small droplets as an insoluble substance. For NAFA, the low bulk water solubility and large estimated average molecular weight further contributes to decreasing the effective hygroscopicity of NAFA.

Compared to the full partitioning model P, the simple model S has two main advantages. By assuming complete partitioning to the surface, there is no need to iterate the partitioning equilibrium to determine the bulk composition at all stages during droplet growth, and therefore no need to know the specific surface activity and impact on bulk water activity of the surface active component. This enables Köhler calculations for unresolved surface active mixtures, as long

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as the overall amount of this mixture in the droplet phase known. Prisle et al. (2011) showed that the simple partitioning model S closely described both experimental CCN activity and predictions with the full partitioning model P for particle mixtures with up to 80% by mass of simple surface active organics, SDS and fatty acid salts. Comparing partitioning models S and P in the present work, as well as to experimental CCN data from Kristensen et al. (2014), we see that this is also the case for complex NAFA–NaCl mixtures.

The simple partitioning model S was developed to specifically describe properties of droplets at the critical point of activation. Indeed, we do not expect that conditions of vanishing surface tension reduction are realized throughout all stages of droplet growth, in particular not at the earliest stages. In the revised manuscript, we have, as mentioned, added full Köhler curves for selected particle compositions, together with predicted droplet surface tension, water activity and NAFA partitioning factors (ratio of NAFA in the surface and bulk), to illustrate the evolution of these properties along the growth curves. We see that the full partitioning model P predicts only a modest surface tension reduction, even at the early stages of droplet growth, which can be rationalized from the corresponding surface/bulk partitioning (surface enhancement) factors, reaching well above three orders of magnitude. The smaller the droplet, the larger the A/V, and except for the earliest stages of droplet growth where overall droplet concentrations are the highest, droplet bulk concentrations are nearly completely depleted by surface adsorption. Therefore, the thermodynamically consistent full partitioning model P describes conditions for a range of droplet sizes, including the critical point of activation, which are closely represented by the simple partitioning model S. On the contrary, the bulk solution model B, which uses the same ternary surface tension–composition parametrization as P, predicts significant surface tension reduction in growing droplets well beyond the point of droplet activation.

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In a macroscopic solution, the situation described by model S is indeed quite unrealistic, but for small droplets with large A/V, it represents conditions predicted with the full model P, as well as observations in CCN experiments, well.

For further comparison to the full model P, and to the experimental data of Kristensen et al. (2014), in the revised manuscript, we have also added Köhler model predictions representing an insoluble surfactant with no impact on droplet water activity (as for model S), but with constant reduced surface tensions corresponding to either 80% or 95% of the value for pure water throughout droplet growth and activation (designated models I80 and I95, respectively). We see that these predictions do not lead to closer agreement with the CCN data or full model predictions, compared to model S, and the agreement decreases when surface tension is further decreased (therefore not included). Is is however possible that such an assumption could provide good agreement with both experimental data and the full model P in cases of less surface active aerosol mixtures, which are less strongly surface adsorbed and depleted from the droplet bulk.

The model presented by Ruehl et al. (2016) is in the "gaseous film" region essentially the same as the simple partitioning model (S) by Prisle et al. (2011). All surface active material is partitioned to the droplet surface, but the total amount is still below the minimum thickness (δ_{org}) necessary to ensure full surface coverage and reduced surface tension. Indeed, Ruehl et al. (2016) find that droplet activation occurs in this gaseous film surface regime, corresponding to the observations of Prisle et al. (2008; 2010; 2011) for the full Gibbsian partitioning model P, which motivated the simple model S. Köhler calculations with our full model P show that activation does not always occur exactly at the point where surface tension reaches that of water (surface thickness of δ_{org}, point

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of film rupture in the model of of Ruehl et al. 2016). Prior to activation, the Ruehl et al. (2016) model yields concentration-dependent reduced droplet surface tensions for the investigated droplet systems. With a surface-composition based surface tension equation, they find a quite different surface tension dependency on droplet size, than seen with the Szyszkowski-type equation in this work. We however also note that the study of Ruehl et al. (2016) involve organics with quite different surfactant characteristics, compared to the NAFA mixtures studied here. They furthermore do not seem to include specific non-ideal solute effects on growing droplet water activity, which could also lead to differences compared to the present work. The model of Ruehl et al. (2016) is fitted to the droplet size–relative humidity data being described, in order to obtain necessary surface tension parameters. As such, their model is analytical, rather than predictive. In the present work, both surface tension and water activity parameters are obtained independently of the predicted CCN measurements by fitting to (marcoscopic) composition-dependent data.

The simple complete phase-separation model of Ovadnevaite et al. (2017) also assumes that surface active droplet components are fully partitioned to the surface, similar to model S of Prisle et al. (2011) and the gaseous film model of Ruehl et al. (2016). The detailed LLPS model of Ovadnevaite et al. (2017) describes the partitioning equilibrium between the aqueous (bulk) and organic (surface) phases in the droplet. Contrary to the full partitioning model P of the present work, and the "compressed film" model of Ruehl et al. (2016), which both consider the surface to be comprised exclusively of surface active organic material, the LLPS model of Ovadnevaite et al. (2017) accounts for presence of small amounts of organic in the aqueous phase, as well as water and water-soluble components in the organic phase. Ovadnevaite et al. (2017) evaluate droplet surface tensions from an empirical mixing rule, based on the mass-weighed composition of the phase-separated organic (surface) phase. Ef-

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fects of solution non-ideality are considered using the well-established AIOMFAC model. Their predictive calculations are based on assuming a proxy composition to represent the organic aerosol mixture, with the inherent uncertainties related to the choice of proxy system and variation of interaction parameters across droplet composition space. The organic proxy mixture used by Ovadnevaite et al. (2017) is less surface active than the NAFA system studied here, which in the Szyszkowski surface tension representation would entail less strong depletion of the droplet bulk phase from surface adsorption and thus higher likelihood of reduced droplet surface tension, including at the point of droplet activation. We also note that the particles representing NUM events observed by Ovadnevaite et al. (2017) are of similar sizes as some of the smallest particles sizes studied in the present work, which activate for smaller growth factors, corresponding to more concentrated solutions, where surface tension is more likely to be reduced in the absence of very strong bulk depletion effects from surface adsorption.

We have added a discussion of these points in the revised manuscript, providing a qualitative comparison of the models of Ruehl et al. (2016) and Ovadnevaite et al. (2017) to the full Gibbsian partitioning model P of the present work and the simple model S of Prisle et al. (2011). We also briefly discuss a new monolayer surface model presented by Malila and Prisle (2018). Models B and K used in this work do not consider bulk/surface partitioning and are therefore mainly used here to highlight the effects of partitioning in activating droplets.

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