Author response to reviewers' comments

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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 framework 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. 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 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 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 number 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 surface 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 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 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.

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 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. Effects 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.

List of changes

1. The model implementation was revised for compatibility with new Matlab updates.

2. All calculations were redone and figures updated. Some smaller changes in results are attributed to a new method for solving for the Köhler curve maximum in the new Matlab update. One significant change of this iteration of the maxima is for the bulk solution model (B) with mass fractions higher than 85%, as described in Section 3, Figs. 2,3,4,5.
3. New calculations were done for an “Insoluble surfactant” representation (I) and added to Figs. 2 and 3, as well as Fig. S3, and presented in new figures.
4. New figures were added for Köhler curves (Fig. 4) and surface tension ((Fig. 4), surface partitioning factor (Fig. S4), and water activity (Fig. S5) along the Köhler curves.
5. Previous figures S1-4 were merged to Fig. S6.
6. Figures 4 and 5 in the original manuscript version and related discussion of the surface tension parametrization for macroscopic and microscopic solution compositions were moved to the SI (Figs. S1 and S2).
7. The whole manuscript and parts of the SI was rewritten, to address reviewer comments as detailed in the response. In particular was added:
8. More detailed description of the mass-based model Section 2.1.
9. Updated presentation of surfactant representations Section 2.3 and Table 1.
10. Discussion of insoluble surfactant representation and modeled droplet properties.
11. Discussion of the infliction points in the Raoult terms shown in Fig 2.
12. Discussion of Köhler curves and properties of growing droplets Section 3.3.
13. Comparison to other partitioning models Section 3.4.1.

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Modeling CCN activity of chemically unresolved ~~model HULIS~~model-HULIS, including composition-dependent surface tension, non-ideality, and surface partitioning

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Abstract. ~~Cloud~~ We present a thermodynamically consistent model that enables self-contained, predictive calculations of droplet growth and activation with considerations of surface adsorption, surface tension reduction, and non-ideal water activity for chemically unresolved, complex surface active aerosol mixtures. The common presence of surface active organic material in atmospheric aerosols is now well-established, whereas the influence of surface activity on aerosol hygroscopic growth and cloud droplet activation remains to be fully constrained. Because specific characterization of key properties, such as water activity and surface tension, are challenging to obtain directly for finite-sized activating droplets, a robust model framework is needed to gain further insight into the droplet equilibrium growth process. The present model is based on coupling Köhler theory with the Gibbs adsorption and Szyszkowski-type surface tension equations and formulated on a mass-basis to allow for a quantitative description of chemically unresolved mixtures. The model is used to calculate cloud condensation nuclei (CCN) activity of aerosol particles comprising ~~surface active~~ Nordic Aquatic Fulvic Acid (NAFA), a surface active model atmospheric humic-like substance (HULIS), and NaCl ~~was modeled with four different approaches to account for NAFA bulk-to-surface partitioning and the combined influence of NAFA and on surface tension and water activity of activating droplets. Calculations were made for particles with~~ with dry diameters of 30–230 nm and compositions ~~covering~~ spanning the full range of relative NAFA and NaCl mixing ratios. ~~Continuous ternary parametrizations~~ Parametrizations of aqueous surface tension and water activity with respect to independently varying NAFA and NaCl mass concentrations were developed ~~from previous measurements on macroscopic bulk solutions and implemented to~~ to obtain continuous descriptions of non-ideal interactions governing both bulk and surface properties during droplet growth and activation. Effects of NAFA surface activity are gauged *via* a ~~Köhler model framework. This enabled comprehensive thermodynamic predictions of cloud droplet activation, including equilibrium surface partitioning, for particles comprising chemically unresolved organic NAFA mixtures. NAFA here serves as a model for surface active atmospheric humic-like substances (HULIS) and for chemically complex organic aerosol in general. Surfactant effects are gauged via predictions of a~~ suite of properties ~~for activating droplets, including critical supersaturation and droplet size, bulk phase composition, surface tension, Kelvin effect, and water activity. Assuming macroscopic solution properties for activating droplets leads to gross overestimations of reported experimental CCN activation, mainly by overestimating surface tension reduction from NAFA solute in droplets.~~ evaluated for growing and activating droplets and results are compared to those of several other predictive Köhler frameworks, where surface active components in droplet solutions are considered in different ways. Failing to account for ~~bulk-to-surface~~ bulk/surface partitioning of NAFA introduces severe biases in evaluated droplet bulk and surface ~~composition and critical size~~compositions, which here specifically affect ~~cloud~~ Köhler activation thermodynamics, but more generally could also impact heterogeneous chemistry on droplet surfaces. ~~Model frameworks based on either including surface~~ Simpler models based on approximating surfactant partitioning and/or neglecting surface tension reduction give similar results ~~for both critical supersaturation and droplet properties and reproduce~~ as the comprehensive partitioning model and reproduce previously reported experimental CCN activity well~~. These perhaps counterintuitive results reflect how the bulk phase is nearly depleted in surface active organic from surface partitioning in submicron droplets with large surface area~~ , reflecting how the finite amounts of surface active material in microscopic droplets are strongly depleted from the bulk phase due to bulk/surface partitioning because surface areas for a given bulk volume ~~.~~ are very large. As a result, ~~NAFA has very little impact on surface tension and water activity at the point of droplet activation. In other words, the predicted surfactant strength~~ both evaluated surfactant strength and hygroscopicity of NAFA is significantly lower in ~~sub-micron~~ finite-sized activating droplets than in macroscopic aqueous solutions of the same overall composition. ~~These results show similar effects of chemically complex surfactants as have previously been seen only for simple surfactants with well-defined molecular properties and add to the growing appreciation of the complex role of surface activity in cloud droplet activation.~~

1 Introduction

The surface activity of atmospheric ~~organic~~ aerosol components and its implications for cloud microphysics have been investigated for several decades. By definition, surface active (surfactant) material adsorb at the surface of a solution, leading to enhanced surface concentrations (activity), compared to the (interior) bulk, and a resulting radial concentration gradient between the surface and bulk phases. Due to this enhanced surface activity, surfactants can typically reduce surface tension of aqueous solutions more efficiently at a given concentration than homogeneously mixed solutes. Shulman et al. (1996) showed that reduced surface tension in aqueous droplets can alter the shape of their equilibrium growth curve as described by Köhler theory (Köhler, 1936) and thereby lower the critical supersaturation threshold for cloud droplet activation. Facchini et al. (1999, 2000) then demonstrated that surface active ~~organic~~ material is indeed present in atmospheric ~~aerosol~~cloud and fog samples, which can significantly reduce aqueous surface ~~tensions in macroscopic samples~~ tension at concentrations comparable to those of activating ~~droplet systems. Surfactants have since~~ droplets. Surface active components have now been found in ~~aerosol~~ aerosols from many different environments ~~(e.g. Petters and Petters, 2016; Kroflič et al., 2018). However, surface active compounds by definition accumulate in a solution~~ (e.g. Petters and Petters, 2016; Gérard et al., 2016; Kroflič et al., 2018).

Köhler calculations generally require composition-dependent droplet properties in some form. The surface equation-of-state for a solution can be given in terms of either the surface or bulk composition, as these quantities are related *via* the equilibrium bulk-to-surface concentration gradient for a given surface active substance. A number of techniques exist to experimentally determine the surface ~~, thus creating a concentration gradient between the (interior) bulk and surface phases. For~~ tension–composition relations for surfactant solutions, which almost exclusively require macroscopic (i.e. millimeter-scale or larger) sample sizes (Fainerman et al., 2002; Hyvärinen et al., 2006; Kristensen et al., 2014; Bzdek et al., 2020). In these macroscopic solutions, surface adsorption and enhanced surface activity involve only a small fraction of the total amount of surface active solute and therefore have negligible effect on the bulk composition. As a consequence, surface tension–composition relations reported in terms of total solute concentrations, which are readily quantified experimentally for macroscopic solutions, closely reflect the corresponding bulk composition.

For finite-sized solutions, such as microscopic and sub-micron ~~droplets with large surface areas for a given bulk volume , this bulk-to-surface partitioning of finite amounts of solute can therefore lead to~~ activating cloud droplets, surface adsorption can significantly deplete the bulk-phase of surface active solute, because the total amount of solute in the system is finite, and the surface area (A) to bulk volume (V) ratio may be several orders of magnitude greater than for macroscopic solutions (Prisle et al., 2010; Lin et al., 2020): For a spherical system, where the diameter d represents the characteristic dimension, $A/V = 6/d = 6 \times 10^6$ m^{-1} for a 1 μm droplet and $A/V = 6000$ m^{-1} for a macroscopic droplet with $d =$1 mm. The highly sensitive variation of A/V with finite solution size introduces a size-dependent ~~bulk phase depletion and~~ shift in both surface and bulk concentrations at the adsorption equilibrium of the surface active species.

The distribution of surface active species between the distinct bulk and surface phases of a solution is referred to as the bulk/surface *partitioning*. Size-dependent partitioning has been predicted to in turn result in size-modulated ~~composition dependent solution properties , including droplet surface tension~~ composition-dependent properties for finite-sized solution droplets (Bianco and Marmur, 1992; Laaksonen, 1993; Sorjamaa et al., 2004; Prisle et al., 2010), including surface tension (a surface property) and water activity ~~(Prisle et al., 2010). These~~ (a bulk property), which are key parameters in determining aerosol water uptake, hygroscopic growth and cloud ~~activation.~~ droplet activation. Until recently, experimental evidence for this effect in cloud microphysics has been indirect, from the reported inability of Köhler models using macroscopic solution property–composition relations to reproduce observed droplet activation. For example, a range of studies have consistently demonstrated that using surface tension and water activity relations based on total solution composition, without explicit consideration of the impact of surface adsorption on bulk composition, can lead to dramatic over-estimations of cloud condensation nuclei (CCN) activity (Li et al., 1998; Sorjamaa et al., 2004; Prisle et al., 2008, 2010; Kristensen et al., 2014; Hansen et al., 2015; Petters a Recently, Bzdek et al. (2020) presented the first measurements of concentration dependent surface tensions for finite-sized, surfactant-containing aqueous droplets and provided the first direct experimental evidence for the influence of bulk-phase depletion from size-dependent bulk/surface partitioning.

Effects of surfactant ~~bulk-to-surface~~ bulk/surface partitioning may greatly impact predictions of the ~~overall cloud formation~~ cloud forming potential of surface active ~~organic~~ aerosol (Laaksonen, 1993; Li et al., 1998; Sorjamaa et al., 2004). ~~The first experimental (Li et al., 1998) and modeling (Sorjamaa et al., 2004) studies focused on the industrial surfactant~~ In Köhler calculations, macroscopic solution property–composition relations are connected to those of growing droplets with changing A/V *via* a partitioning model, which is typically based on a suitable adsorption isotherm and surface tension equation of state for the surface active components. An overview of the most widely used partitioning models in Köhler modeling is given by Malila and Prisle (2018). Thermodynamic process models, such as those presented by Prisle et al. (2010), Topping (2010), Raatikainen and Laaksonen (2011), Petters and Kreidenweis (2013) and Malila and Prisle (2018), generally rely on input of compound-specific properties with well-characterized composition dependencies. Due to the challenges involved in obtaining sufficient amounts of atmospheric samples and characterizing their composition and composition-dependent properties in aqueous solution, including surface activity (e.g. Kroflič et al., 2018; Prisle et al., 2019), many process-level experimental and modeling studies have used sodium dodecyl sulfate (SDS) and similar industrial surfactants with relatively well-known properties ~~, as model compound for the surface active organic mixtures present in~~ as model compounds for surface active components of real atmospheric aerosols ~~. Prisle et al. (2008, 2010) then demonstrated a similarly dramatic effect for particles comprising a series of atmospheric straight chain~~ (e.g. Li et al., 1998; Sorjamaa et al., 2004; Harmon et al., 2010; Prisle et al., 2011; Raatikainen and La

The first atmospheric surfactants used in Köhler calculations together with a thermodynamic partitioning model were straight-chain fatty acid sodium salts ~~(FAS). These surface active organics belong to one of the major compound classes~~ (Prisle et al., 2008, 2010, 2011; Forestieri et al., 2018), which are widely identified in atmospheric aerosol samples ~~(e.g. Mochida et al., 200~~ Both SDS~~and FAS~~ , fatty acids, and their salts are relatively strong surfactants (Prisle et al., 2008, 2010, and references therein), ~~however these studies showed that both experimental and~~ yet the modeled effect of surface tension on CCN activation was very modest, due to strong depletion of ~~surfactant~~ the surfactant molecules from the bulk phase in activating droplets arising from surface partitioning. ~~This at first led to an understanding that completely neglecting surface activity of organic aerosol was sufficient for purposes of estimating atmospheric organic aerosol CCN activity in large scale simulations (e.g. Prisle et al., 2012). However, different studies have come to diverging conclusions regarding the general applicability of this approximation (e.g. Petters and Petters, 2016) and recent studies have found evidence for significant enhancement of hygroscopicity of secondary organic aerosol (Ruehl et al., 2016), marine primary organics (Ovadnevaite et al., 2017), limonene-derived organosulfate products (Hansen et al., 2015), and water soluble pollen extracts (**?**), from surface tension effects.~~

~~The role of surfactants in cloud droplet activation remains ambiguous and the conditions for which surface active organics can enhance CCN activity must be established for a broad range of atmospheric organic aerosol compositions. Due to the challenges involved in obtaining atmospheric samples and characterizing their surfactant properties (e.g. Kroflič et al., 2018), SDS and similar industrial surfactants have been the preferred model compound of several process-level thermodynamic studies (e.g. Sorjamaa et al., 2004; Harmon et al., 2010; Raatikainen and Laaksonen, 2011; Petters and Kreidenweis, 2013). These compounds are however not immediately relevant in the atmosphere, just as the~~ Overall, these model predictions reproduced experimental observations of CCN activity well. The atmospherically relevant surfactants so far studied in terms of detailed compound-specific solution properties (see e.g. overview by Petters and Petters, 2016) comprise ~~only a~~ a relatively narrow selection of often simple, homologous molecules, which most likely do not ~~span the full breadth of~~ represent the properties of all atmospheric surface active ~~organic aerosol CCN activity. In addition~~compounds. Furthermore, the binary and ternary aqueous droplet mixtures ~~typically studied~~ which are typically the focus of process-level studies may constitute too simple proxy systems to capture the ~~breadth~~ variation of properties displayed by chemically complex surface active ~~organic aerosols~~ aerosol mixtures in the atmosphere. ~~This~~ Significant variation in aerosol surface activity may be reflected in the somewhat diverging messages regarding the importance of surface tension for closure of CCN number concentrations from different studies ~~(e.g. Wex et al., 2007; Varga et al., 2007; Asa-Awuku et al., 2008; Booth et al., 2009; Poulain et al., 2010; Frosch et al., 2011)~~(e.g. Wex et

Atmospheric aerosol samples, as well as those generated in more elaborate laboratory experiments, often comprise complex mixtures which are chemically either partially or entirely unresolved. A major challenge in establishing ~~more~~ general results for ~~surface active CCN activity~~ the role of surface active aerosol in cloud microphysics relates to the ~~comprehensive composition dependent~~ composition-dependent thermodynamic description and process modeling of such chemically diverse and ~~typically unresolved organic mixtures. Process level thermodynamic models that account for bulk-to-surface partitioning of surface active organics, such as those presented by e. g. Prisle et al. (2010), Topping (2010), Raatikainen and Laaksonen (2011), and Petters and Kreidenweis (2013), require input of compound-specific properties with well-characterized composition dependencies. These data are generally not available for all relevant mixtures, in particular for chemically unresolved atmospheric organic aerosol. To this effect~~unresolved aerosol mixtures. Even in the hypothetical case where all aerosol components and their quantities would be known, it is often not realistic to obtain a well-constrained description of their interactions in all solution states corresponding to growing droplets. To enable thermodynamic calculations, one approach is to assume a well-known proxy compound or mixture to represent the properties of the complex system. A key challenge of this approach concerns how representative the chosen proxy is of the actual aerosol mixture and in particular how well it represents the response of the mixture 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. Alternatively, Prisle et al. (2011) proposed a very simple framework for representing the overall effect of ~~(organic)~~ aerosol surface activity on CCN activation. This ~~representation~~ model rather crudely assumes that ~~droplet surface tension at the point of activation is not reduced from that of water, despite the surface active organic being~~ surface active components are completely partitioned to the droplet surface ~~. It is equivalent to assuming an~~ with a resulting effective hygroscopicity parameter of $\kappa = 0$ (Petters and Kreidenweis, 2007) ~~for surface active organic components in the mixture~~and vanishing impact on droplets surface tension. The simple representation was demonstrated to perform ~~very~~ well for SDS and ~~FAS~~ fatty acid salts with 8–12 carbon atoms ($\mathrm{C}_8, \mathrm{C}_{10}, \mathrm{C}_{12}$), the activation behavior of which it was first proposed to emulate, but a more general applicability still remains to be ~~validated~~established.

~~HUmic LIke Substances (HULIS) comprise another important group of atmospheric surface active organics (e.g. Kiss et al., 2005; Dinar~~
~~Kristensen et al. (2014) measured the CCN activity of~~

Here, we present a framework that enables predictive, thermodynamically consistent calculations of droplet growth and activation for chemically unresolved, complex surface active aerosol mixtures. Following the approach of Prisle et al. (2010), Köhler theory is coupled with a partitioning model based on the Gibbs adsorption and Szyszkowski-type surface tension equations. To allow for a quantitative description of chemically unresolved components, the model is formulated on a mass-basis and continuous parametrizations for bulk water activity and surface tension in aqueous solutions are constructed from macroscopic measurements, where composition-dependency is described in terms of mass-concentrations without specific knowledge of the molecular identity of all solution components.

The model is applied to evaluate a suite of properties, including critical supersaturation and droplet size, bulk-phase composition, water activity, surface tension and Kelvin effect, for growing and activating droplets formed from particles comprising Nordic Aquatic Fulic Acid (NAFA) ~~,~~ mixed with sodium chloride (NaCl). NAFA is one of several commercial reference compounds used as models for atmospheric ~~HULIS, mixed with sodium chloride (). In addition, they measured the influence of various NAFA–~~HUmic LIke Substances (HULIS), which comprise another major group of atmospheric surface active organics (e.g. Kiss et al., 2005; Dinar et al., 2006b; Graber and Rudich, 2006). Kristensen et al. (2014) and Lin et al. (2020) report a comprehensive data set, including measurements of CCN activity for particles with a range of sizes comprising NAFA and NaCl ~~mixtures on surface activity~~ in various mixing ratios, as well as surface tension and water activity of macroscopic aqueous ~~solutions and found that NAFA~~ NAFA–NaCl solutions. NAFA significantly reduces surface tension in ~~aqueous solution, in agreement with other studies for~~ macroscopic aqueous solutions, similar to other model HULIS (e.g. Kiss et al., 2005; Aumann et al., 1967). However, Kristensen et al. (2014) found that CCN activity of both pure NAFA and mixed NAFA–NaCl particles was ~~grossly overestimated by simple~~ significantly overestimated by Köhler ~~theory~~ calculations assuming the impact of NAFA surface activity on droplet surface tension to be equivalent to that measured in the corresponding macroscopic solutions. ~~It therefore seems likely that~~ This strongly suggests that size-dependent bulk/surface partitioning of NAFA in microscopic droplets also needs to be taken into account to explain the observed CCN activity~~of NAFA–mixtures.~~

~~Here, we present a modified version of the comprehensive thermodynamic model framework of Prisle et al. (2010), which allows detailed evaluations of surfactant bulk-to-surface partitioning and cloud droplet activation for particles comprising chemically unresolved NAFA. This is achieved by developing continuous ternary parametrizations of water activity and surface tension with respect to independent variations in both NAFA and mass concentrations in aqueous solution, based on the macroscopic solution measurements by Kristensen et al. (2014). The mass-concentration based parametrizations are then implemented to the Köhler model framework. This allows us to~~. The predictive thermodynamic framework provides a means to gain insight into the detailed process-level mechanisms governing the particle size and composition dependent variations in CCN activity of ~~NAFA. We also test the applicability of the simple representation by Prisle et al. (2011) for these NAFA–particle mixtures, which are exactly the kind of surface active and chemically unresolved organic aerosol mixturesfor which the simple representation was originally developed. For reference and additional insight, we include calculations using the commonly used representations of (surface active) organic aerosol in Köhler theory, by either assuming activating droplets have properties corresponding to a macroscopic aqueous solution with the same total composition, or simply treating the organic as a regular, fully soluble and homogeneously mixed (i.e. notsurface active) solute.~~ chemically complex, unresolved surface active NAFA aerosol mixtures.

2 Theory and modeling

CCN activity for NAFA particles of varying dry sizes and mixing ratios with ~~sodium chloride~~ NaCl salt was calculated using ~~the methodology of Prisle et al. (2010). Critical supersaturations (SS_c) are iterated as the maximum of the equilibrium droplet growth curve described by the~~ a framework based on the Köhler equation ~~(Köhler, 1936)~~ (Köhler, 1936; Prisle et al., 2010) in the form

$$\frac{SS}{[100\%]} \equiv \frac{p_\mathrm{w}}{p^0_\mathrm{w}} - 1 = a_\mathrm{w} \exp\left(\frac{4\sigma\nu_\mathrm{w}}{RTd}\right) - 1\,. \tag{1}$$

~~The Köhler curve gives~~ Equation 1 describes the equilibrium water vapor supersaturation (SS) over a spherical solution droplet as a function of its diameter (d): p_w is the equilibrium partial pressure of water over the solution droplet, p^0_w is the saturation vapor pressure over a planar surface of pure water, a_w and σ are the water activity and surface tension of the droplet solution, ν_w is the partial molar volume of water in solution, approximated ~~by $M_\mathrm{w}/\rho_\mathrm{w}$,~~ as the ratio of pure water molar mass and mass density $M_\mathrm{w}/\rho_\mathrm{w}$, R is the universal gas constant, and T is the Kelvin temperature. The ~~droplet size where SS_c occurs is here referred to as the critical droplet diameter d_c. In addition, only the initially~~ solution droplet is formed as water condenses onto an initially dry particle. Only the dry particle before any water uptake has occurred is here referred to as a ~~particle~~ "particle" and dry particle diameters (as well as other properties) are designated in upper case symbols, as D_p. After water uptake, the wet aerosol particle is referred to as a (solution) droplet, and corresponding diameters (and other properties) are designated in lower case symbols, as d. For each dry particle size and composition, the critical supersaturation (SS_c) is evaluated as the maximum of the equilibrium droplet growth (Köhler) curve described by Eq. 1. The droplet size where SS_c occurs is here referred to as the critical droplet diameter d_c, or the *point of activation*. When droplets have grown past their respective critical point to sizes $d > d_\mathrm{c}$, they are ~~referred to~~ described as *activated* cloud droplets. At earlier points $d \leq d_\mathrm{c}$ on the Köhler curves, droplets are considered to be in the process of *activating*.

The water activity (also called the Raoult term) describes the suppression of equilibrium water partial pressure over an aqueous solution by dissolved solutes, compared to the saturation vapor pressure of pure water, as

$$p_\mathrm{w} = a_\mathrm{w} p^0_\mathrm{w} = \gamma_\mathrm{w} x_\mathrm{w} p^0_\mathrm{w}\,. \tag{2}$$

Here, x_w is the water (mole or mass) fraction in solution and γ_w is the corresponding (mole or mass fraction based) activity coefficient of water. The exponential (or Kelvin) term describes the enhancement of vapor pressure over the convex side of a curved droplet surface, compared to a planar ~~liquid surface~~ surface of the same liquid, and depends explicitly on the droplet surface tension. Both water activity and Kelvin term are ~~described as~~ functions of droplet ~~bulk~~ composition, determining x_w and thus $\gamma_\mathrm{w} = \gamma_\mathrm{w}(x_\mathrm{w})$ and a_w, as well as any concentration dependent ~~surface tension reduction~~ change in droplet solution surface tension from the pure water value, ~~$\Delta\sigma = \sigma_w - \sigma$~~ $\Delta\sigma = \sigma_\mathrm{w} - \sigma$.

The total (T) amount of solute in ~~droplets~~ the growing droplets remains constant and is determined from the dry particle compositions in terms of relative mass fractions ~~of NAFA and , where ($W_\mathrm{p,NAFA} + W_\mathrm{p,NaCl} = 1$)~~ $W_\mathrm{p,s}$ of each solute s, where $\sum_s W_\mathrm{p,s} = 1$. Assuming volume additivity in spherical particles, the total dry mass of each solute is then given from their bulk mass densities ~~ρ_i as~~ ρ_s as

$$m^T{}_{is} = W_{\mathrm{p},i\mathrm{p},s}\frac{\pi}{6}D_\mathrm{p}^3\left(\sum{}_i\frac{W_{\mathrm{p},i}}{\rho_i}{}_j\frac{W_{\mathrm{p},s}}{\rho_j}\right)^{-1}. \tag{3}$$

In our calculations, we have used $\rho_{\mathrm{NaCl}} = 2.165\,\mathrm{g\,cm^{-3}}$ and $\rho_{\mathrm{NAFA}} = 1.6\,\mathrm{g\,cm^{-3}}$~~for the unknown NAFA density . The~~. The NAFA density is not available in the literature and is therefore assumed to be similar to that of Suwannee River Fulvic Acid, another common reference humic substance (Dinar et al., 2006a). In principle, this quantity can readily be determined by simple weighing of a well-defined volume of the sample, but the resulting value is highly dependent on the packing of the sample material and we have therefore refrained from obtaining a more precise experimental estimate here. The droplet temperature is assumed to be $T = 303$ K, reflecting the range of effective temperatures from about $298 - 313$ K in the CCN counter between measurements at different supersaturations (T.B. Kristensen, personal communication). The sensitivity of calculations to the assumed ~~temperature and~~ value of ρ_{NAFA} and variations in experimental droplet temperature is discussed in the Supporting Information (SI).

2.1 ~~Surfactant representations~~

At each droplet size, the total amount of water is calculated by assuming volume additivity also of water and dry particle components within the droplet phase, as

$$m_\mathrm{w}^T = \rho_\mathrm{w}\frac{\pi}{6}(d^3 - D_\mathrm{p}^3)\,. \tag{4}$$

The total droplet composition $\{x_i^T\} = \mathbf{x^T}$ is then given in terms of the mass fractions of each component i as

$$x_i^T = \frac{m_i^T}{\sum_j m_j^T} \tag{5}$$

~~Cloud droplet activation is calculated including the influence of surfactant properties according to four different representations (summarized in Table 1) :~~

2.1 Surfactant partitioning

~~.~~When surface active material adsorbs at the droplet surface, it leads to a partitioning of the total mass of surface active solute m_{sft}^T between the surface (S) and bulk (B) phases of the solution droplet. This partitioning depletes the droplet bulk concentration, compared to the total concentration $x_{\mathrm{sft}}^B < x_{\mathrm{sft}}^T$ and changes the overall bulk composition, compared to the total composition of the droplet $\{x_i^B\} = \mathbf{x^B} \neq \mathbf{x^T}$. To calculate the resulting amount of solute in the droplet bulk (and surface), we use a partitioning model based on the Gibbs adsorption equation (Gibbs et al., 1928) in the form:

$$RT\sum_i \frac{m_i^T}{M_i}\frac{\partial \ln(a_i)}{\partial m_{\mathrm{sft}}^B} + A\frac{\partial\sigma}{\partial m_{\mathrm{sft}}^B} = 0\,, \tag{6}$$

where $A = \pi d^2$ is the droplet surface area, m_i^T and M_i are the total and molar mass of each droplet component i, a_i is the activity of each component in the droplet solution, and $m^B_{\rm sft}$ is the mass of partitioning (surface active) species in the droplet bulk. For chemically well-defined components, here water and NaCl, M_i are well-known quantities. For NAFA, we here assume an average molar mass of $\bar{M}_{\rm NAFA} = 4266\,{\rm g\,mol^{-1}}$ according to the estimate of Mäkelä and Manninen (2008). This corresponds to an assumption of the average mass of a partitioning unit. The sensitivity of calculations to variations by up to an order of magnitude in the assumed value of $\bar{M}_{\rm NAFA}$ is discussed in the SI. Activities for non-volatile solutes are very challenging to measure directly, but can in binary solutions be inferred from measurements of the solvent activity *via* the Gibbs-Duhem equation. Since this is not possible for ternary and higher-order mixtures, $a_{\rm NAFA}$ and $a_{\rm NaCl}$ are approximated as the corresponding mass fraction concentrations. Previous estimates for ternary surfactant–NaCl aqueous mixtures showed that this assumption had only minor effects in Köhler calculations (Prisle et al., 2010). The composition-dependent droplet water activity a_w, which also enters directly into Eq.1, is evaluated from an experimentally-based parameterization as described in Section 2.2.

~~.~~The bulk/surface partitioning equilibrium is solved iteratively from Eq. 6 at each droplet size d and total composition $\mathbf{x^T}$, constrained by mass conservation for all droplet components, $m_i^T = m_i^B + m_i^S$, and by choosing the position of the Gibbs surface to yield the droplet bulk-phase volume equal to the total droplet volume, $V = \pi d^3/6$ (Prisle et al., 2010).

~~, however, the bulk compositions at each droplet size generally differ.~~

~~.~~

~~Properties included in the different representations of NAFA CCN activity used in calculations. When ternary surface tension is notused, it is set constant to the value for pure water ($\sigma_{\rm w}$).partitioning $\sigma = \sigma(\mathbf{x^B})$ $a_{\rm w} = a_{\rm w}(\mathbf{x^B})$(P)partitioning x x x (S) simple x - x (B) bulk- x x (K) basic/water - - x~~

2.2 Ternary parametrizations

Iterations of critical supersaturations from Eq.1 require continuous functions for ~~concentration dependent variations in~~concentration-depend variations in surface tension and water activity of the growing droplets. Here, both σ and $a_{\rm w}$ ~~of growing droplets~~are described as functions of droplet bulk composition $\mathbf{x^B}$, which is the basis for using the Gibbs adsorption equation in the form given in Eq. 6. At equilibrium, the surface and bulk compositions of a given surface active substance are related via the concentration gradient resulting from its surface activity and mass conservation within the solution, just as the the activities of water and all other components are the same in all phases of the solution. Although the surface tension of a solution may also be given in terms of the surface composition (Ruehl et al., 2016), a major advantage of using bulk-composition based relations for solution properties is that these can be readily obtained from measurements for macroscopic solutions, where the bulk-phase composition is directly constrained in terms of the total dissolved mass. The absolute surface composition is on the other hand not easily quantified by direct measurement.

The key to applying composition-dependent properties obtained for macroscopic systems to finite-sized droplets, is to correct the bulk (or surface) concentrations of droplet components using a partitioning model. When partitioning of ~~surfactant molecules~~ surface active solute to the droplet surface is considered~~using representation (P)~~, the bulk concentration ~~of NAFA~~

~~changes~~ changes along the Köhler growth curve, due to both dilution ~~and changing ratio of~~ as the droplet grows and changing bulk/surface partitioning, for example expressed in terms of the surface partitioning factor $m^S_{\mathrm{sft}}/m^B_{\mathrm{sft}}$, with changing ratio of the droplet surface area and bulk volume. For ternary water–NAFA–NaCl droplet compositions, the relative ~~mixing ratio of NAFA and~~ solute mass fractions in the droplet bulk phase ~~for example given as the solute mass fraction $w_i = m^B_i / \sum_j m^B_j$ (where m^B_i~~

$$w_s = \frac{m^B_s}{\sum_j m^B_j}\,, \tag{7}$$

where m^B_s is the mass of solute ~~i in the bulk, $j = \mathrm{NAFA}, \mathrm{NaCl}$, and $w_{\mathrm{NAFA}} + w_{\mathrm{NaCl}} = 1$) therefore changes~~ s in the droplet bulk and $\sum_s w_s = 1$, of NAFA and NaCl therefore change in a continuous fashion from ~~that of~~ the corresponding dry particle composition (~~$W_{\mathrm{p},i}$~~$W_{\mathrm{p},s}$), as a result of ~~NAFA surface partitioning, as droplets grow according to Eq. 1.~~ changing NAFA partitioning in the growing droplets. The effect of bulk/surface partitioning is to move the droplet bulk (and surface) solution mixing state in the 2-dimensional NAFA–NaCl concentration domain, compared to the total droplet mixing state, or a macroscopic solution with the same composition. As a consequence, continuous ~~ternary~~ parametrizations with respect to independent variations in ~~droplet NAFA and~~ all component concentrations are needed to evaluate droplet properties over the full range of ~~droplet~~ mixing states realized during droplet growth and activation.

~~Strictly, only representation (P) requires the use of the continuous ternary parametrizations, since only in these calculations does the relative NAFA–solute mixing ratio change from that of the dry particles as the droplets grow ($W_{\mathrm{p},i} \neq w_i$). In representation (S), the relative bulk phase mixing state of NAFA and changes discontinuously at the onset of droplet growth, from the nominal dry particle value to $w_{\mathrm{NAFA}} = 0$ and $w_{\mathrm{NaCl}} = 1$ in droplets where NAFA is completely partitioned to the surface. When representations (B) and (K) are used, the relative mixing ratio of NAFA and solutes remains equal to the nominal value of the dry particles and does not change with concentration of the growing droplets ($W_{\mathrm{p},i} = w_i$). The individual binary parametrizations given for each nominal NAFA–solute mixing ratio by Kristensen et al. (2014) could therefore in principle be employed in these cases. For consistency, we here use the ternary parametrizations in all calculations, at essentially no additional computational cost. This allows us to explore additional features of the different model representations, in terms of predicted droplet properties for continuous variation in dry particle compositions. Finally, we note that with representation (S), dissolved NAFA mass does not affect the water activity which is therefore determined from the contribution only, according to the binary water activity parametrization given by Prisle (2006).~~

~~Ternary parametrizations of~~ Parametrizations of both σ and a_{w} were obtained by fitting continuous functions of NAFA and NaCl aqueous concentrations to the experimental surface tensions and ~~osmolality-derived water activities measured by Kristensen et al. (2014)~~ water activities reported by Kristensen et al. (2014) and Lin et al. (2020) for macroscopic solutions of same solute compositions as the original dry particles, using the least squares method. By using mass-based concentrations, which are readily available from experimental parameters, a quantitative description is obtained for all solution components, including the chemically unresolved NAFA.

2.2.1 ~~Parametrization of~~ Surface tension σ

NAFA–NaCl aqueous surface tensions (in $\mathrm{mN\ m^{-1}}$) were fitted with the Szyszkowski equation in the form (Meissner and Michaels, 1949):

$$\sigma = \sigma_{\mathrm{w}} - q_{\mathrm{st1}} \ln\left(1 + \frac{C_{\mathrm{NAFA}}}{q_{\mathrm{st2}}}\right), \tag{8}$$

where ~~$\sigma_{\mathrm{w}} = 93.6635 + 0.009133T - 0.000275T^2$~~ $\sigma_{\mathrm{w}} = 93.6635 + 0.009133\,T - 0.000275\,T^2$ (Dillmann and Meier, 1991; Vanhanen et a the temperature-dependent surface tension of pure water (in $\mathrm{mN\ m^{-1}}$) and C_{NAFA} is the mass concentration of NAFA (in $\mathrm{g\ L^{-1}}$). Dependency of σ on NaCl concentration enters through the fitting parameters q_{st1} and q_{st2}, which are both functions of the relative NAFA–NaCl mass fraction in solution.

Kristensen et al. (2014) and Lin et al. (2020) report that measured aqueous NAFA surface tension ~~for a given sample droplet~~ decreases with time after formation of the sample surface. This is likely ~~owing to both kinetic~~ due to both dynamic effects of surface adsorption and structural rearrangements in the surface phase, as well as potentially to continually increased concentrations of the pendant ~~droplets~~ drop samples from evaporation of water over the course of measurements. Fitting parameters for the surface tension parametrization (Eq. 8) used in the present calculations were obtained from ~~measurements performed at~~ measurement data corresponding to times $t = 600$ s after generation of the pendant ~~drop. At this selected time lapse, measurements were available for the widest range of solutions, and generally the steepest and the majority of the total surface tension decrease had occurred. Furthermore, we estimate that the~~ drops. Following considerations of Prisle et al. (2008), the ratio of these measurement times to those of the cloud droplet activation measurements is here estimated to be roughly of the same order of magnitude ~~($\sim 10^2$)~~ as the diameter ratio of the droplets involved in the two types of measurement ~~. We therefore assume that any potential kinetic~~ ($\sim 10^2$). With this simple argument, any potential dynamic effects of surfactant ~~molecules~~ solute diffusing to the droplet surface, ~~such as any speculated~~ leading to incomplete (non-equilibrium) NAFA partitioning, are assumed to be at least comparable between the surface tension parametrizations and the droplet activation measurements, if present at all. Using a comprehensive set of time-evolving surface tension measurements for aqueous NAFA–NaCl mixtures with a wide range of compositions, Lin et al. (2020) presented a detailed assessment of the effects of time-dependent surface adsorption in Köhler calcuations. At the selected time lapse of $t = 600$ s, measurement data were available from Kristensen et al. (2014) and Lin et al. (2020) for the widest range of solutions, and generally the steepest and the majority of the total surface tension decrease with respect to measurment time had occurred at this point.

The surface tension fitting parameters q_{st1} (in $\mathrm{mN\ m^{-1}}$) and q_{st2} (in $\mathrm{L\ g^{-1}}$) for times $t = 600$ s are given as

$$q_{\mathrm{st1}} = 10.46 - 4.810\,w_{\mathrm{NAFA}} \tag{9}$$

and

$$q_{\mathrm{st2}} = 0.5947 - 0.3278\,w_{\mathrm{NAFA}}\,\cancel{.}, \tag{10}$$

~~Here, as before,~~ where w_{NAFA} is the (dimensionless) mass fraction of NAFA solute relative to NaCl in the solution bulk phase ~~.~~ given in Eq. 7. Fits were made ~~under the conditions~~ with the constraints that $q_{\mathrm{st1}} \geq 0$ and $q_{\mathrm{st2}} > 0$ for all $w_{\mathrm{NAFA}} \in 0-1$.

We also made ternary fits to the surface tension data using the Szyszkowski-type equation given by Prisle et al. (2010), which contains an additional term explicitly including the positive aqueous surface tension gradient with respect to NaCl concentration, as well as having both fitting parameters depend quadratically, instead of linearly, on w_{NAFA}. The more elaborate ~~equation~~ equations did not significantly improve the fit to data, while introducing several additional fitting parameters to the model. In our calculations, we therefore used the simpler Eq. 8 with implicit NaCl dependency and linear variation of the fit parameters with w_{NAFA}.

2.2.2 ~~Parametrization of~~ Water activity a_w

~~Water~~ Osmolality-derived water activities were fitted as functions of NaCl and NAFA mass concentrations (C_{NaCl} and C_{NAFA}, both in $\mathrm{g\ L^{-1}}$) in the form:

$$a_{\mathrm{w}} = 1 + q_{\mathrm{a1}} C_{\mathrm{NaCl}} + q_{\mathrm{a2}} C_{\mathrm{NAFA}}\,, \tag{11}$$

with fitting parameters $q_{\mathrm{a1}} = -5.68 \cdot 10^{-4}\ \mathrm{L\ g^{-1}}$ and $q_{\mathrm{a2}} = -2.68 \cdot 10^{-5}\ \mathrm{L\ g^{-1}}$. Several other, more complex functions were tested as well, but the simple linear relations gave the most reasonable fits to the data over the measured composition ranges. Water actvities derived from osmometry in principle include all non-ideal solution effects, in particular concentration-dependent NAFA dissociation and effects of any non-ideal interactions among the resulting solute entities~~, on the activity of water in solution.~~. Still, the linear relationship ~~in~~ on mass concentrations of solute with unknown molar content ~~and activity coefficients given by Eq. 11~~ may not be thermodynamically consistent over the full range of water–NAFA–NaCl mixing states. Indeed, for the limiting case of binary solutions, ~~it~~ Eq. 11 does fail to comply with the Gibbs-Duhem relation in the limit of pure NAFA ($m_{\mathrm{w}} = m_{\mathrm{NaCl}} = 0$). This state is, however, never realized in our calculations, where droplet growth ~~starts~~ is initiated at a finite growth factor and tends toward infinite dilution. Zamora and Jacobson (2013) derived water activities from measured hygroscopic growth factors for NAFA–NaCl mixtures and also found near-linear relationships between water activity and total solute (molal) concentration.

2.3 Surfactant representations

For each dry particle composition and size, cloud droplet activation is calculated by considering the influence of NAFA surface activity according to five different representations (summarized in Table 1):

- **(P)** The full partitioning model decribed in Section 2.1: For each droplet size, the NAFA bulk/surface partitioning equilibrium is solved iteratively from Eq. 6 to determine the droplet bulk phase composition $\{x_i^B\} = \mathbf{x^B}$, from which droplet surface tension and water activity are evaluated according to concentration-dependent ternary parametrizations, $\sigma = \sigma(\mathbf{x^B})$ and $a_{\mathrm{w}} = a_{\mathrm{w}}(\mathbf{x^B})$, according to Eqs. 8 and 11. By using measurement-based parametrizations which rely only on *mass* concentrations and mass mixing ratios of organic and inorganic components, a quantitative description is obtained with respect to all droplet components, including the chemically unresolved NAFA. This comprehensive thermodynamic formulation serves as a benchmark for the evaluation of effects of NAFA surface activity in cloud droplet activation, as well as for the performance of the other representations applied.

(S) The simple partitioning model of Prisle et al. (2011): All surfactant solute is assumed to be completely partitioned to the droplet surface, such that $m^B_{\text{sft}} = 0$ for all droplet sizes and compositions, and the surface active particle components do not affect either water activity or surface tension at the point of activation. This representation is a simple empirical model based on the predictions of the thermodynamically consistent partitioning model of Prisle et al. (2010) for droplets comprising simple, strong, molecular surfactants (such as SDS) at the critical point of activation. Because the surface active components do not contribute to the composition-dependent droplet properties and the partitioning equilibrium does not need iteration, this representation is computationally simple and immediately applicable to chemically unresolved complex surface active mixtures. When all surfactant mass is depleted from the bulk, concentration-dependent droplet water activity is evaluated from the binary aqueous NaCl parametrization given by (Prisle, 2006) based on data from Low (1969):

$$a_{\text{w}} = 1 - 0.031715 b_{\text{NaCl}} + 0.0012582 b^2_{\text{NaCl}} - 0.000022921 b^3_{\text{NaCl}} . \tag{12}$$

Here, b_{NaCl} is the molal concentration of NaCl, which is readily determined from the mass concentration *via* the well-known molar mass of NaCl. Droplet surface tension is constant $\sigma = \sigma_{\text{w}}$.

(I) Insoluble surfactant model: Similar to (S), all surfactant solute is assumed to be completely partitioned to the droplet surface ($m^B_{\text{sft}} = 0$), but the surface tension is reduced by a constant amount to either $\sigma = 0.95\sigma_{\text{w}}$ or $0.80\sigma_{\text{w}}$ throughout droplet growth. This corresponds to a simplified representation of an insoluble surfactant, where the surface active component does not dissolve into the bulk solution, but forms a phase-separated layer on the surface which reduces solution surface tension according to the surface coverage (Ruehl et al., 2016). Due to the lack of quantitative surface-composition based surface tension relations for chemically unresolved NAFA, the surface tension reduction is here represented with a constant value.

(B) Bulk solution model: The droplet is assumed to have the same properties as a macroscopic (bulk) solution with corresponding total composition. The surface partitioning factor is assumed to be negligible, such that the droplet bulk phase composition is determined directly from the total composition without iteration ($\mathbf{x^B} = \mathbf{x^T}$). Droplet surface tension and water activity are evaluated according to the same concentration-dependent mass-based ternary parametrizations given in Eqs. 8 and 11 as for **(P)**. However, the bulk compositions at each droplet size will generally differ between the two representations.

(K) Basic Köhler model: Effects of surface activity are disregarded altogether. As for **(B)**, the droplet bulk phase composition is equal to the total droplet composition, without correction for surface partitioning ($\mathbf{x^B} = \mathbf{x^T}$). The surface tension is assumed to be constant for all droplet sizes and compositions and equal to that of pure water ($\sigma = \sigma_{\text{w}}$). Droplet water activity is evaluated according to the concentration-dependent mass-based ternary parametrization in Eq. 11, using the total droplet composition $a_{\text{w}} = a_{\text{w}}(\mathbf{x^T})$.

Representations (P), (S), and (I) include considerations of the impact of surface adsorption on bulk/surface partitioning, whereas (B) and (K) are both bulk solution representations. Surface tension is reduced in (P) and (B) according to composition

Table 1. Properties included in the different representations of NAFA surface activity used in Köhler calculations.

model	partitioning	$\sigma = \sigma_{\mathrm{w}}(\mathbf{x^B})$	$a_{\mathrm{w}} = a_{\mathrm{w}}(\mathbf{x^B})$
(P) full partitioning	Eq. 6	Eq. 8	Eq. 11
(S) simple partitioning	$m^B_{\mathrm{NAFA}} = 0$	σ_{w}	Eq. 12
(I) insoluble surfactant	$m^B_{\mathrm{NAFA}} = 0$	$0.80\sigma_{\mathrm{w}}, 0.95\sigma_{\mathrm{w}}$	Eq. 12
(B) bulk solution	no, $\mathbf{x^B} = \mathbf{x^T}$	Eq. 8	Eq. 11
(K) basic Köhler	no, $\mathbf{x^B} = \mathbf{x^T}$	σ_{w}	Eq. 11

dependent relations, and by a constant value in (I). As the surface active component is completely partitioned to the surface in (S) and (I), only NaCl impacts water activity in these representations, whereas ternary water activity relations are used in (P), (B), and (K).

Strictly, only representation (P) requires the use of fully continuous ternary parametrizations, since only in these calculations does the relative NAFA–NaCl solute mixing ratio change from that of the dry particles as the droplets grow ($w_i \neq W_{\mathrm{p},i}$). In representations (S) and (I), the relative bulk phase mixing state of NAFA and NaCl changes discontinuously at the onset of droplet growth, from the nominal dry particle value to $\{w_{\mathrm{NAFA}} = 0, w_{\mathrm{NaCl}} = 1\}$ in droplets where NAFA is completely partitioned to the surface. When representations (B) and (K) are used, the relative mixing ratio of NAFA and NaCl solutes remains equal to the nominal value of the dry particles and does not change with concentration of the growing droplets ($w_i = W_{\mathrm{p},i}$). The individual binary parametrizations (1-dimensional composition space) given for each nominal NAFA–NaCl solute mixing ratio by Kristensen et al. (2014) could therefore in principle be employed in these cases. For consistency, the ternary parametrizations given in Eqs. 8 and 11 are here used in all calculations, at essentially no additional computational cost. This allows us to compare features of the different surfactant representations, in terms of predicted droplet properties for continuous variation in dry particle compositions.

3 Results and discussion

In the following, we present results of modeled CCN activity and droplet properties during growth and at the critical point of activation for mixed NAFA–NaCl particles, using the ~~four different frameworks for including aqueous properties of NAFA in the~~ different representations of NAFA surface active properties in aqueous solution droplets. By analyzing and comparing the results of each representation, ~~we evaluate the~~ various effects of NAFA surface activity on predicted CCN activity are assessed. Model sensitivity to ~~various~~ selected input parameters, including ~~the choice of surface tension parametrization, assumed NAFA average molecular weight and mass density , temperature, and~~ assumed NAFA mass density and average molar mass, droplet temperature, choice of surface tension equation, and the effect of potential sample impurity in the droplet activation measurements of Kristensen et al. (2014) is presented in the SI.

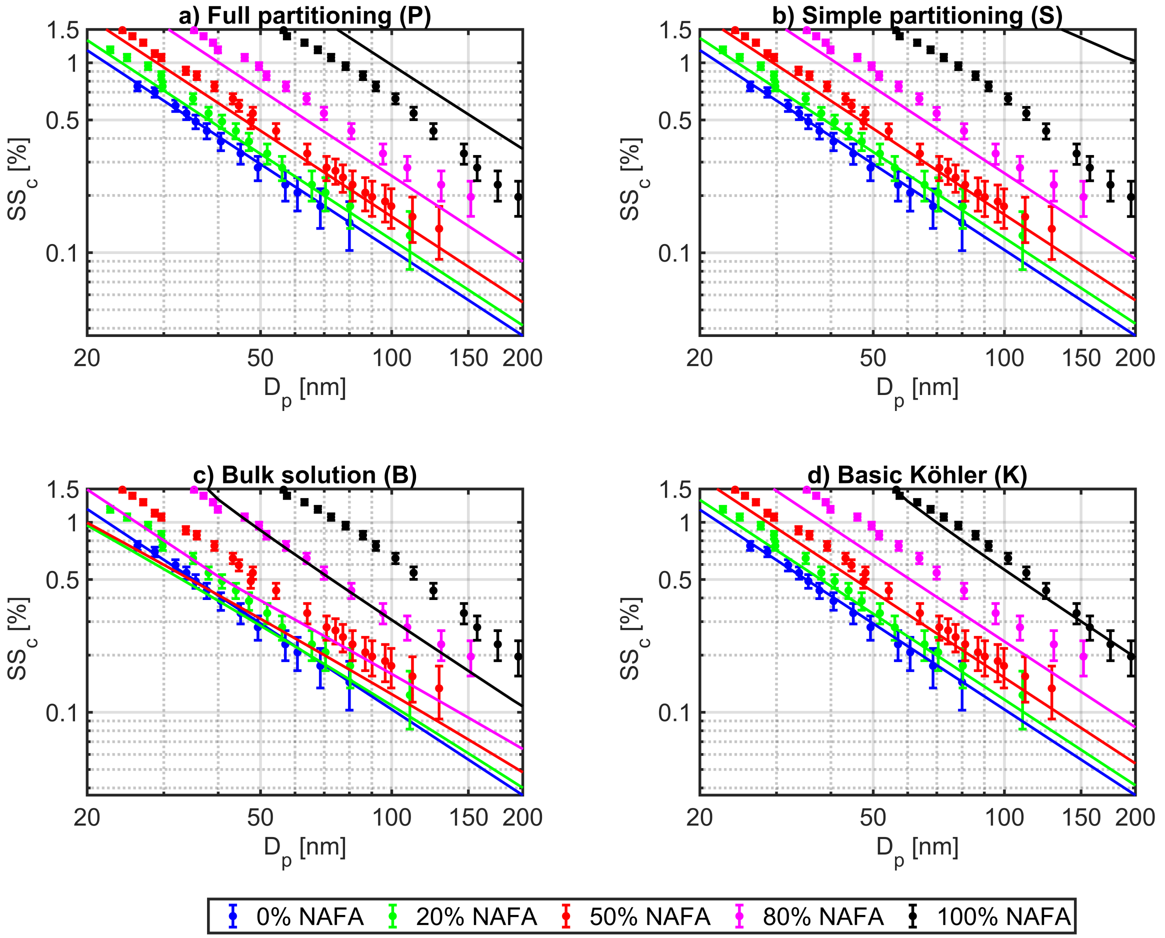
3.1 CCN activity

Modeled critical supersaturations (SS_c) as functions of dry particle diameter (D_p) are presented in Figure 1 for particles with dry NAFA mass fractions ($W_\mathrm{p,NAFA}$) of 0% (blue), 20%, (green), 50% (red), 80% (purple), and 100% (black), relative to NaCl. Results of Köhler calculations with each of the four ~~different~~ representations of surfactant effects ~~on CCN activity are shown as curves in separate panels and~~ (P), (S), (B), and (K) are shown in panels a), b), c), and d), respectively, together with the experimental values for particles with equivalent dry compositions reported by Kristensen et al. (2014) ~~are shown in each panel~~ for comparison. Error bars on the experimental data are estimated as ±1 standard deviations on measured SS_c, as reported by Kristensen et al. (2014). ~~Calculations using the representation (S) are not meaningful for the case of pure NAFA, as NAFA is assumed to have effective hygroscopicity parameter $\kappa = 0$. Therefore, results are in this case shown only for mixtures with up to 80%NAFA. All representations give similar results for pure particles, as expected. However, the water activity parametrization for binary used in (S) introduces some differences, compared to the ternary parametrization (Eq. 11) used in the remaining three models. The binary parametrization of Prisle (2006) is optimized for representing the slight changes in dissociation factor for in very dilute solutions and the effect of this can also be seen in calculations with (S) for the largest particles, which activate as highly diluted droplets.~~ Model results for representation (I) are shown in the SI.

~~For all representations~~

All representations of NAFA surface activity give similar results in the limit of pure NaCl particles, as expected. For each representation, the modeled CCN activity decreases (SS_c increases) with increasing $W_\mathrm{p,NAFA}$ for ~~each particle sizeinvestigated~~a given particle size, in agreement with the experimental trend. This shows that upon varying the dry particle composition from pure NaCl to pure NAFA, any effect of decreased droplet surface tension at the point of activation, from the presence of surface active NAFA in the droplet phase, cannot overcome the simultaneous increase in water activity (Eq. 2), arising from a potential combination of *i*) increasing droplet non-ideality (specifically leading to increased $\gamma_\mathrm{w} > 1$), *ii*) depletion of solute from the droplet bulk phase ~~solute~~ due to NAFA surface partitioning, and *iii*) the much higher average ~~molecular~~ molar mass of NAFA~~(e.g. Mäkelä and Manninen (2008) give the value 4266 g mol^{-1}),~~ , compared to pure NaCl ~~. We~~ (both leading to increased x_w^B). Several studies have previously observed the same trend, ~~both experimentally and~~ experimentally or in model calculations, for ~~simpler~~ aerosol systems comprising both simple strongly surface active ~~sodium dodecyl sulfate (SDS)~~ molecules, such as SDS and fatty acid sodium salts~~(FAS)~~ , as well as complex macromolecules and surface active mixtures, in various mixing ratios with NaCl ~~(Prisle et al., 2010, 2008; Sorjamaa et al., 2004)~~(Li et al., 1998; Prisle et al., 2008, 2010; Hansen et al., 20

The overall good performance of calculations using (P) are reassuring in terms of our ability to capture relevant properties of the activating droplets within the comprehensive thermodynamic description. Each of the representations (P), (S), and (K) describe the experimental data fairly well, except in the case of ~~calculations using (P) with respect to~~ pure NAFA particles~~. Here,~~ , where (P) ~~underestimates~~ and (S) underestimate CCN activity well outside the reported experimental uncertainty. In the absence of hygroscopic NaCl, predictions with model (S) correspond to condensation of water into a pure aqueous droplet phase in the presence of insoluble material, which is adsorbed at the droplet surface without attaining full coverage. Similarly for the insoluble surfactant model (I), shown in Fig. S3 in the SI, but here the reduced surface tension brings predictions



~~Critical supersaturations (SS_c) for mixed NAFA–particles, calculated (curves) using the four different surfactant representations described in Section 2.3: (a) comprehensive partitioning (P), (b) simple partitioning (S), (c) bulk solution (B), and (d) basic Köhler theory (K), in each case compared to experimental values (dots) measured by Kristensen et al. (2014). Colors indicate original dry particle fraction of NAFA ($W_{p,NAFA}$) relative to . Calculations are made using a mass density of $\rho_{NAFA} = 1.6$ g cm^{-3} for NAFA. Error bars on experimental data represent ±1 standard deviations on SS_c as reported by Kristensen et al. (2014).~~

Figure 1. Critical supersaturations (SS_c) for mixed NAFA–NaCl particles, calculated (curves) using the different representations of NAFA surface activity described in Section 2.3: (a) full partitioning model (P), (b) simple partitioning model (S), (c) bulk solution model (B), and (d) basic Köhler model (K), in each case compared to experimental values (dots) measured by Kristensen et al. (2014). Colors indicate original dry particle fraction of NAFA ($W_{p,NAFA}$) relative to NaCl. Calculations are made using a NAFA mass density of $\rho_{NAFA} = 1.6$ g cm^{-3}. Error bars on experimental data represent ±1 standard deviations on SS_c as reported by Kristensen et al. (2014).

somewhat closer to experimental values for pure NAFA particles, compared to (S). To reconcile predictions of model (I) with measured SS_c for pure NAFA particles would however require much stronger surface tension reductions than the 5–20% included in the present calculations, at the expense of increasingly poor agreement with experimental values for all other particle compositions. In general, it is clear that model (I) does not represent experimental CCN data well across the full range of NAFA–NaCl particle sizes and compositions investigated. This suggests that discrepancies observed for the other partitioning models (P) and (S) with respect to pure NAFA particles cannot be attributed to surface tension effects alone. It is possible that relatively small amounts of hygroscopic impurities could be present in the organic aerosol mass and thus enhancing experimental CCN activity, as described by Bilde and Svenningsson (2004). The model sensitivity analysis presented in the SI ~~show~~ shows that even 3% by mass of impurities ~~with~~ in the NAFA mixture with hygroscopic properties corresponding to those of NaCl would be sufficient to reconcile the calculations of model (P) ~~calculations~~ with experimental data for pure NAFA particles. ~~The overall good performance of calculations using (P) are reassuring in terms of our ability to capture relevant properties of the activating droplets within the comprehensive thermodynamic description. Of models (P), (S), and (K) , the latter seem~~ Model (K) tends to overestimate mixed NAFA–NaCl CCN activity ~~the most~~slightly more than (P) and (S), hinting that NAFA bulk depletion from surface partitioning may indeed have a more significant impact on decreasing CCN activity than surface tension reduction has on increasing it.

The most prominent feature of Fig. 1 is how Köhler calculations using the bulk solution representation (B) clearly and consistently underestimate experimental critical supersaturations for all particle sizes and compositions. ~~This was also noted by Kristensen et al. (2014), using a simplified model based on similar assumptions as (B). The significant exaggeration of CCN activity in this framework was also consistently found in our previous studies~~ Similar observations have been made in several previous studies at sub- and supersaturated conditions of particles comprising ~~the simple surfactants SDS and FAS,~~ both chemically simple and complex surfactants and for both pure surfactant particles and in various mixtures with ~~(Prisle et al., 2010, 2008; Sorjamaa et al., 2004)~~inorganic salts (Li et al., 1998; Rood and Williams, 2001; Sorjamaa et al., 2004; Prisle et a Thus, the dramatic increase in CCN activity ~~anticipated by Facchini et al. (1999), from including organic~~ initially anticipated from the results of Facchini et al. (1999), by including aerosol surface activity equivalent to macroscopic solutions in the Köhler framework, was ~~not found to reproduce experimental observations either for these particles comprising a more complex~~ found also for these particles comprising a more complex atmospherically relevant surface active mixture to not reproduce experimental CCN observations.

Kristensen et al. (2014) compared their measured CCN activities to two simple Köhler models based on similar assumptions as representations (B) – macroscopic solution, concentration-dependent surface tension and water activity – and (K) – macroscopic solution, constant surface tension equal to that of pure 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 partitioning model (P) and therefore for consistency run with the continuous ternary surface tension and water activity parametrizations presented in Eqs. 8 and 11, even if these are not needed in absence of bulk/surface partitioning calculations. Kristensen et al. (2014) used simpler parametrizations with a 1-dimensional composition domain, which are not continuous with respect to variations in the relative NAFA–NaCl mass fractions w_NAFA and ~~perhaps atmospherically relevant~~

~~organic surfactant mixture.~~ w_{NaCl} and have slightly different forms than the full ternary functions used here, even at the lines of intersection. Furthermore, the surface tension parametrizations used by Kristensen et al. (2014) are made for data points corresponding to measurement times t= 0 s after the formation of the surface and therefore based on higher surface tension values for a given solution composition, compared to the data from measurement times t= 600 s used in this work. As higher macroscopic surface tensions correspond to lower surface activity of NAFA, predictions of SS_{c} will similarly be biased higher, in the absence of partitioning considerations. Our calculations with model (B) would therefore also be closer to the experimental values of Kristensen et al. (2014) if we had used their surface tension parametrizations, but as clearly seen from Fig. 7 in Kristensen et al. (2014), this would still not bring model predictions even close to agreement with experiments.

Similar to the present model (K), Kristensen et al. (2014) also find that a basic Köhler model, where NAFA surface activity is completely ignored, gives good agreement with measured CCN activity for NAFA–NaCl particles with up to 50% NAFA, as well as for pure NAFA, but not for particle mixtures with 80% NAFA. This seemingly counter-intuitive result for particle mixtures comprising strongly surface active material with significant ability to lower surface tension in macroscopic solutions has previously been seen also for simple, strong surfactants, such as SDS and C8-C12 fatty acid salts (Sorjamaa et al., 2004; Prisle et al., 200 On the other hand, several recent studies have shown properties for both simple and complex atmospheric aerosol, e.g. secondary organic aerosol (Ruehl et al., 2016), marine primary organics (Ovadnevaite et al., 2017), limonene-derived organosulfate products (Hansen et al., 2015), and water-soluble pollen extracts (Prisle et al., 2019) which are consistent with an enhancement of aerosol hygroscopicity by surfactants, at least partly due to reduced surface tension. This suggests that model (K) is likely too simple to fully capture CCN activity of different types of surface active material across all atmospherically relevant particle compositions and conditions and that, generally, a full partitioning model is needed for robust predictions. In cases where the basic Köhler model (K) gives good agreement with experimental CCN activity, it also closely traces predictions with the comprehensive partitioning model (P).

3.2 Droplet properties at activation

Figure 2~~presents in panel (a) calculated~~ a presents critical supersaturations for 50 nm dry particles calculated with each model representation as a function of NAFA mass fraction $W_{\mathrm{p,NAFA}}$ in the dry particles. Experimental values from Kristensen et al. (2014) for particles with ~~approximate dry sizes of 50 nm~~ similar dry sizes are shown for reference. ~~Direct~~ Immediate comparison with experimental values is not always possible along ~~this~~ the particle composition dimension, as Kristensen et al. (2014) did not measure the exact same particle sizes for ~~different dry particle compositions~~each dry particle composition. This is because they used an experimental setup ~~allowing them to scan a range~~ scanning a set of pre-selected supersaturations, rather than ~~dry~~ particle sizes. ~~In the same figure~~Corresponding to each value of SS_{c} shown in panel (a), other panels ~~present for calculations on~~ in Fig. 2 show for the same 50 nm particles: (b) the ~~corresponding~~ individual Kelvin and Raoult terms~~calculated at the critical point of droplet activation, i.e. for the droplet sizes d_{c}, where the equilibrium Köhler curve reaches the critical supersaturation SS_{c}~~, (c) droplet diameter growth factor ~~at activation~~ $GF_{\mathrm{c}} = d_{\mathrm{c}}/D_{\mathrm{p}}$, and (d) droplet surface tension σ_{c}, also ~~evaluated~~ calculated at the critical point d_{c} of the Köhler curve. Qualitatively similar results were obtained for other ~~particle sizes as well. Any effects present~~ dry particle sizes, but model differences are more pronounced ~~and therefore shown here for~~

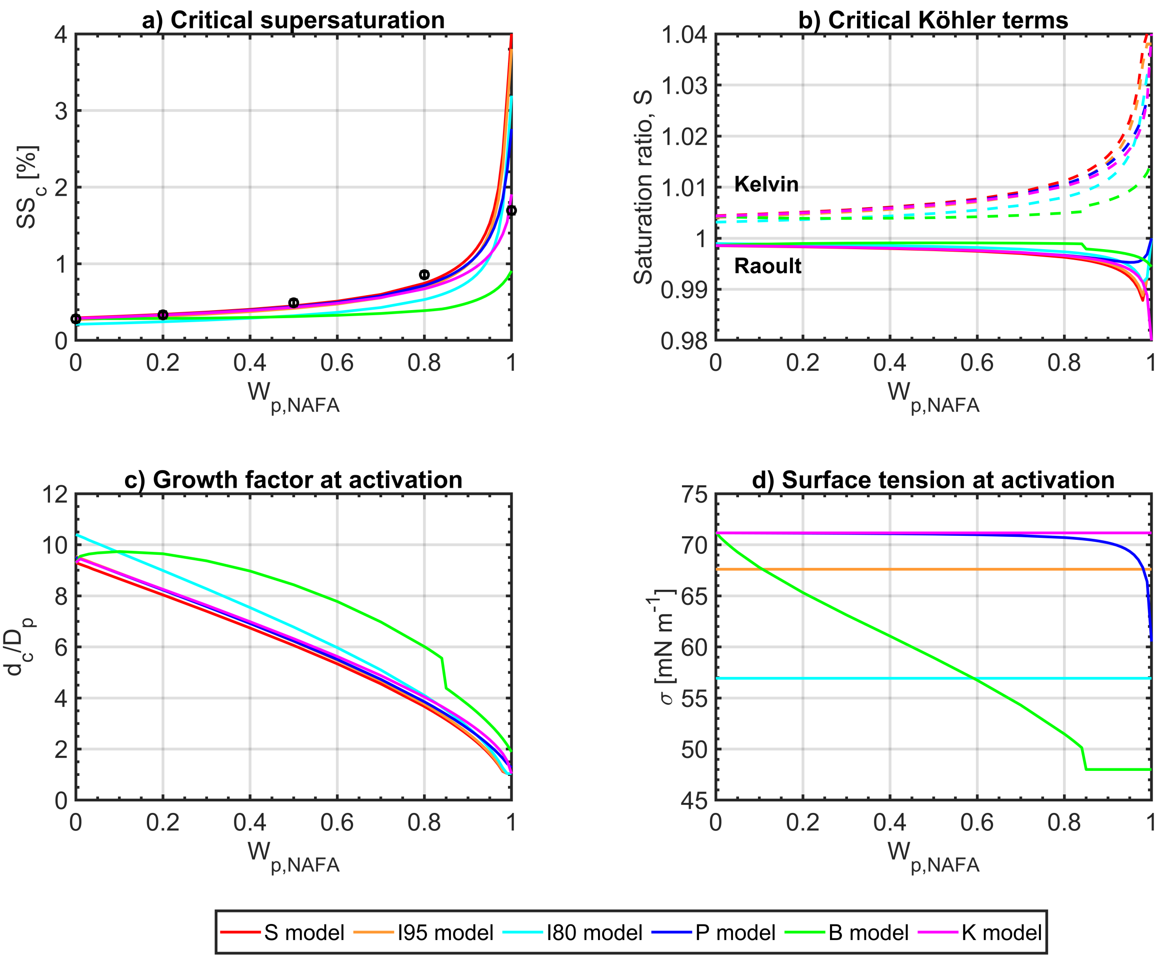


Figure 2. ~~Critical supersaturations~~ Properties of activating droplets calculated ~~for 50 nm dry particles~~ with ~~the four different~~ representations ~~of NAFA CCN activity,~~ (P), (S), (~~B~~I), (B) and (K) ~~,~~ at the critical point of droplet activation d_c for 50 nm dry particles as ~~a function~~ functions of dry particle NAFA mass fraction $W_{\mathrm{p,NAFA}}$: (a) critical supersaturations SS_{c}, ~~together with the~~ (b) Kelvin and Raoult terms corresponding to each SS_{c} at the critical point of the ~~corresponding~~ Köhler curve, (~~b~~c) ~~,~~ droplet diameter growth factor, and (~~c~~d) ~~and~~ droplet surface tension. In panel (~~d~~a), ~~all evaluated~~ experimental values from Kristensen et al. (2014) for ~~the same dry~~ particles ~~at the critical point of droplet activation, d_c~~ with similar dry sizes are shown for reference.

~~particles with smaller dry diameters: these activate for higher critical supersaturations (?), and thus for~~ for smaller particles, which generally activate for smaller critical sizes, corresponding to smaller critical growth factors~~and~~ , with more concentrated droplet compositions ~~, and with~~ and larger surface area-to-bulk volume ratios, introducing more pronounced surface partitioning for a given total composition.

Results in Fig. 2 ~~demonstrate~~ illustrate how the simple ~~surfactant representation~~ representations (S) ~~traces the~~ and (I), as well as the basic Köhler model (K) all predict very similar properties of activating droplets to those of the comprehensive partitioning model (P) for essentially the entire range of NAFA mass fractions in the particles. Not only critical supersaturations, but also the individual Kelvin and Raoult terms at the point of droplet activation, are fairly similar ~~between (P) and (S), and~~ and predicted droplet sizes at activation (as represented by the droplet growth factors) also agree well. This was not immediately expected, ~~as~~ since model (S) was proposed to emulate specifically SS_c, not necessarily ~~individual~~ other droplet properties at ~~d_c~~ the critical point (Prisle et al., 2011), and since NAFA is seen from experimental data to give significant surface tension reductions in macroscopic solutions (Kristensen et al., 2014), contrary to the assumptions of both (S) and (K). The similarity of all activation parameters indicates that the underlying assumptions of ~~the simple representation, as predicted by the comprehensive model~~ ~~,~~ both the simple representations and the basic Köhler model are reasonably representative for the NAFA particle systems in question~~. The basic Köhler model (K) predicts nearly identical droplet activation properties to those of (P), for particle compositions with up to about 80% by mass of NAFA.~~ , as predicted by the comprehensive model (P). This close agreement between basic Köhler predictions and comprehensive partitioning thermodynamics was also observed ~~for mixed~~ in previous studies for mixed surfactant–NaCl particles with SDS and ~~FAS in previous studies~~ fatty acid salts (Prisle et al., 2010, 2008). For NAFA particles, the agreement extends to even larger surfactant fractions (up to about 80% by mass of NAFA) than seen in these earlier studies, where models agreed for dry particle surfactant mass fractions up to about 50%.

~~Panel (d) in~~ It is important to note that properties in Fig. 2 correspond to critical droplets of different sizes d_c. Therefore, in addition to the overall variation in total solute composition given by $W_\mathrm{p,NAFA}$, also the droplet dilution state, as reflected in the varying activation growth factors GF_c (panel c), and the ensuing size-dependent bulk/surface partitioning of NAFA predicted with representation (P) vary between the droplets. Total composition, dilution, and partitioning each affect the droplet bulk solution composition, from which the droplet surface tension (panel d) and Kelvin and Raoult terms (panel b) are evaluated. Variations of critical droplet properties with $W_\mathrm{p,NAFA}$ therefore do not *a priori* reflect continuous variation in all underlying droplet properties, as they represent only the maxima of individual Köhler curves corresponding to each particle composition.

The Raoult terms shown in Fig. 2~~shows that the predicted surface tension at droplet activation is overall only modestly reduced within the (P) framework. Indeed, for~~ b each vary as functions of $W_\mathrm{p,NAFA}$, replacing hygroscopic NaCl with the significantly less hygroscopic component NAFA, as well as the critical droplet dilution state, both affecting the overall amount of water and solute in the droplets, and in the case of representations (P), (S), and (I) also the extent of NAFA bulk/surface partitioning. Each affect the composition of the droplet bulk phase, which govern a_w according to Eq. 2 in general and Eqs. 11 or 12 for the present calculations in particular. The calculated critical Raoult terms are seen to be *higher* for the bulk solution representation (B) than the other representations, despite that (P), (S) and (I) consider bulk depletion of NAFA, whereas (B), like (K), does not. This is due to the significantly higher dilution factor of activating droplets predicted by (B), as is seen from GF_c in Fig. 2c. For representations (P), (S) and (I), both Raoult terms and growth factors of activating droplets are very similar. For all representations, the predicted reduction of water activity at droplet activation is modest across the dry particle composition range.

For representations (P), (S), and (I), an infliction point is seen in the Raoult terms for very high $W_{\mathrm{p,NAFA}}$, whereas for (B) and (K), the Raoult terms decrease with increasing $W_{\mathrm{p,NAFA}}$ throughout the dry particle composition range. In the absence of bulk/surface partitioning, droplet concentrations continue to increase with decreasing dilution of the total solute mass, as seen from the growth factors GF_{c} Fig. 2c. When NAFA bulk/surface partitioning is considered, the effect of decreasing dilution is first strong enough to overcome the decrease in total amount of hygroscopic material with increasing $W_{\mathrm{p,NAFA}}$ and the depletion of NAFA from the droplet bulk, leading to decreasing Raoult terms, but eventually the balance reverses, as the total amount of NaCl becomes too small to compensate for the surface active component which is largely depleted from the bulk. With the full partitioning model, the Raoult term changes smoothly, whereas sharp infliction points are seen for the simple models (S) and (I), where partitioning occurs as a step function. Bulk compositions of activating droplets are discussed in more detail related to Fig. 3 below.

For representation (B), the Raoult term has a step change with respect to dry particle composition for $W_{\mathrm{p,NAFA}} = 0.85$. The increasing concentrations of both NAFA and NaCl are clearly seen in Figs. 3a and b below. This is caused by a step decrease in the critical droplet growth factors GF_{c} (Fig. 2c), leading a to a simultaneous step increase in the Kelvin term (Fig. 2b). As seen in Fig. 2a, the opposing changes in the Kelvin and Raoult terms caused by decreasing d_{c} cancel out, so that the resulting SS_{c} change smoothly with $W_{\mathrm{p,NAFA}}$. At the same dry particle composition, critical droplet surface tensions σ_{c} predicted with representation (B) reach a constant minimum value in Fig. 2d. This corresponds to droplets exceeding a critical micelle concentration-type transition for NAFA, which is estimated from the surface tension data of (Kristensen et al., 2014) to occur for various NAFA–NaCl mixtures at $\sigma = 48\ \mathrm{mN\ m^{-1}}$. Figures 4 and 5 (discussed in more detail below) show how the predicted critical point d_{c} shifts between two local maxima on the Köhler curve, from the larger to the smaller droplet size, corresponding to droplets with surface tensions above or at the minimum value, respectively. This causes the discontinuous shift in d_{c} and critical droplet properties seen for representation (B) in Figs. 2 and 3. A similar shift is not seen for calculations with representation (P), because droplet surface tension never reaches the minimum value $\sigma = 48\mathrm{mN\ m^{-1}}$ (Figs. 2d and 5).

The Kelvin term at droplet activation depends on the critical droplet size d_{c}, determining the curvature effect according to Eq. 1, together with the droplet surface tension as a function of droplet bulk composition, which in turn is governed by the droplet dilution state and size-dependent bulk/surface partitioning. The critical Kelvin terms for each NAFA representation in Fig. 2b generally follow the corresponding trends in d_{c} as given by GF_{c} (Fig. 2c). For representations (P), (S), and (I), GF_{c} values are mutually very similar across the entire dry particle composition range. Figure 2d shows how droplet surface tension at activation is reduced according to Eq. 8 in calculations with (P) and (B), or fixed to σ_{w}, $\sigma = 0.95\,\sigma_{\mathrm{w}} \approx 68\ \mathrm{mN\ m^{-1}}$, and $\sigma = 0.80\,\sigma_{\mathrm{w}} \approx 57\ \mathrm{mN\ m^{-1}}$ for models (K), (I95), and (I80), respectively. When the critical surface tension is significantly reduced in calculations with (B) and (I80), the corresponding Kelvin terms are somewhat lower than for (P), (S), and (I), where surface tension is only modestly reduced at activation, or not at all.

Predictions with representation (B) in Fig. 2d show that NAFA can significantly reduce surface tension of activating droplets when they are considered similar to macroscopic solutions, whereas for representation (P) the predicted surface tensions at droplet activation are overall only modestly reduced. For particles with less than 80% by mass of NAFA, the surface tensions in activating droplets are essentially the same as for pure water and only for the very highest mass fractions of NAFA

$(W_{\rm p,NAFA} > 0.95)$ is the surface tension reduced by more than 5% from the pure water value. This is one of the fundamental assumptions underlying calculations with both (S) and (K) – and the validity of this assumption as predicted with (P) for all but the largest dry particle NAFA fractions is one of the main reasons for the simultaneous close agreement between calculations using (S) and (K), and the comprehensive framework of (P). ~~For the highest NAFA fractions, $\sigma_{\rm c}$ is predicted with (P) to be moderately reduced, but never by more than about 10 $\rm mN\,m^{-1}$ from the pure water value. Nevertheless, the~~ Furthermore, the effect of this modest surface tension reduction ~~on~~ at the point of droplet activation must be more than counterbalanced by bulk depletion from NAFA surface partitioning, since the predicted $SS_{\rm c}$ are higher for (P) than for (K), but slightly ~~lower in (P~~higher in (S) than for (~~S~~P), at the highest NAFA fractions. This is also reflected in the corresponding Raoult terms.

~~We note how the calculated Raoult termsin panel (b) show that the predicted water activity of activating droplets is higherfor the bulk solution representation (B) than the other three representations, despite that (P) and (S) consider bulk depletion of NAFA, whereas (B), like (K), does not. This is due to the much higher dilution factor of activating droplets predicted by (B), as is seen from the significantly larger $GF_{\rm c}$ in panel (c).~~

3.2.1 Bulk composition of activating droplets

3.3 ~~Effects of NAFA partitioning~~

Figure 3 presents ~~calculated~~ mass concentrations of (a) NAFA and (b) NaCl ~~mass concentrations~~ in the droplet bulk, ~~C$_{\rm NAFA}$ and C$_{\rm NaCl}$,~~ $C_{\rm NAFA}$ and $C_{\rm NaCl}$ (both in g L^{-1}~~, at~~) calculated at the critical point of activation $d_{\rm c}$ for the same particles with dry diameters of 50 nm ~~,~~ and compositions $W_{\rm p,NAFA}$ as in Fig. 2. These are the solute concentrations governing the evaluated droplet surface ~~tension~~ tensions and water activities at activation. ~~The two lower panels in Fig. 3 illustrate the extent of calculated bulk–surface partitioning of NAFA in activating droplets: Panel (c) presents the surface–bulk partitioning factor of NAFA, in terms of the mass ratio of NAFA solute in the droplet surface and bulk $m^S_{\rm NAFA}/m^B_{\rm NAFA}$, calculated with representation (P). In representation (S), this value is 1 at all droplet sizes, and in both (B) and (K), it is 0. Panel (d) presents the bulk mass fraction of solute comprised by NAFA, $w_{\rm NAFA} = m^B_{\rm NAFA}/(m^B_{\rm NAFA} + m^B_{\rm NaCl})$, at the point of droplet activation, calculated with representations (~~For the non-partitioning salt, $C_{\rm NaCl}$ is determined by the total amount of NaCl in the dry particle, given from $W_{\rm p,NAFA}$, and the droplet dilution state at activation, $GF_{\rm c}$ (Fig. 2c). For representations (P)~~, (B), and (K). For calculations with (B)and (K), (green and pink lines, respectively) the ratio of C$_{\rm NAFA}$ (panel a) and C$_{\rm NaCl}$ (panel b)scale with the nominal value of the dry particle composition $W_{\rm p,NAFA}$, as it should in the absence of~~, (S) and (I), $C_{\rm NAFA}$ is in addition affected by bulk depletion from ~~surface partitioning of NAFA. This is also seen directly from $w_{\rm NAFA}$ in panel (d). With representation (S~~the size-dependent or step-wise bulk/surface partitioning. In calculations with (S) and (I), the bulk NAFA concentration ~~and solute fraction is vanishing at all droplet sizes.~~

~~When partitioning is considered in~~ is vanishing due to complete partitioning to the droplet surface, however, also for the comprehensive partitioning model (P) ~~,~~ are NAFA bulk concentrations ~~are~~ nearly vanishing at the point of activation across ~~the dry particle composition range. Concentrations~~ all dry particle compositions. As before, qualitatively similar results were obtained for other particle sizes. For larger particles, concentrations are even more dilute than those presented here for 50 nm particles.

In model (K), concentrations of *both* NAFA and NaCl in activating droplets increase with NAFA mass fraction in the dry particles, except ~~(i) for calculations with (B) in general, and (ii) in all representations for~~ for particles with the very largest dry NAFA fractions. This reflects how particles ~~become less CCN active, as the NAFA fraction increases, or as surface tension according to macroscopic solution properties are reconsidered, and thus particles activate for higher critical supersaturations, smaller relative growth factors, and thus~~ activate for still more concentrated droplet compositions, as ~~is also~~ seen in Fig. 2~~(c)~~c. Across the ~~four representations,~~ all representations, evaluated C_{NaCl} at droplet activation for a given dry particle composition follow the trend in GF_{c}. In particular, for all representations except (B), activating droplets become more concentrated in the inorganic salt, even if $W_{\mathrm{p,NaCl}}$ decreases. ~~We note again, that qualitatively similar results were obtained for other particle sizes as well.For larger particles, concentrations are even more dilute than those presented here for 50 nm particles~~For calculations with representation (B), C_{NAFA} increases with $W_{\mathrm{p,NAFA}}$ and decreasing GF_{c}, as expected. C_{NaCl} first decreases slightly, as the amount of NaCl in the particles decreases with increasing $W_{\mathrm{p,NAFA}}$, reflecting also a state of increasing, or relatively high, dilution, as activation occurs for large d_{c} when droplet surface tension is increasingly reduced (Fig. 2d). A discontinuous increase is seen with (B) for both C_{NAFA} and C_{NaCl} at $W_{\mathrm{p,NAFA}} = 0.85$, reflecting the sudden decrease in GF_{c} (Fig. 2c) as droplet activation shifts from the local maximum at larger, to that at smaller, d_{c} (Figs. 4 and 5). For all representations, C_{NaCl} show an infliction point for the largest $W_{\mathrm{p,NAFA}}$, where concentrations eventually fall, as decreasing dilution can no longer counter the decreasing total NaCl content in the droplets. This infliction point is visible in the Raoult terms of the partitioning representations (P), (S), and (I) seen in Fig. 2b, but not strong enough to translate into a similar infliction the Raoult terms of the bulk solution models (B) and (K).

~~Mass concentrations C_i in g L^{-1} of (a) NAFA and (b) in activating droplets calculated with the different representations (P), (S), (B), and (K), for dry particles with diameters of 50 nm. For the same particles are also shown (c) NAFA mass partitioning factor in terms of the surface–bulk mass ratio of NAFA, $m^S_{\mathrm{NAFA}}/m^B_{\mathrm{NAFA}}$, and (d) mass fraction of bulk solute in activating droplets comprised by NAFA, $w_{\mathrm{NAFA}} = m^B_{\mathrm{NAFA}}/(m^B_{\mathrm{NAFA}} + m^B_{\mathrm{NaCl}})$, both at the point of droplet activation.~~

The NAFA surface partitioning factor at droplet activation, in terms of the mass ratio of NAFA solute in the droplet surface and bulk, $m^S_{\mathrm{NAFA}}/m^B_{\mathrm{NAFA}}$, calculated with representation (P), is shown in Fig. 3c. In representations (S) and (I), this value is infinite at all droplet sizes, and in models (B) and (K), it is 0. Fig. 3d shows the resulting droplet bulk composition in terms of the mass fraction of solute comprised by NAFA, $w_{\mathrm{NAFA}} = m^B_{\mathrm{NAFA}}/(m^B_{\mathrm{NAFA}} + m^B_{\mathrm{NaCl}})$, at the point of droplet activation. For calculations with (B) and (K), this ratio is identical to the dry particle composition $W_{\mathrm{p,NAFA}}$, as it should in the absence of bulk depletion from surface partitioning of NAFA. With representations (S) and (I), the NAFA bulk solute fraction is vanishing, as $C_{\mathrm{NAFA}} = 0$ g L^{-1} (Fig. 3a). Partitioning of NAFA profoundly changes the droplet bulk ~~composition~~ phase mixing state at the point of activation, compared to the relative NAFA–NaCl ratio in the original dry particles. For 50 nm particles in Fig. 3~~(c), the NAFA partitioning factor~~ c, $m^S_{\mathrm{NAFA}}/m^B_{\mathrm{NAFA}}$ in activating droplets calculated from the comprehensive partitioning model (P) is larger than 500 for all particle compositions~~, and for~~. For all dry particle sizes and NAFA mass fractions ~~,~~ investigated (Fig. 1), calculated $m^S_{\mathrm{NAFA}}/m^B_{\mathrm{NAFA}}$ at the point of activation is greater than two orders of magnitude (not shown). ~~Put another~~

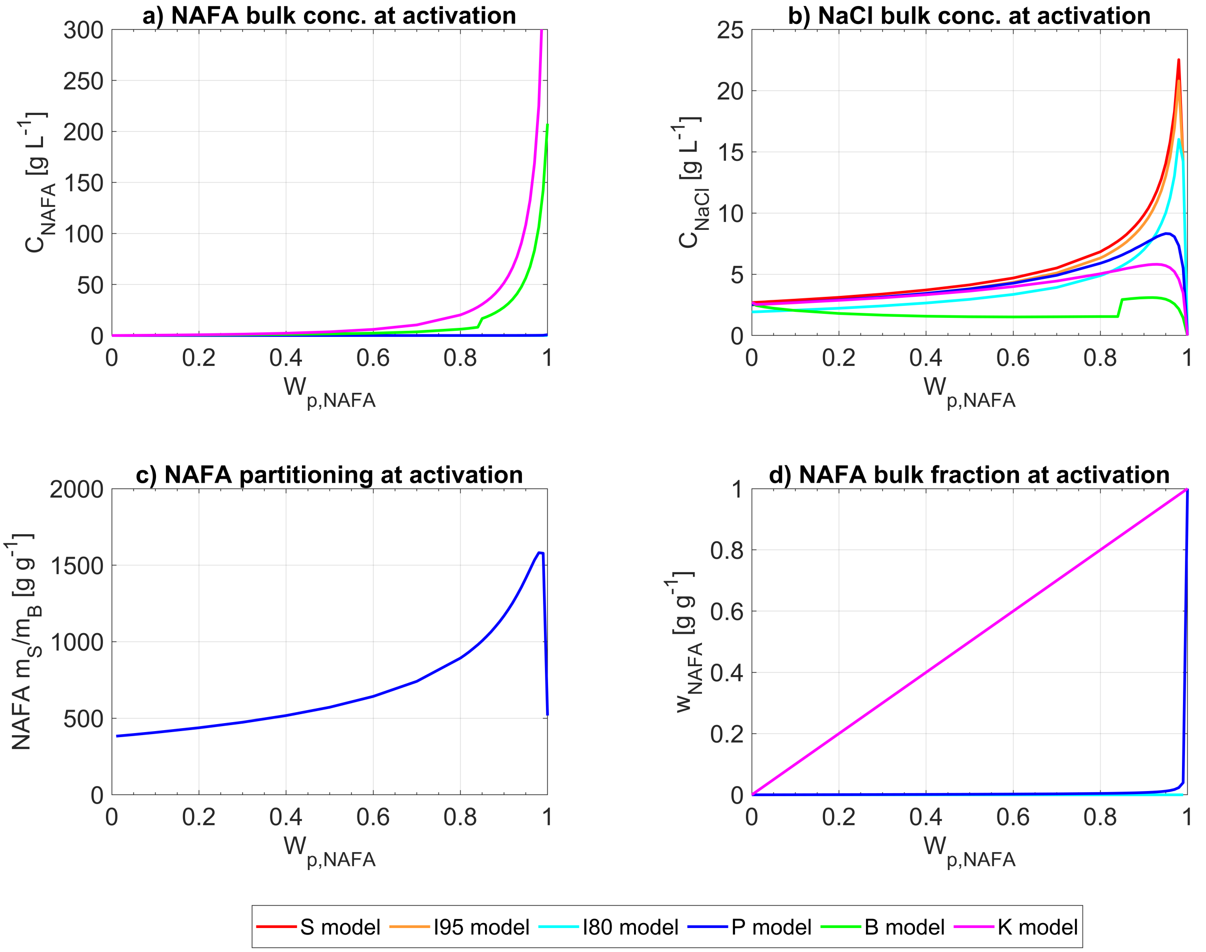


Figure 3. Mass concentrations C_i (in g L^{-1}) of (a) NAFA and (b) NaCl in activating droplets calculated with the different representations (P), (S), (I), (B), and (K), for dry particles with diameters of 50 nm. For the same particles are also shown (c) NAFA surface partitioning factor $m^S_{\mathrm{NAFA}}/m^B_{\mathrm{NAFA}}$, and (d) mass fraction of bulk solute comprised by NAFA, $w_{\mathrm{NAFA}} = m^B_{\mathrm{NAFA}}/(m^B_{\mathrm{NAFA}} + m^B_{\mathrm{NaCl}})$, evaluated at the point of droplet activation.

~~way,~~ As a result, except for the very largest dry particle NAFA fractions, the concentration of NAFA (Fig. 3a) and the relative amount of droplet solute comprised by NAFA ~~shown in panel (d)~~ (Fig. 3d) in activating droplets is all but vanishing~~, even when the partitioning equilibrium is evaluated in the most comprehensive framework (P).~~ .

These observations support the applicability of the underlying assumptions in the simple representation (S) for NAFA CCN activity, that the surfactant bulk concentration at droplet activation is effectively 0 and the overall impact of NAFA on particle hygroscopicity is vanishing.

3.3 ~~NAFA impact on surface tension~~Properties of growing droplets along Köhler curves

3.3.1 ~~Macroscopic solutions~~

~~NAFA is surface active and significantly reduces surface tension in macroscopic aqueous solutions, as is also the case for other model HULIS like Suwannee River Fulvic Acid (SRFA) and Humic acids (e.g. Kiss et al., 2005; Aumann et al., 1967; Kristensen et al., 201~~ ~~In Figure **??** (~~Figure 4 shows the Köhler curves for selected dry particle compositions $W_{\mathrm{p,NAFA}} =$ (a) ~~, modeled variation in aqueous surface tension as a function of NAFA mass concentration using the ternary Eq. 8 is compared to the underlying measurements of Kristensen et al. (2014) for macroscopic bulk solutions with mass mixing ratios of 20, 50, 80~~0.20, (b) 0.50, (c) 0.80, and ~~100% NAFA relative to . To obtain a smooth fit with continuous independent variations in both NAFA and concentrations, the ternary parametrization does not always represent data quite as well as individual fits to one dimensional concentration domains with fixed w_{NAFA} (not shown) might, for especially dilute solutions. To facilitate comparison with experimental data, surface tensions in Fig. **??** are predicted for 298 K. Calculations~~ (d) 0.95, calculated with each model representation for the 50 nm particles described in Figs. 2 and 3. The droplet surface tensions evaluated along the Köhler curves are shown in Fig. 5 and the corresponding NAFA surface partitioning factors $m^{S}_{\mathrm{NAFA}}/m^{B}_{\mathrm{NAFA}}$ and water activities of the growing droplets are presented in Figs. S4 and S5 of the SI. For all curves representing calculated properties of the growing droplets, the respective critical points of droplet activation (SS_{c}) presented in Figs. 1 and S3 are indicated with asterisks.

All representations used in calculations of CCN activity ~~in this work are made for temperatures of 303 K, yielding potentially lower aqueous surface tensions due to the temperature dependence of Eq. 8. The effect on Köhler calculations is however negligible (see SI for more details).~~

~~At a given C_{NAFA} , the surface tension reduction increases with concentration of (i.e. with decreasing w_{NAFA})until at least 80% of the solute mass is comprised by .This is a clear demonstration of salting out of NAFA by the inorganic salt in these solute composition and concentration ranges (e.g. **?**). Salting out is likely caused by increased non-ideality ("ionic strength")in solutions with larger~~ produce meaningful Köhler curves and other solution properties for the growing droplets. The close agreement between representations (P), (S), (I95) and (K) for calculated droplets properties at the point of activation d_{c} is seen in Fig. 4 along the full Köhler curves, expect for the highest NAFA fraction in the dry particles (panel d). For $W_{\mathrm{p,NAFA}} = 0.95$, clear differences in the shapes of the Köhler curves can be seen, as the differences between the NAFA representations become more prominent relative to the still smaller amount of hygroscopic NaCl ~~concentrations affecting the solubility and/or surface propensity of NAFA by enhancing the organic activity~~in the droplets.

~~Panel (b) in Fig. **??** shows the variation in ternary surface tension fitting parameters given by Eqs. 9 and 10 across the full range of NAFA solute mass fractions w_{NAFA}. By analogy to the Szyszkowski equation (**?**), parameter q_{st1} can be interpreted as related to the maximum surface excess $\Gamma^{\mathrm{max}}_{\mathrm{NAFA}}$ (notably, defined on a $\mathrm{mmol/m^2}$ concentration scale) by~~

~~$q_{\mathrm{st1}} = RT\Gamma^{\mathrm{max}}_{\mathrm{NAFA}}$,~~

~~and parameter q_{st2} as the (inverse of the) surface activity coefficient (with respect to a mass-concentration scale and infinite dilution reference state), see also Aumann et al. (1967). Fig. **??** (b) shows how NAFA surface activity is predicted to increase~~

~~(the inverse of q_{st2} increases) with increasing w_{NAFA}, while the corresponding maximum surface excess (and q_{st1})simultaneously decrease. The latter effect may be caused by concurrent increased depletion of salt ions from the aqueous surface as~~ For both representations (I80) and (B), the predicted droplet surface tension is significantly reduced during droplet growth and well beyond the point of activation. At a given droplet size d, the ~~salt fraction increases. Interestingly, we find very similar values for both Γ^{max} and surface adsorption parameter q_{st2} as Aumann et al. (1967) for Suwannee River Fulvic Acid in both binary aqueous solution and a 25% solute mass mixture with . Their data for SRFA has been included in Fig. **??** (b)for comparison.~~

~~Macroscopic surface tension of aqueous NAFA–solutions: (a) Surface tension as function of NAFA mass concentration in solutions with different NAFA and mixing ratios, as predicted with the ternary parametrization in Eq. 8 for 298 K, and compared to data from Kristensen et al. (2014). (b) Variation in the Szyszkowski fitting parameters given in Eqs. 9 and 10 and related maximum surface excess $\Gamma^{\mathrm{max}}_{\mathrm{NAFA}}$ from Eq. **??** with NAFA mass fraction relative to . Similar data for Suwannee River Fulvic Acid from Aumann et al. (1967) is shown for comparison.~~

3.3.1 ~~Activating droplets~~

~~It was seen already in Fig. 3 how activating droplets formed on NAFA containing particles are predicted to be fairly dilute aqueous solutions, with bulk solute compositions w_i significantly different from the original dry particle composition $W_{\mathrm{p},i}$ when NAFA bulk–surface partitioning is taken into account. For example, mass concentrations of NAFA and are $0.0066\ \mathrm{gL}^{-1}$ and $3.80\ \mathrm{gL}^{-1}$, respectively,~~ equilibrium supersaturation SS is higher for representation (B) than for (I80) when the concentration-dependen droplet surface tension is higher in (B) than the fixed surface tension of $\sigma = 0.80\sigma_{\mathrm{w}}$ in (I80), and vice versa. When partitioning is included in the calculations with representations (P), (I95), and (S), the order of the Köhler curves at each d, as well as the values of SS_{c} at the critical points, do not simply follow the relative magnitudes of the droplet surface tensions. In calculations with representation (P), surface tension is reduced for the more concentrated droplets at the earlier stages of the Köhler growth curves, but only for the highest $W_{\mathrm{p,NAFA}}$ is the reduction maintained until the critical point. Even for droplets much smaller and more concentrated than at the point of ~~droplet activation , calculated with model (P)for 50 nm particles with dry mass fractions of 50% NAFA. For 100 and 150 nm particles of the same composition, the corresponding values (not shown) are 0.0065 and $0.0064\ \mathrm{gL}^{-1}$ NAFA, and 1.34 and $0.736\ \mathrm{gL}^{-1}$. The relative solute mass fractions of NAFA w_{NAFA} in the activating droplets are thus 0.0017, 0.0049, and 0.0086 for the 50, 100, and 150 nm dry particles, respectively.~~ activation ($d < d_{\mathrm{c}}$), surface tension is never reduced by more than about 10% from the pure water value. This reflects the very small amounts of NAFA solute remaining in the droplet bulk phase, when bulk/surface partitioning is taken into consideration.

~~Surface tensions as function of NAFA mass concentration C_{NAFA} predicted with Eq. 8 for aqueous solutions with NAFA solute mass fractions w_{NAFA} of 0.001, 0.01, 0.1, and 1, relative to .~~

~~Modeled surface tensions for aqueous solutions with NAFA solute mass fractions w_{NAFA} of 0.001, 0.01, 0.1, and 1, respectively, are shown in Fig. **??** as functions of surfactant mass concentration. There are virtually no differences between surface tensions modeled for different mixing ratios $w_{\mathrm{NAFA}} < 0.1$ (all fall under the pink line for $w_{\mathrm{NAFA}} = 0.1$). Solute mixing states $w_{\mathrm{NAFA}} > 0.1$ are not realized for activating droplets when partitioning~~ The degree of partitioning to the surface is significant already at the much higher droplet concentrations at the early stages of the Köhler curves before activation and generally the amount of NAFA in the droplet surface is ~~included and these results are shown in Fig. ?? merely to illustrate the surfactant fractions at which changes due to solute mixing state do begin to occur.~~

~~In the NAFA concentration range up to 10^{-2} $\mathrm{gL^{-1}}$, the predicted ternary surface tensions are virtually identical to σ_w~~2-3 orders of magnitude higher than the amount left in the bulk (Fig.~~These are solutions representative of droplets at d_c for particles with a dry NAFA mass fraction of 50%. For some of the highest fractions of NAFA, as in the case of $W_\mathrm{p,NAFA} = 0.95$, the concentrations predicted with model (P) in activating droplets formed on 50, 100, and 150 nm dry particles are 0.1121, 0.1271, and 0.1306 $\mathrm{gL^{-1}}$ of NAFA, and 9.2485, 3.6409, and 2.0446 $\mathrm{gL^{-1}}$ of , respectively, and the corresponding values of w_NAFA are 0.0120, 0.0337, and 0.0600.~~

~~It is crucial to keep in mind that none of the~~S4). Typically, $m^S_\mathrm{NAFA}/m^B_\mathrm{NAFA}$ is even higher for droplet sizes $d < d_\mathrm{c}$ than at the critical point, illustrating that partitioning has even greater effect on droplet bulk concentration than smaller degrees of dilution in smaller droplets. As a consequence, even if NAFA is able to significantly reduce surface tension in macroscopic solutions, the same effect is not seen in microscopic activating droplets, even at similar total droplet concentrations. A comparison of surface ~~tension values for solution compositions representative of activating NAFA–~~tension variations predicted with Eq. 8 in macroscopic and microscopic droplet solutions due to changes in bulk composition from NAFA partitioning is discussed in more detail in the SI. Fig. S5 shows how droplet water activity increases as droplets grow and dilute along the Köhler curve. The water activity is significantly reduced early in droplet growth, but except for the largest $W_\mathrm{p,NAFA}$ is very close to 1 at d_c. Predicted droplet a_w only differ significantly between the different representations when NAFA fractions in the dry particles are very large. As NAFA is much less hygroscopic than NaCl~~droplets in Fig~~, and the resulting reduction of water activity is even smaller for sub-micron droplets due to strong bulk/surface partitioning, a_w is governed by the hygroscopic salt and variations mainly reflect the varying droplet dilution state. ~~?? are constrained by the measurement data of Kristensen et al. (2014). In model (P), w_NAFA is significantly decreased from $W_\mathrm{p,NAFA}$ of the original dry particle, due to bulk depletion of NAFA, but not of the salt, and typically $C_\mathrm{NAFA} << C_\mathrm{NaCl}$. An important implication of this is that the ternary surface tension and water activity parametrizations used for calculating properties during droplet growth and activation are both extrapolated far beyond the well-constrained composition domains for making the comprehensive partitioning calculations in this work. All model calculations using the (P) representation should therefore be taken with an appropriate "grain of salt", even if we anticipate that the results presented here will qualitatively remain valid under improved constraints of ternary aqueous solution properties. As a consequence, we strongly recommend that this potentially large change in droplet composition from corresponding macroscopic solutions is taken into consideration when measuring aqueous surface tension of various organic aerosol components for the purpose of analyzing or predicting aerosol CCN activity . We are also aware, however, of the significant challenges involved in measuring accurate surface tension–concentration isotherms for such low organic concentrations and in preparing samples with the appropriate well-defined organic–inorganic mixing ratios.~~

3.3.1 ~~Consequences for Köhler modeling~~

3.4 Consequences for Köhler modeling

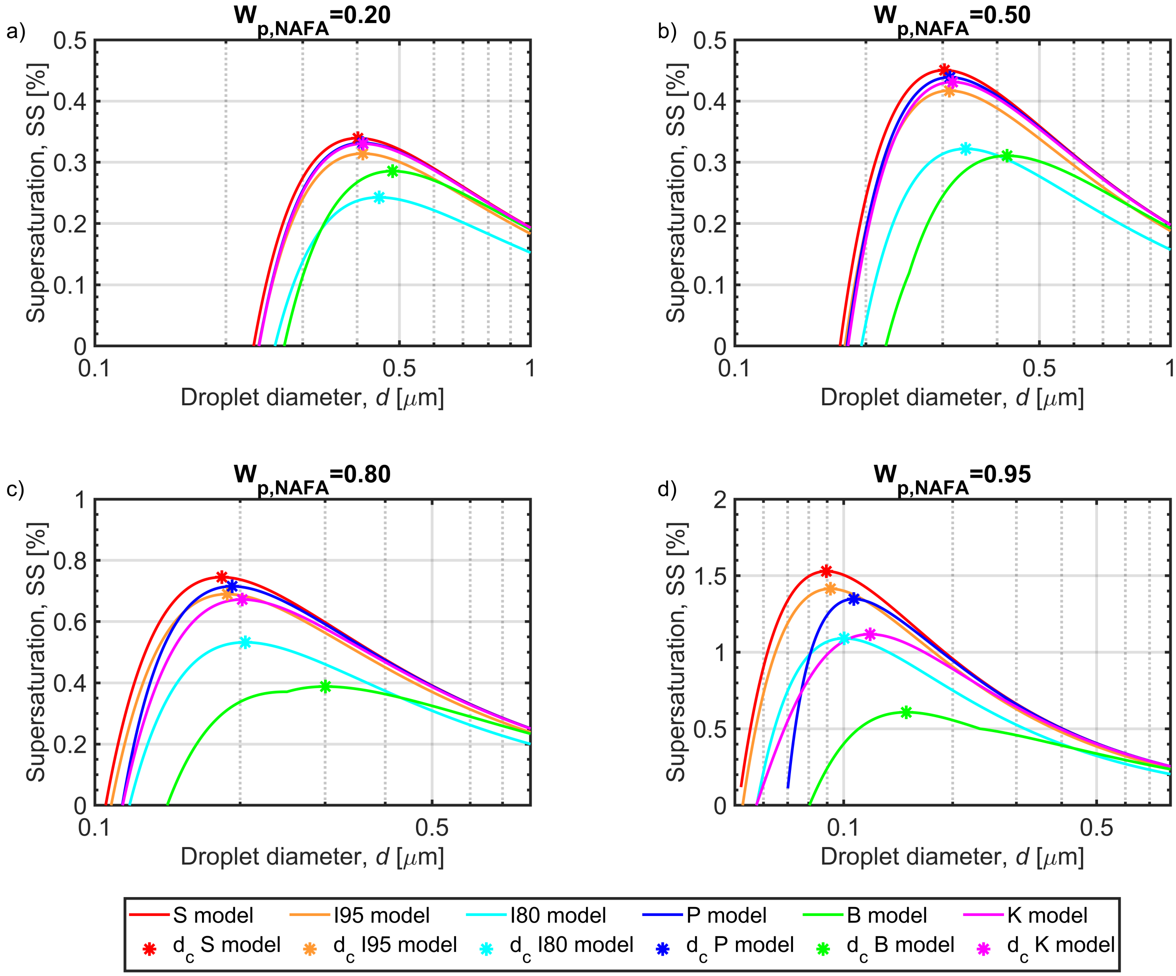


Figure 4. Köhler curves for growing aqueous NAFA–NaCl droplets formed from 50 nm dry particles with NAFA mass fractions of (a) 0.20, (b) 0.50, (c) 0.80, and (d) 0.95, calculated with the different models described in Section 2.3. The critical points of droplet activation (SS_c) presented in Figs. 1 and S3 are indicated with asterisks on each Köhler curve. Note that the supersaturation (SS) scale is different between the panels.

~~Here, we summarize the key points of the preceding discussion relevant for modeling of CCN activity.~~ The preceding discussion ~~demonstrates how the full~~ highlights how the comprehensive thermodynamic partitioning model (P) consistently during droplet growth and at the point of activation predicts the vast majority of NAFA ~~solute~~ in the droplet to be depleted from the ~~droplet~~ bulk by partitioning to the surface~~at the point of droplet activation~~. Except for particles with the very highest ~~NAFA~~ dry mass fractions, ~~close to 100%,~~ NAFA contributes next to none of the solute in the droplet bulk phase, which governs the equilibrium surface tension and water activity ~~properties~~ of the droplet. ~~Consequently, the surface tension~~ Even if NAFA effectively reduces

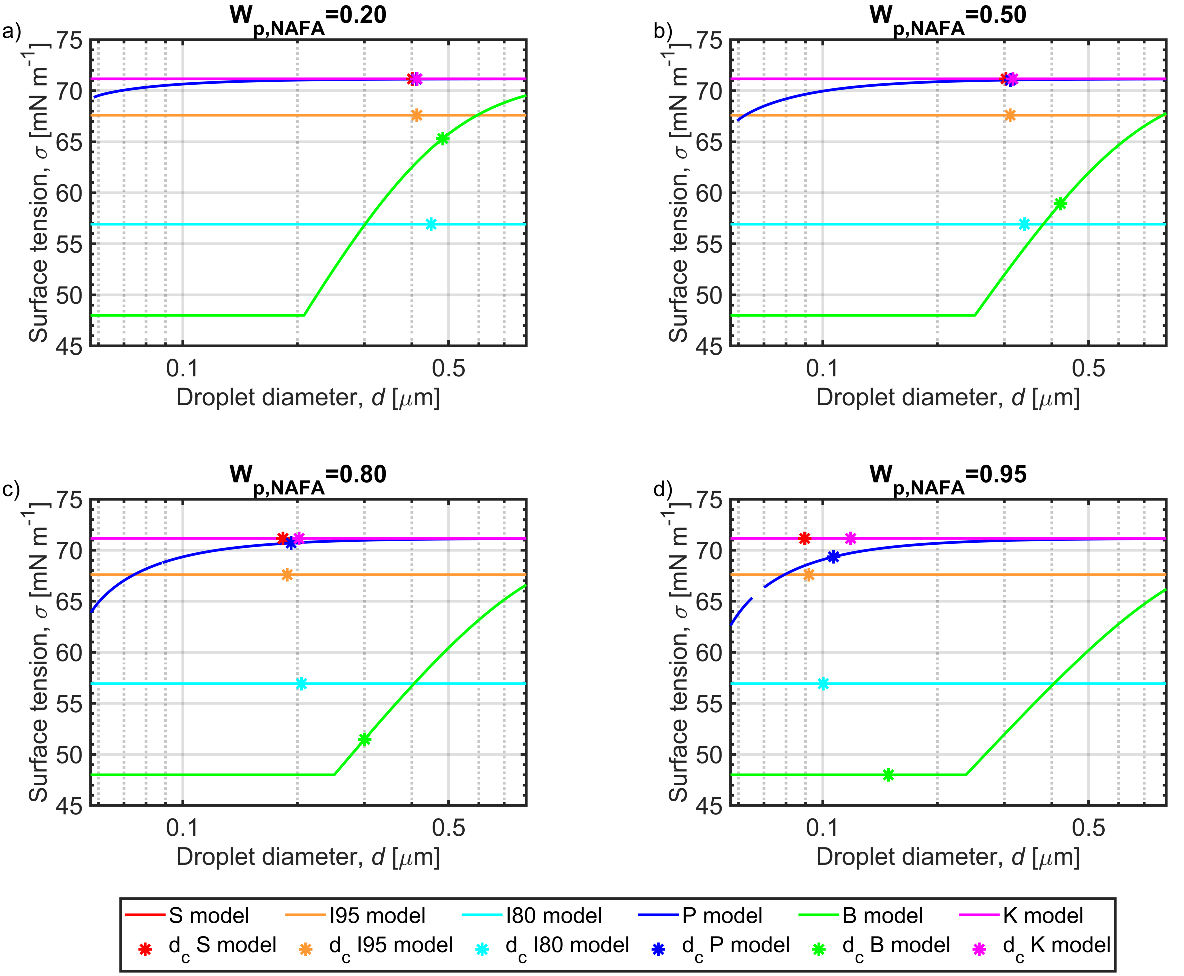


Figure 5. Surface tension along Köhler curves for growing aqueous NAFA–NaCl droplets formed from 50 nm dry particles with NAFA mass fractions of (a) 0.20, (b) 0.50, (c) 0.80, and (d) 0.95, calculated with the different models described in Section 2.3. The critical points of droplet activation (SS_c) presented in Figs. 1 and S3 are indicated with asterisks on each surface tension curve.

surface tension in macroscopic solution, at droplet activation~~predicted with (P) is barely lowered~~ , the predicted surface tension is barely reduced at all for particles with less than 80% NAFA ~~mass~~ and for still higher NAFA fractions, the maximum surface tension reduction ~~never reaches more than~~ only amounts to around 10 ~~mN/m~~ mN m^{-1} from the pure water value ~~. This occurs even if particles with larger NAFA fractions activate for droplets with smaller critical growth factors and thus relatively higher total solute concentrations.For these droplets, NAFA partitioning to the surface is enhanced by~~ across the investigated dry particle size range. For particles even smaller than those considered here, cloud droplet activation may occur for sufficiently small and therefore concentrated droplets that surface tension could be further reduced at d_c. However, extrapolating the experimental and modeling trends in Fig. 1, corresponding SS_c would be similarly higher (exceeding 1.5%) and likely represent supersaturation conditions which are rarely met in the atmosphere.

The basis for this seemingly counter-intuitive droplet state is the comparatively very large surface areas ~~compared to the volume~~ (A) relative to the finite volume (V) of the bulk ~~. The impact of NAFA surface activity is therefore not the same in sub-micron droplets as in macroscopic aqueous solutions where partitioning has negligible effect on bulk composition. Moreover, NAFA surfactant strength is significantly modulated by droplet size and must be taken into account in the cloud activation process. These observations explain the~~ for microscopic activating cloud droplets, compared to a macroscopic solution (Prisle et al., 2010; Bzdek et al., 2020). Even when essentially all the surface active material is adsorbed at the droplet surface, the finite-sized solution droplets do not comprise enough surface active solute altogether to generate sufficient surface concentrations to significantly reduce droplet surface tension. Predictions with the thermodynamic partitioning model show how adsorption to the large droplet surfaces depletes the bulk of surface active solute, leaving the resulting amount dissolved in the bulk phase at a given total concentration in the droplet essentially vanishing. The equilibrium bulk-to-surface concentration gradient governing the adsorption of a given surface active substance is therefore established for a droplet solution state of dilute concentrations in both bulk and surface phases. This leads to the strongly surface active component effectively behaving in small droplets as an insoluble and slightly or even non-surface active substance. For NAFA in the present work, pronounced bulk phase depletion further diminishes the low intrinsic hygroscopicity, in terms of impact om bulk water activity, due to low aqueous solubility and large estimated average molar mass, to yield a nearly vanishing effective hygroscopicity in activating droplets.

These mechanisms explain the observed good performance of the simple partitioning model (S), where contributions from NAFA ~~on~~ to both water activity and surface tension reduction ~~effectively are~~ are effectively set to zero, with respect to the comprehensive partitioning model (P). The simple model (S) is an empirical model developed to emulate the properties of strong surfactants in activating droplets predicted with a thermodynamic partitioning model based on similar Szyszkowski-type surface tension and Gibbs adsorption equations as used for the present mass-based framework (Prisle et al., 2008, 2010, 2011). As the simple partitioning model (S) was developed to specifically describe properties of droplets at the critical point of activation, it was not *a priori* expected that conditions of vanishing surface tension and water activity reduction would be realized throughout droplet growth and activation, in particular not at the earlier stages along the Köhler curve. However, the smaller the droplet, the larger the A/V and resulting surface/bulk partitioning (surface enhancement) factor, 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, in the case of NAFA particles, as for the simple, strong surfactants SDS and fatty acid salts, conditions described with the thermodynamic partitioning model (P) are closely represented by the simple partitioning model (S) for a range of droplet sizes, including the critical point of activation.

In a macroscopic solution, a strong surfactant which is fully partitioned to the surface would be expected to signaficantly reduce solution surface tension and the situation described by model (S) would be quite unrealistic. However, Köhler model predictions with the insoluble surfactant representation (I), where NAFA has no impact on droplet water activity and surface tension is moderately reduced, do not represent either the CCN data of Kristensen et al. (2014) or the full partitioning model predictions, well and the agreement decreases when surface tension is further decreased (therefore not included here). Specifically, insoluble surfactant representation fails to reproduce the variation of CCN activity with dry particle mixing state, and therefore the composition-dependent balance between Kelvin and Raoult terms. Is is however entirely possible that the properties described by representation (I) 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.

Similar mechanisms as predicted with the thermodynamic partitioning model for activation of NAFA particles in this work could be present for the bacterial biopolymers investigated by Dawson et al. (2016) as proxy for complex marine hydrogels. These substances produce significant surface tension reduction in macroscopic solutions, which is not reflected in experimental hygroscopic properties for aerosol mixtures with various salts. Dawson et al. (2016) provide crosslinking between polymers and formation of insoluble complexes as possible explanations. Another mechanism could be bulk depletion from surface partitioning, which was predicted to impact the Köhler curves for NAFA particles also at much earlier stages than the critical point of activation.

The very poor performance of model (B) with respect to both CCN data from Kristensen et al. (2014) and predictions of the thermodynamic partitioning model (P), in contrast to the good performance of (S), shows that for the studied NAFA–NaCl mixtures, the most significant ~~surfactant impact~~ impact of surface activity on cloud microphysics is on ~~bulk phase~~ bulk-phase depletion from surface partitioning, and notably *not* on surface tension reduction in activating droplets. ~~Therefore, including surface tension~~ Calculations with model (P) use the same composition-dependent surface tension and water activity relations as model (B), based on measurements made for macroscopic solutions (Eqs. 8 and 11). Several previous studies have highlighted that application of macroscopic relations without correcting the droplet bulk composition for depletion of surface active components from bulk/surface partitioning onto the large droplet surfaces fails to reproduce experimentally observed CCN activity for a variety of surface active organic aerosol (Prisle et al., 2008, 2010, 2011; Petters and Petters, 2016; Forestieri et al., 2018; Lin et al., 2018). When macroscopic composition-dependent relations for surface tension, as well as other solution properties, are connected to microscopic droplet states *via* a bulk/surface partitioning model, the effect of bulk/surface partitioning in droplets is to move the solution mixing state to a different point in the composition domain, as illustrated in Figs. 2 and 3 for the present case of NAFA–NaCl droplet mixtures.

Including surface tension effects of surface active ~~organic aerosol~~ aerosol components without considering the altered ~~bulk–surface~~ bulk-phase composition from surface partitioning will lead to greater errors in estimating CCN activity than neglecting surface activity altogether~~.~~: The basic Köhler model (K) which disregards all effects pertaining to NAFA surface activity is ~~therefore~~ able to capture both measured CCN activity of the mixed NAFA–NaCl particles and Köhler predictions with model (P) surprisingly well, even if NAFA ~~is indeed fairly surface active and has~~ indeed shows significant surfactant strength in ~~bulk~~ macroscopic aqueous solutions. ~~These conclusions are similar to those of~~ Similar conclusions were made in previous studies for ~~mixtures of~~ particle mixtures of strong, simple surfactants SDS and ~~FAS~~ fatty acid salts with NaCl (Sorjamaa et al., 2004; Prisle et al., 2008, 2010; Forestieri et al., 2018)~~This~~. Detailed analysis showed that the good agreement of the basic Köhler model with measured CCN activity and close resemblance to predictions from the comprehensive partitioning model are in large part due to cancellation effects between the perturbations in predicted Kelvin (surface tension depression) and Raoult (water activity depression) terms of the Köhler curves, introduced by a full account of surface activity, compared to the basic Köhler model (Prisle et al., 2008, 2010). Here, we see the same cancellation between differences in the critical Kelvin and Raoult terms for NAFA–NaCl particles, when comparing predictions from models (K) and (P). Evident as a close similarity between the basic Köhler and comprehensive partitioning model predictions, as well as experiments, this may prove to be a signature feature of ~~surface activity impact on CCN activity for relatively strong surfactants.~~ CCN activity for relatively strong surfactants, in particular for compounds and mixtures with large $\bar{M}_i$, including macromolecules such as model-HULIS and biopolymers (Dawson et al., 2016).

This nearly full cancellation of surface activity effects on Kelvin and Raoult terms may not be present in droplet activation for all types of surface active aerosol components and mixtures. Which general features of these systems are driving the impact of surface activity in cloud microphysics remains to firmly established *via* predictive, thermodynamically consistent Köhler modeling using independently derived mixture-specific model parameters.

3.4.1 Other surface partitioning models

Several bulk/surface partitioning models have been presented and deployed in Köhler calculations to reproduce measured CCN activity for surface active aerosol systems with varying degrees of success. Common for these models is that macroscopic solution property–composition relations are connected to those of a growing droplet with changing A/V based on an adsorption isotherm and surface tension equation of state for the surface active components. As in the present work, Gibbsian adsorption with Szyszkowski-type surface tension equations have been most widely used, however, to our knowledge, this is the first time such a comprehensive, predictive Gibbsian bulk/surface partitioning framework has been applied on a mass-basis, allowing for thermodynamically consistent Köhler modeling of complex, chemically unresolved surface active aerosol. 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 construction of suitable multi-dimensional parametrizations are still non-trivial and require significant amounts of sample material to obtain a sufficient number of data points for robust fits.

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 less than what is necessary to reach a minimum surface concentration, expressed *via* the δ_{org} parameter (interpreted as a minimum surface thickness), that enables full surface coverage and reduced surface tension. Ruehl et al. (2016) found that droplet activation typically occurs in this gaseous film surface regime, analogously to the observations of the present work and Prisle et al. (2010, 2011) for the full Gibbsian partitioning model and simple model (S). Köhler calculations with the full partitioning model however show that activation does not always occur exactly at the point where surface tension reaches that of water (δ_{org}, point of film rupture in Ruehl's model). Prior to activation, the Ruehl et al. (2016) model accounts for concentration-dependent reduced surface tensions of the investigated droplet systems. Using 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. However, their study also involves surface active aerosols with quite different characteristics, compared to the NAFA mixtures studied here. They furthermore do not seem to include effects of non-ideal solute interactions on growing droplet water activity, which could also lead to differences compared to the present work. The model of Ruehl et al. (2016) is first fitted to the droplet size–relative humidity data being described, in order to obtain the necessary surface tension and adsorption parameters. As such, their model is analytical, rather than predictive, and could not be fitted to the CCN data for supersaturated conditions used to validate model prediction of this work. 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 components are fully partitioned to the droplet surface, similar to the model of Prisle et al. (2011) and the gaseous film model of Ruehl et al. (2016). The detailed liquid-liquid phase separation (LLPS) model of Ovadnevaite et al. (2017) describes the composition-dependent partitioning equilibrium between an aqueous (bulk) and organic (surface) phase of a 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 the surface active 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. They evaluate droplet surface tensions from an empirical mixing rule, based on the mass-weighed composition of the phase-separated organic (surface) phase. Effects of solution non-ideality in the aqueous phase are considered using the well-established AIOMFAC model. Their predictive calculations are enabled by assuming a well-defined proxy mixture to represent the surface active aerosol component, with the inherent uncertainties related to the choice of proxy system and variation of solute-solvent and solute-solute interaction parameters across droplet composition space. The proxy mixture used by Ovadnevaite et al. (2017) appears to be less surface active than the NAFA system studied here. In the Gibbsian–Szyszkowski partitioning representation (P), this would entail less strong depletion of the surface active component from the droplet bulk phase due to surface adsorption and thus higher likelihood of (moderately) reduced droplet surface tension, including at the point of droplet activation. The particles representing so-called nascent ultrafine mode (NUM) events observed by Ovadnevaite et al. (2017) are of similar sizes as some of the smallest particle sizes studied in the present work, which activate for smaller growth factors, corresponding to more concentrated solutions, where surface tension is indeed more likely to be reduced in the absence of strong bulk depletion effects from surface adsorption.

Similarly to the Ovadnevaite et al. (2017) LLPS model, the monolayer partitioning model of Malila and Prisle (2018) allows for partitioning of all droplet components between both bulk and surface phases. The partitioning occurs according to a semi-empirical mixing rule to yield surface-composition dependent solution surface tension matching the surface tension evaluated for the corresponding bulk-composition. Instead of assuming a proxy solution mixture as for the LLPS model, effects of non-ideality on surface adsorption are accounted for by using experimentally-based composition-dependent solution properties. By using mass-based relations and assuming an average volume of the partitioning unit (Lin et al., 2018) analogously to the approach of the present work, this allows for applications to chemically unresolved surface active mixtures without explicitly defining all specific interactions between solution components. The monolayer model of Malila and Prisle (2018) provides an alternative to the Gibbsian models for performing predictive Köhler predictions of droplet growth and activation with independently determined interaction parameters for both well-known and unresolved droplet mixtures. The monolayer model has been found to predict lower droplet surface tensions than the Gibbsian models, because the surface partitioning factor $m^S_{\mathrm{sft}}/m^B_{\mathrm{sft}}$ is restricted to a finite value by the volume of the surface monolayer, leading to less strong depletion of the droplet bulk (Malila and Prisle, 2018; Lin et al., 2018, 2020; Bzdek et al., 2020).

It is occasionally questioned whether partitioning models are valid at all for CCN measurements, due to the long equilibration times of (macroscopic) surface tension (Fainerman et al., 2002; Noziere et al., 2014; Van den Bogaert and Joos, 1979, 1980; Wen et al., 19 to particle and droplet residence times in commonly used cloud condensation nucleus counters (Prisle et al., 2008; Kristensen et al., 2014). Lin et al. (2020) presented a detailed analysis of the effects of using 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 in droplets is seen when using surface tension parametrizations corresponding to successively longer measurement times, but the effects of this surface adsorption on the individual Kelvin and Raoult terms of the droplet growth curve nearly cancel at every time step. We are currently not aware of any experiment that would allow verification of these predictions and only of this single existing data set to enable similar calculations with considerations of time dependence in connection with bulk/surface partitioning, therefore the general nature of these phenomena is currently unclear.

3.4.2 Large-scale applications

Thermodynamically consistent, predictive partitioning models enable investigating details about how droplet properties change under the impact of surface activity as they grow and activate. However, the double iterative scheme employed in the comprehensive model (P) is computationally not feasible for applications to large-scale simulations (Prisle et al., 2012) Representation (K) is computationally much simpler to use than the comprehensive partitioning model (P) and has thus been favored over the latter for calculations of CCN activity, in light of the ambiguity of performance of the two models with respect to data ~~(Prisle et al., 2008, 2010)~~ as well as in global simulations (Prisle et al., 2012). ~~The~~ However, the simple representation (S) is ~~however at least as easy as (K) to implement and run in large scale modeling (Prisle et al., 2011, 2012) . Furthermore, representation (S) specifically does not require knowledge of composition and composition-dependent properties for surface active organic mixtures and is computationally much less demanding that the double iterative scheme employed in the comprehensive model (P). Both~~ equally easy to implement in a large-scale framework (Prisle et al., 2011, 2012) and has the additional advantage that contributions of the surface active components to both hygroscopicity and surface tension are known without specific knowledge of the composition of the particle mixtures. These features make (S) applicable to larger scale modelling of CCN activation for real atmospheric aerosols (Prisle et al., 2011, 2012). The good performance of (S) with respect to both data and comprehensive calculations for mixed NAFA–NaCl particles renders the simple representation as a promising candidate for representing effects of strong surface activity on CCN potential of other complex and unresolved organic aerosol mixtures. ~~The validity of the representation must however be established for a wider range of surface active organic aerosol types. Several recent studies have for example shown properties of atmospheric organic aerosol, e.g. SOA (Ruehl et al., 2016), primary marine~~

~~OA (Ovadnevaite et al., 2017), and water-soluble pollen extracts (?) which are consistent with a greater enhancement of aerosol hygroscopicity by surfactants, at least partly due to decreased surface tension. Which general features of these systems are driving the impact of surface tension remains to firmly established.~~

4 Conclusions

We ~~adapted the comprehensive~~ present a framework for including bulk/surface partitioning of chemically unresolved surface active components in Köhler ~~model of Prisle et al. (2010), including bulk–surface partitioning in~~ modeling of growing droplets, ~~for~~ using mass-based Gibbs adsorption and Szyszkowski surface tension equations. The comprehensive framework (P) was applied to calculate CCN activity for particles comprising chemically unresolved NAFA ~~and its~~ in mixtures with NaCl. ~~This required input of~~ Continuous, ternary parametrizations of surface tension and water activity as functions of both NAFA and NaCl aqueous mass concentrations~~. We then calculated CCN activity of particles comprising NAFA and using the comprehensive framework (P) to benchmark three~~ , as required input for the model, were constructed from measurements. Comprehensive, thermodynamically consistent predictions were used to benchmark four alternative representations of the effect of NAFA surface activity in cloud droplet activation: (S) the simple partitioning representation proposed by Prisle et al. (2011), where NAFA is assumed to have zero intrinsic influence on both surface tension and water activity of droplets, (I) considering NAFA as a fully surface-partitioned, insoluble surfactant with fixed surface tension reduction, (B) assuming that droplets comprising NAFA and NaCl have identical properties to macroscopic bulk solutions of the same overall composition, and (K) treating NAFA and NaCl alike as regular soluble and homogeneouly distributed (non-surface active) solutes.

Results of our calculations show ~~how~~ that assuming macroscopic solution properties for activating droplets in the micron and sub-micron size range lead to gross overestimations of measured ~~particle~~ CCN activity, whereas other frameworks including bulk-surface partitioning and/or omitting surface tension reduction ~~all~~ each describe the previously reported CCN data for NAFA–NaCl particles well. These latter models give mutually similar results for both ~~calculated~~ critical supersaturations, as well as a number of other ~~critical properties of~~ properties calculated for activating droplets. ~~This reflects how the NAFA partitioning equilibrium is strongly shifted toward the surface, as assumed in the simple representation (S), and as a consequence, droplet surface tension is rarely reduced from that of pure water, as assumed in both the simple (S) and basic Köhler (K) models.~~

NAFA has significant surfactant strength in macroscopic aqueous solutions, but due to ~~surface partitioning in combination with~~ the very large surface-to-volume ratios of sub-micron activating droplets, the NAFA partitioning equilibrium is strongly shifted toward the surface and the same total compositions do not lead to similar, if any, reductions in droplet surface tension ~~. Likely due to its high average molecular weight compared to hygroscopic salts,~~ as in macroscopic solutions. NAFA has only modest influence on water activity in both macroscopic aqueous solutions and activating droplets alike, at least in part due to its high average molar mass, compared to hygroscopic salts. In sub-micron droplets, the weak intrinsic impact on water activity is further dampened by surface partitioning of NAFA.

~~This work demonstrates how, even~~ With experimentally constrained accounts of non-ideal interactions in both water activity and NAFA surface activity, we therefore predict cloud microphysical behavior for chemically complex ~~model organic aerosol mixtures with significant surfactant strength in macroscopic solution, the overall effect of surface activity on cloud activation can be similar to that found for much simpler surfactants with more~~ aerosol mixtures which closely resembles that previously seen for systems comprising simple, strong surfactants with well-defined molecular properties. ~~We show that also for the complex NAFA mixtures, sub-micron droplet properties can be~~ Sub-micron droplet properties are governed by size-modulated influences of surface activity on both water activity and curvature terms of the Köhler curve ~~.~~ and the "missing Raoult effect" from bulk-phase depletion due to surface adsorption overpowers any enhancement of droplet growth and activation from decreased surface tension. We are currently not aware of any other chemically unresolved or complex aerosol system for which experimental data are available to enable a similar analysis. However, we hope that the presented framework will motivate more measurements to provide thermodynamically consistent characterization for a broad range of surface active aerosol systems. This will contribute significantly to clarify the compositions and conditions where each of the effects of aerosol surface activity is dominating cloud microphysics. From the early ~~studies of~~ demonstrations of reduced surface tension of atmospheric cloud water ~~(Facchini et al., 1999) to recent demonstrations of surfactant effects for actual atmospheric organic aerosol (Ruehl et al., 2016; Ovadnevaite et al., 2017; ?)~~to the remaining diverging observations for surface tension effects in cloud microphysics, the present results underscore that organic surface activity may be one of the key features to constrain for the understanding and modeling of aerosol–cloud–climate interactions (Prisle et al., 2012; Lowe et al., 2019).

Finally, ~~understanding organic aerosol surface activity~~ surface activity of aerosol components may have important implications for other atmospheric processes in addition to cloud microphysics, including heterogeneous chemistry on aqueous droplet surfaces. Owing to the large surface areas, aqueous surface chemistry may be significantly enhanced on submicron droplets. One example is the photosensitized limonene uptake by Humic Acid, another ~~model-HULIS~~atmospheric model HULIS, recently described by Tsui and McNeill (2018). A comprehensive description of droplet surface composition, including size-dependent surface ~~excess~~ adsorption and response to changing ambient humidity and droplet growth, may be crucial for understanding and predicting the extent of such processes.

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