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

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Abstract. Cloud condensation nuclei (CCN) activity of aerosol particles comprising surface active Nordic Aquatic Fulvic Acid (NAFA) and $NaCl$ was modeled with four different approaches to account for NAFA bulk-to-surface partitioning and the combined influence of NAFA and $NaCl$ on surface tension and water activity of activating droplets. Calculations were made for particles with dry diameters of 30–230 nm and compositions covering the full range of relative NAFA and $NaCl$

5 mixing ratios. Continuous ternary 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 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

10 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. Failing to account for bulk-to-surface partitioning of NAFA introduces severe biases in evaluated droplet bulk and surface composition and critical size, which here

15 specifically affect cloud activation thermodynamics, but more generally could also impact heterogeneous chemistry on droplet surfaces. Model frameworks based on either including surface partitioning and/or neglecting surface tension reduction give similar results for both critical supersaturation and droplet properties and reproduce 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 for a given bulk volume. As a result, NAFA has very little impact on

20 surface tension and water activity at the point of droplet activation. In other words, the predicted surfactant strength of NAFA is significantly lower in sub-micron 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. 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, which can significantly reduce aqueous surface tensions in macroscopic samples at concentrations comparable to those of activating droplet systems. Surfactants have since been found in aerosol from many different environments (e.g. Petters and Petters, 2016; Kroflič et al., 2018). However, surface active compounds by definition accumulate in a solution surface, thus creating a concentration gradient between the (interior) bulk and surface phases. For 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 size-dependent bulk phase depletion and result in size-modulated composition dependent solution properties, including droplet surface tension and water activity (Prisle et al., 2010). These are key parameters in determining aerosol water uptake, hygroscopic growth and cloud activation.

Effects of surfactant bulk-to-surface partitioning may greatly impact predictions of the overall cloud formation 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 sodium dodecyl sulfate (SDS) with relatively well-known properties, as model compound for the surface active organic mixtures present in real atmospheric aerosols. Prisle et al. (2008, 2010) then demonstrated a similarly dramatic effect for particles comprising a series of atmospheric straight chain fatty acid sodium salts (FAS). These surface active organics belong to one of the major compound classes identified in atmospheric aerosol samples (e.g. Mochida et al., 2002; Cheng et al., 2004; Forestieri et al., 2018). Both SDS and FAS are relatively strong surfactants (Prisle et al., 2008, 2010, and references therein), however these studies showed that both experimental and modeled effect of surface tension on CCN activation was very modest, due to strong depletion of surfactant 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 (Prisle et al., 2018), 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 atmospherically relevant surfactants so far studied (see e.g. overview by Petters and Petters, 2016) comprise only a narrow selection of often homologous molecules,

5 which most likely do not span the full breadth of atmospheric surface active organic aerosol CCN activity. In addition, the binary and ternary aqueous droplet mixtures typically studied may constitute too simple proxy systems to capture the breadth of properties displayed by chemically complex surface active organic aerosols in the atmosphere. This 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;

10 Frosch et al., 2011).

A major challenge in establishing more general results for surface active CCN activity relates to the comprehensive composition dependent thermodynamic description and process modeling of 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 Kreiden-

15 weis (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, Prisle et al. (2011) proposed a very simple framework for representing the overall effect of (organic) surface activity on CCN activation. This representation 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 completely partitioned to the droplet surface. It is equivalent to as-

20 suming an effective hygroscopicity parameter of $\kappa = 0$ (Petters and Kreidenweis, 2007) for surface active organic components in the mixture. The simple representation was demonstrated to perform very well for SDS and FAS with 8–12 carbon atoms (C_8, C_{10}, C_{12}), the activation behavior of which it was first proposed to emulate, but a more general applicability still remains to be validated.

HUmic LIke Substances (HULIS) comprise another important group of atmospheric surface active organics (e.g. Kiss et al.,

25 2005; Dinar et al., 2006; Graber and Rudich, 2006). Kristensen et al. (2014) measured the CCN activity of particles comprising Nordic Aquatic Fulic Acid (NAFA), one of several commercial reference compounds used as models for atmospheric HULIS, mixed with sodium chloride (NaCl). In addition, they measured the influence of various NAFA–NaCl mixtures on surface activity and water activity of macroscopic aqueous solutions and found that NAFA reduces surface tension in aqueous solution, in agreement with other studies for model HULIS (e.g. Kiss et al., 2005; Aumann et al., 2010). However, Kristensen et al.

30 (2014) found that CCN activity of pure NAFA and mixed NAFA–NaCl particles was grossly overestimated by simple Köhler theory 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 surface partitioning of NAFA in droplets also needs to be taken into account to explain the observed CCN activity of NAFA–NaCl mixtures.

Here, we present a modified version of the comprehensive thermodynamic model framework of Prisle et al. (2010), which

35 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 $NaCl$ 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 gain insight into the detailed process-level mechanisms

5 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–$NaCl$ particle mixtures, which are exactly the kind of surface active and chemically unresolved organic aerosol mixtures for 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 solu-

10 tion with the same total composition, or simply treating the organic as a regular, fully soluble and homogeneously mixed (i.e. *not* surface active) solute.

2 Theory and modeling

CCN activity for NAFA particles of varying dry sizes and mixing ratios with sodium chloride salt was calculated using the methodology of Prisle et al. (2010). Critical supersaturations (SS_c) are iterated as the maximum of the equilibrium droplet

15 growth curve described by the Köhler equation (Köhler, 1936) in the form

$$\frac{SS}{[100\%]} \equiv \frac{p_w}{p_w^0} - 1 = a_w \exp\left(\frac{4\sigma\nu_w}{RTd}\right) - 1 . \tag{1}$$

The Köhler curve gives 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_w^0 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

20 molar volume of water in solution, approximated by M_w/ρ_w, the ratio of pure water molar mass and mass density, 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 dry particle before any water uptake has occurred is referred to as a 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

25 lower case symbols, as d. When droplets have grown past their respective critical point to sizes $d > d_c$, they are referred to as *activated* cloud droplets.

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

$$p_w = a_w p_w^0 = \gamma_w x_w p_w^0 . \tag{2}$$

30 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, and depends explicitly on 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 from the pure water value, $\Delta\sigma = \sigma_w - \sigma$.

The total amount of solute in droplets is determined from dry particle compositions in terms of relative mass fractions of

5 NAFA and NaCl, where $(W_{\mathrm{p,NAFA}} + W_{\mathrm{p,NaCl}} = 1)$. Assuming volume additivity in spherical particles, total dry mass of each solute is given from their bulk mass densities ρ_i as

$$m_i^T = W_{\mathrm{p},i}\frac{\pi}{6}D_{\mathrm{P}}^3\left(\sum_i \frac{W_{\mathrm{p},i}}{\rho_i}\right)^{-1} \qquad (3)$$

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 temperature is assumed to be $T = 303$ K, reflecting the range of effective temperatures from about $298 - 313$ K in the CCN counter

10 between measurements at different supersaturations (T.B. Kristensen, personal communication). The sensitivity of calculations to the assumed temperature and ρ_{NAFA} is discussed in the Supporting Information (SI).

2.1 Surfactant representations

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

15 **(P)** The comprehensive partitioning model of Prisle et al. (2010): For each droplet size, the NAFA bulk–to–surface partitioning equilibrium is iterated 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 $a_{\mathrm{w}} = a_{\mathrm{w}}(\mathbf{x^B})$. For the present version of this model, we have developed measurement-based parametrizations which rely only on *mass* concentrations and mass mixing ratios of organic and inorganic components. The mass-based parametriza-

20 tions circumvent the model requirements for droplet composition and composition-dependent properties in molar quantities, which are not available for chemically unresolved mixtures, such as NAFA. This version of the comprehensive thermodynamic formulation is computationally inefficient, but serves here as a benchmark for the evaluation of the other representations applied.

(S) The simple representation of Prisle et al. (2011): The surfactant is assumed to be completely partitioned to the droplet

25 surface, such that the partitioning equilibrium does not need iteration. All surfactant (SFT) mass is depleted from the bulk $(x_{\mathrm{SFT}}^B = 0)$ and therefore does not affect either water activity or surface tension at the point of activation. Concentration-dependent water activity is evaluated from the binary aqueous NaCl parametrization given by (Prisle, 2006) based on data from Low (1969): $a_{\mathrm{w}} = 1 - 0.031715b_{\mathrm{NaCl}} + 0.0012582b_{\mathrm{NaCl}}^2 - 0.000022921b_{\mathrm{NaCl}}^3$. Here, b_{NaCl} is the molal concentration of NaCl, which is readily determined from the mass concentration via the well-known molecular weight

30 of NaCl. This representation is computationally the simplest of those used in this work.

Table 1. Properties included in the different representations of NAFA CCN activity used in calculations. When ternary surface tension is *not* used, it is set constant to the value for pure water (σ_w).

	partitioning	$\sigma = \sigma(\mathbf{x^B})$	$a_\mathrm{w} = a_\mathrm{w}(\mathbf{x^B})$
(P) partitioning	x	x	x
(S) simple	x	-	x
(B) bulk	-	x	x
(K) basic/water	-	-	x

(B) The droplet is assumed to have the same properties as a macroscopic (bulk) solution with corresponding total composition: Here, surfactant partitioning has negligible effect on solution bulk phase composition, which is then determined directly from the total droplet 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 as for **(P)**, however, the bulk compositions at each droplet size generally differ.

(K) Basic Köhler theory: Surface activity effects are disregarded altogether. As for **(B)**, the droplet bulk phase composition is equal to the total droplet composition, without consideration of 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 ($\sigma = \sigma_\mathrm{w}$). Droplet water activity is evaluated according to the concentration-dependent mass-based ternary parametrization, using total droplet composition ($\mathbf{x^T}$).

2.2 Ternary parametrizations

Iterations of critical supersaturations from Eq.1 require continuous functions for concentration dependent variations in σ and a_w of growing droplets. When partitioning of surfactant molecules to the droplet surface is considered using representation (P), the bulk concentration of NAFA changes due to both dilution and changing ratio of droplet surface area and bulk volume. For ternary water–NAFA–NaCl droplet compositions, the relative mixing ratio of NAFA and NaCl in the droplet bulk phase for example given as the solute mass fraction $w_i = m_i^B / \sum_j m_j^B$ (where m_i^B is the mass of solute i in the bulk, $j = \mathrm{NAFA}, \mathrm{NaCl}$, and $w_\mathrm{NAFA} + w_\mathrm{NaCl} = 1$) therefore changes in a continuous fashion from that of the corresponding dry particle composition ($W_{\mathrm{p},i}$), as a result of NAFA surface partitioning, as droplets grow according to Eq.1. As a consequence, continuous ternary parametrizations with respect to independent variations in droplet NAFA and NaCl concentrations are needed to evaluate droplet properties over the full range of droplet mixing states realized during growth and activation.

Strictly, only representation (P) requires the use of the 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 ($W_{\mathrm{p},i} \neq w_i$). In representation (S), 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 $w_\mathrm{NAFA} = 0$ 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 NaCl 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–NaCl 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

5 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 NaCl contribution only, according to the binary NaCl water activity parametrization given by Prisle (2006).

Ternary parametrizations of both σ and a_{w} were obtained by fitting continuous functions of NAFA and NaCl aqueous concentrations to the surface tensions and osmolality-derived water activities measured by Kristensen et al. (2014) for macroscopic

10 solutions of same solute compositions as the original dry particles, using the least squares method.

2.2.1 Parametrization of σ

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

$$\sigma = \sigma_{\mathrm{w}} - q_{\mathrm{st1}} \ln\left(1 + \frac{C_{\mathrm{NAFA}}}{q_{\mathrm{st2}}}\right), \tag{4}$$

where $\sigma_{\mathrm{w}} = 93.6635 + 0.009133T - 0.000275T^2$ is the temperature-dependent surface tension of pure water (in $\mathrm{mN\ m^{-1}}$)

15 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) report that measured aqueous NAFA surface tension for a given sample droplet decreases with time. This is likely owing to both kinetic effects of surface adsorption and structural rearrangements in the surface phase, as well as to continually increased concentrations of the pendant droplets from evaporation of water over the course of measurements.

20 Fitting parameters for the surface tension parametrization (Eq. 4) used in the present calculations were obtained from measurements performed at $t = 600$ 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 ratio of these measurement times to those of the cloud droplet activation measurements is roughly of the same order of magnitude ($\sim 10^2$) as the diameter ratio of the droplets involved in the two types of measurement.

25 We therefore assume that any potential kinetic effects of surfactant molecules diffusing to the droplet surface, such as any speculated incomplete (non-equilibrium) NAFA partitioning, are at least comparable between the surface tension parametrizations and the droplet activation measurements, if present at all.

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

$$q_{\mathrm{st1}} = 10.46 - 4.810 w_{\mathrm{NAFA}} \tag{5}$$

30 and

$$q_{\mathrm{st2}} = 0.5947 - 0.3278 w_{\mathrm{NAFA}}. \tag{6}$$

Here, as before, w_{NAFA} is the (dimensionless) mass fraction of NAFA solute relative to NaCl in the solution bulk phase. Fits were made under the conditions 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 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

5   as having both fitting parameters depend quadratically instead of linearly on w_{NAFA}. The more elaborate equation 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. 4 with implicit NaCl dependency and linear variation of the fit parameters with w_{NAFA}.

2.2.2 Parametrization of a_w

Water activities were fitted as functions of NaCl and NAFA mass concentrations (C_{NaCl} and C_{NAFA}, both in g L^{-1}) in the

10   form:

$$a_{\mathrm{w}} = 1 + q_{\mathrm{a1}} C_{\mathrm{NaCl}} + q_{\mathrm{a2}} C_{\mathrm{NAFA}}\,, \tag{7}$$

with fitting parameters $q_{\mathrm{a1}} = -5.68 \cdot 10^{-4}$ L g^{-1} and $q_{\mathrm{a2}} = -2.68 \cdot 10^{-5}$ 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-

15   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 mass concentrations of solute with unknown molar content and activity co-efficients given by Eq. 7 may not be thermodynamically consistent over the full range of water–NAFA–NaCl mixing states. Indeed, for binary solutions, it does fail to comply with the Gibbs-Duhem relation in the limit of pure NAFA. This state is, how-ever, never realized in our calculations, where droplet growth starts at a finite growth factor and tends toward infinite dilution.

20   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.

3   Results and discussion

In the following, we present results of modeled CCN activity and droplet properties at the critical point of activation for mixed NAFA–NaCl particles, using the four different frameworks for including aqueous properties of NAFA in the droplets. By

25   analyzing and comparing the results of each representation, we evaluate the effects of NAFA surface activity on predicted CCN activity. Model sensitivity to various input parameters, including the choice of surface tension parametrization, assumed NAFA average molecular weight and mass density, temperature, and effect of potential sample impurity in the 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 ($W_{p,NAFA}$) 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

5   shown as curves in separate panels and 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 NaCl

10   particles, as expected. However, the water activity parametrization for binary NaCl used in (S) introduces some differences, compared to the ternary parametrization (Eq. 7) used in the remaining three models. The binary NaCl parametrization of Prisle (2006) is optimized for representing the slight changes in dissociation factor for NaCl 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.

For all representations, the modeled CCN activity decreases (SS_c increases) with increasing $W_{p,NAFA}$ for each particle size

15   investigated, 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, arising from a potential combination of *i*) increasing droplet non-ideality, *ii*) depletion of the droplet bulk phase solute due to NAFA surface partitioning, and *iii*) the much higher average molecular mass of NAFA (e.g. Mäkelä and Manninen (2008) give the value 4266 $g\,mol^{-1}$),

20   compared to pure NaCl. We have previously observed the same trend, both experimentally and in model calculations, for simpler aerosol systems comprising strongly surface active sodium dodecyl sulfate (SDS) and fatty acid sodium salts (FAS) in various mixing ratios with NaCl (Prisle et al., 2010, 2008; Sorjamaa et al., 2004).

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, (P) underestimates CCN activity well outside the reported experimental

25   uncertainty. It is possible that relatively small amounts of hygroscopic impurities could be present in the organic aerosol mass and thus enhancing CCN activity, as described by Bilde and Svenningsson (2004). The model sensitivity analysis presented in the SI show that even 3% by mass of impurities with properties corresponding to those of NaCl would be sufficient to reconcile the (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

30   thermodynamic description. Of models (P), (S), and (K), the latter seem to overestimate mixed NAFA–NaCl CCN activity the most, 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
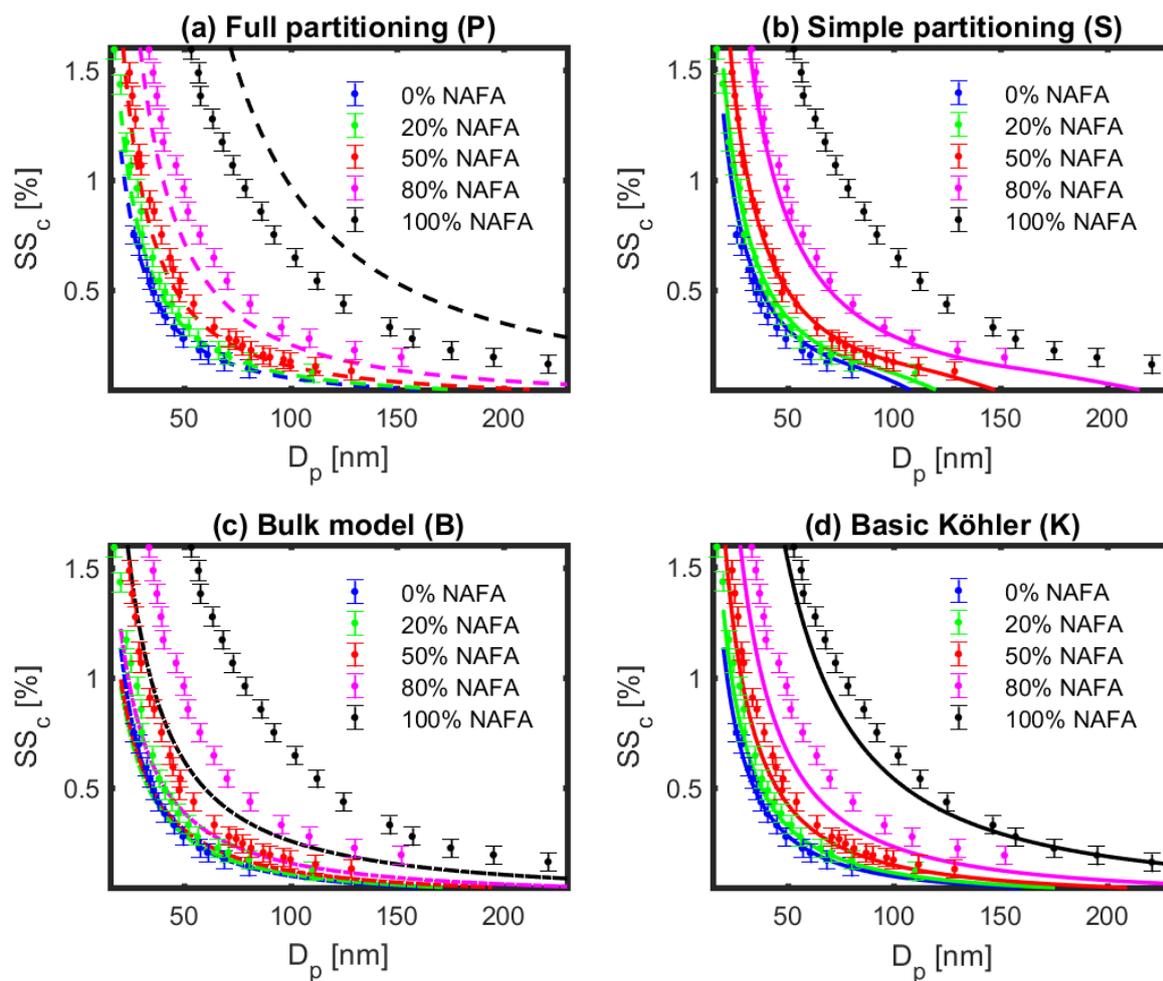
Figure 1. Critical supersaturations (SS_c) for mixed NAFA–NaCl particles, calculated (curves) using the four different surfactant representations described in Section 2.1: (a) comprehensive partitioning (P), (b) simple partitioning (S), (c) bulk solution (B), and (d) basic Köhler theory (K), in each 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 NaCl. Calculations are made using a mass density of $\rho_{NAFA} = 1.6 \, \mathrm{g \, cm^{-3}}$ for NAFA. Error bars on experimental data represent ± 1 standard deviations on SS_c as reported by Kristensen et al. (2014).

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 of particles comprising the simple surfactants SDS and FAS, for both pure surfactant particles and in various mixtures with NaCl (Prisle et al., 2010, 2008; Sorjamaa et al., 2004). Thus, the dramatic increase in CCN activity anticipated by Facchini et al. (1999), from including organic 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 and perhaps atmospherically relevant organic surfactant mixture.

3.2 Droplet properties at activation

Figure 2 presents in panel (a) calculated critical supersaturations for 50 nm dry particles as a function of NAFA mass fraction

5   $W_{p,NAFA}$ in the dry particles. Experimental values from Kristensen et al. (2014) for particles with approximate dry sizes of 50 nm are shown for reference. Direct comparison with experimental values is not always possible along this dimension, as Kristensen et al. (2014) did not measure the exact same particle sizes for different dry particle compositions. This is because they used an experimental setup allowing them to scan a range of pre-selected supersaturations, rather than dry particle sizes. In the same figure, other panels present for calculations on the same 50 nm particles: (b) the corresponding Kelvin and Raoult

10   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 $GF_c = d_c/D_p$, and (d) droplet surface tension σ_c, also evaluated at the critical point. Qualitatively similar results were obtained for other particle sizes as well. Any effects present are more pronounced and therefore shown here for particles with smaller dry diameters: these activate for higher critical supersaturations (Seinfeld and Pandis, 2006), and thus for smaller critical sizes, smaller critical growth factors and more

15   concentrated droplet compositions, and with larger surface area-to-bulk volume ratios, introducing more pronounced surface partitioning for a given total composition.

Results in Fig. 2 demonstrate how the simple surfactant representation (S) traces 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 predicted droplet sizes at

20   activation (as represented by droplet growth factors) also agree well. This was not immediately expected, as (S) was proposed to emulate SS_c, not necessarily individual droplet properties at d_c. The similarity of all activation parameters indicates that the underlying assumptions of the simple representation, as predicted by the comprehensive 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. This close agreement between basic Köhler

25   predictions and comprehensive partitioning thermodynamics was also observed for mixed particles with SDS and FAS in previous studies (Prisle et al., 2010, 2008). For NAFA particles, the agreement extends to even larger surfactant fractions than seen in these earlier studies, where models agreed for dry particle surfactant mass fractions up to about 50%.

Panel (d) in Fig. 2 shows that the predicted surface tension at droplet activation is overall only modestly reduced within the (P) framework. Indeed, for particles with less than 80% by mass of NAFA, the surface tensions in activating droplets are

30   essentially the same as for pure water. 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, σ_c is predicted with (P) to be moderately reduced, but never by more than about $10\,\mathrm{mN\,m^{-1}}$ from the pure water value. Nevertheless, the effect of this surface tension reduction on droplet activation must be
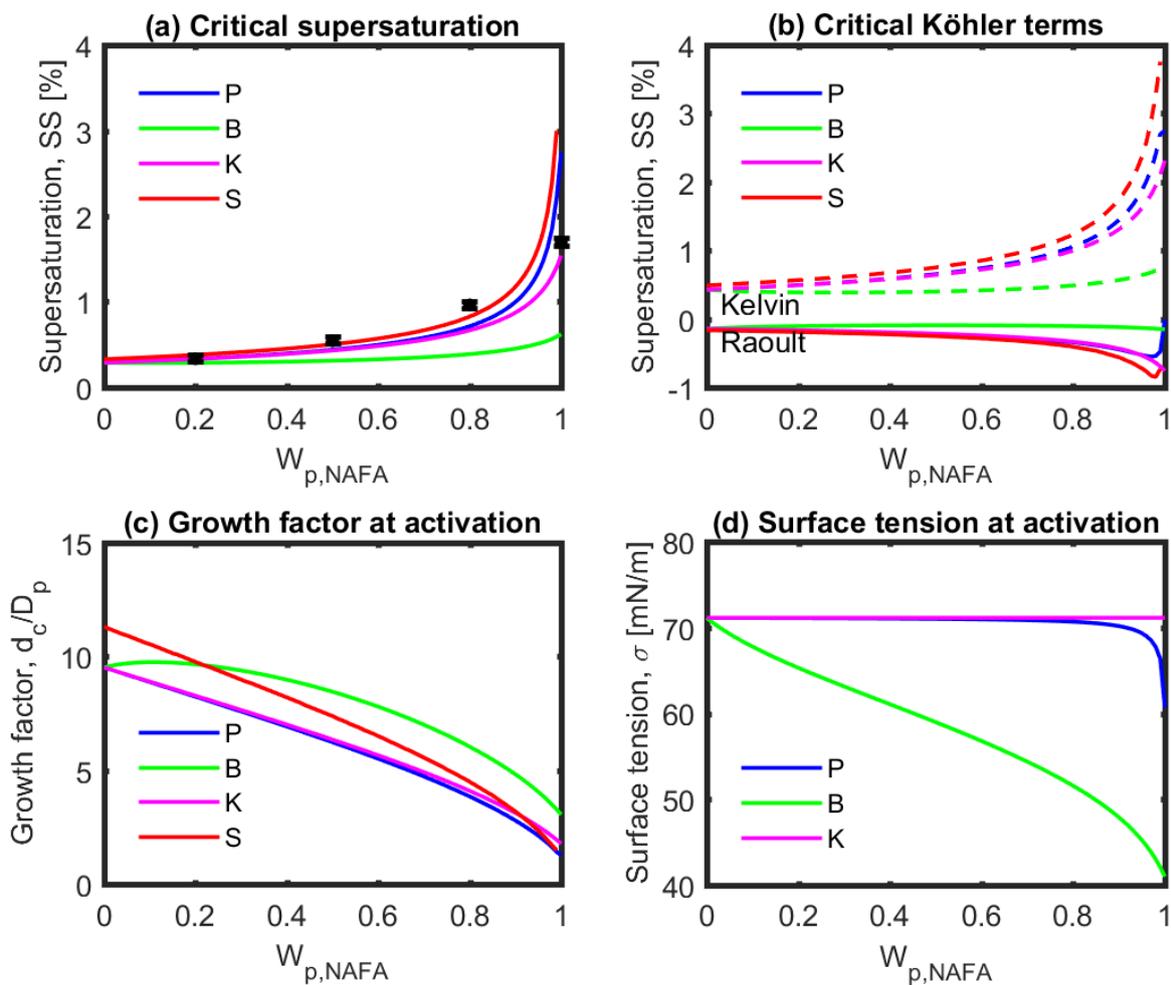
Figure 2. Critical supersaturations calculated for 50 nm dry particles with the four different representations of NAFA CCN activity, (P), (S), (B), and (K), as a function of dry particle NAFA mass fraction $W_{\mathrm{p,NAFA}}$ (a), together with the Kelvin and Raoult terms of the corresponding Köhler curve (b), droplet diameter growth factor (c) and surface tension (d), all evaluated for the same dry particles at the critical point of droplet activation, d_{c}.

more than counterbalanced by bulk depletion from NAFA surface partitioning, since predicted SS_{c} are higher for (P) than for (K), but slightly lower in (P) than for (S), at the highest NAFA fractions.

We note how the calculated Raoult terms in panel (b) show that the predicted water activity of activating droplets is *higher* for 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_c in panel (c).

3.3 Effects of NAFA partitioning

Figure 3 presents calculated (a) NAFA and (b) NaCl mass concentrations in the droplet bulk, C_{NAFA} and C_{NaCl}, both in

5 $g\,L^{-1}$, at d_c for particles with dry diameters of 50 nm. These are the solute concentrations governing the evaluated droplet surface tension 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_{NAFA}^S/m_{NAFA}^B, 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

10 comprised by NAFA, $w_{NAFA} = m_{NAFA}^B/(m_{NAFA}^B + m_{NaCl}^B)$, at the point of droplet activation, calculated with representations (P), (B), and (K). For calculations with (B) and (K), (green and pink lines, respectively) the ratio of C_{NAFA} (panel a) and C_{NaCl} (panel b) scale with the nominal value of the dry particle composition $W_{p,NAFA}$, as it should in the absence of bulk depletion from surface partitioning of NAFA. This is also seen directly from w_{NAFA} in panel (d). With representation (S), the bulk NAFA concentration and solute fraction is vanishing at all droplet sizes.

15 When partitioning is considered in (P), NAFA bulk concentrations are vanishing at the point of activation across the dry particle composition range. 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 particles with the 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,

20 smaller relative growth factors, and thus more concentrated droplet compositions, as is also seen in Fig. 2(c). Across the four representations, C_{NaCl} at activation for a given particle composition follow the trend in GF_c. In particular, activating droplets become more concentrated in the inorganic salt, even if $W_{p,NaCl}$ 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.

25 Partitioning of NAFA profoundly changes the droplet bulk composition 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 m_{NAFA}^S/m_{NAFA}^B in activating droplets is larger than 500 for all particle compositions, and for all dry particle sizes and NAFA mass fractions, m_{NAFA}^S/m_{NAFA}^B is greater than two orders of magnitude (not shown). Put another way, except for the very largest dry particle NAFA fractions, the relative amount of droplet solute comprised by NAFA shown in panel (d) is all but vanishing, even when

30 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.
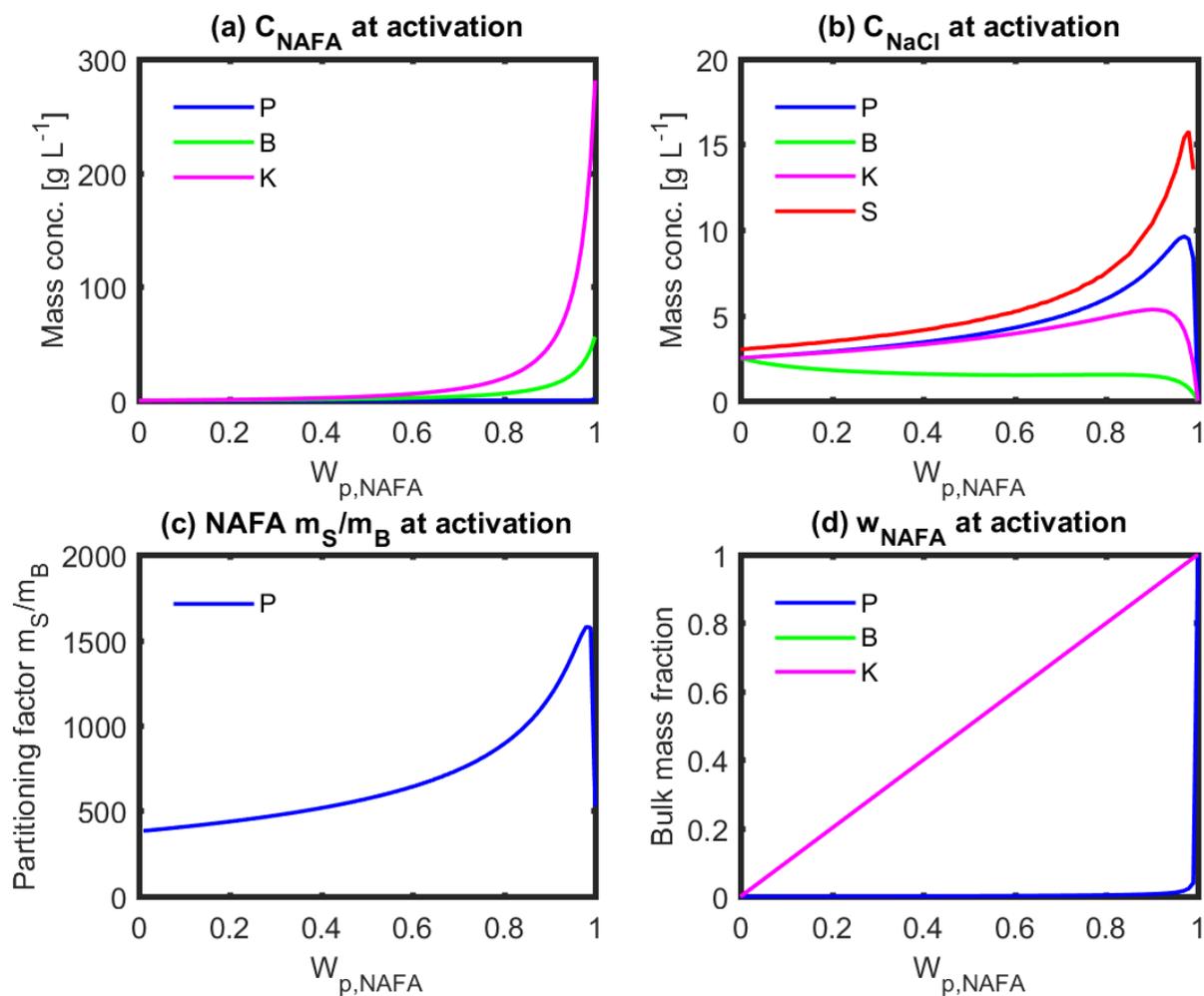
Figure 3. Mass concentrations C_i in g L^{-1} of (a) NAFA and (b) NaCl in activating droplets calculated with the different representations (P), (S), (B), and (K), for dry particles with diameters of 50 nm. For the same particles are also shown (c) NAFA mass partitioning factor in terms of the surface–bulk mass ratio of NAFA, $m_{\mathrm{NAFA}}^S/m_{\mathrm{NAFA}}^B$, and (d) mass fraction of bulk solute in activating droplets comprised by NAFA, $w_{\mathrm{NAFA}} = m_{\mathrm{NAFA}}^B/(m_{\mathrm{NAFA}}^B + m_{\mathrm{NaCl}}^B)$, both at the point of droplet activation.

3.4 NAFA impact on surface tension

3.4.1 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., 2010;

Kristensen et al., 2014). In Figure 4 (a), modeled variation in aqueous surface tension as a function of NAFA mass concentration using the ternary Eq. 4 is compared to the underlying measurements of Kristensen et al. (2014) for macroscopic bulk solutions with mass mixing ratios of 20, 50, 80, and 100% NAFA relative to $NaCl$. To obtain a smooth fit with continuous independent variations in both NAFA and $NaCl$ concentrations, the ternary parametrization does not always represent data quite as well as

5 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. 4 are predicted for 298 K. 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. 4. 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 $NaCl$ (i.e. with decreasing w_{NAFA}) until

10 at least 80% of the solute mass is comprised by $NaCl$. This is a clear demonstration of salting out of NAFA by the inorganic salt in these solute composition and concentration ranges (e.g. Tuckermann, 2007). Salting out is likely caused by increased non-ideality ("ionic strength") in solutions with larger $NaCl$ concentrations affecting the solubility and/or surface propensity of NAFA by enhancing the organic activity.

Panel (b) in Fig. 4 shows the variation in ternary surface tension fitting parameters given by Eqs. 5 and 6 across the full range

15 of NAFA solute mass fractions w_{NAFA}. By analogy to the Szyszkowski equation (Szyskowski, 1908), parameter q_{st1} can be interpreted as related to the maximum surface excess Γ_{NAFA}^{max} (notably, defined on a $mmol/m^2$ concentration scale) by

$$q_{st1} = RT\Gamma_{NAFA}^{max}\,, \qquad\qquad (8)$$

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. (2010). Fig. 4 (b) shows how NAFA surface activity is predicted to increase (the

20 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 the salt fraction increases. Interestingly, we find very similar values for both Γ^{max} and surface adsorption parameter q_{st2} as Aumann et al. (2010) for Suwannee River Fulvic Acid in both binary aqueous solution and a 25% solute mass mixture with $NaCl$. Their data for SRFA has been included in Fig. 4 (b) for comparison.

25 ### 3.4.2 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 $W_{p,i}$ when NAFA bulk–surface partitioning is taken into account. For example, mass concentrations of NAFA and $NaCl$ are $0.0066\ gL^{-1}$ and $3.80\ gL^{-1}$, respectively, at the point of droplet activation, calculated with model (P) for 50 nm particles with dry mass

30 fractions of 50% NAFA. For 100 and 150 nm particles of the same composition, the corresponding values (not shown) are 0.0065 and $0.0064\ gL^{-1}$ NAFA, and 1.34 and $0.736\ gL^{-1}$ $NaCl$. 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.
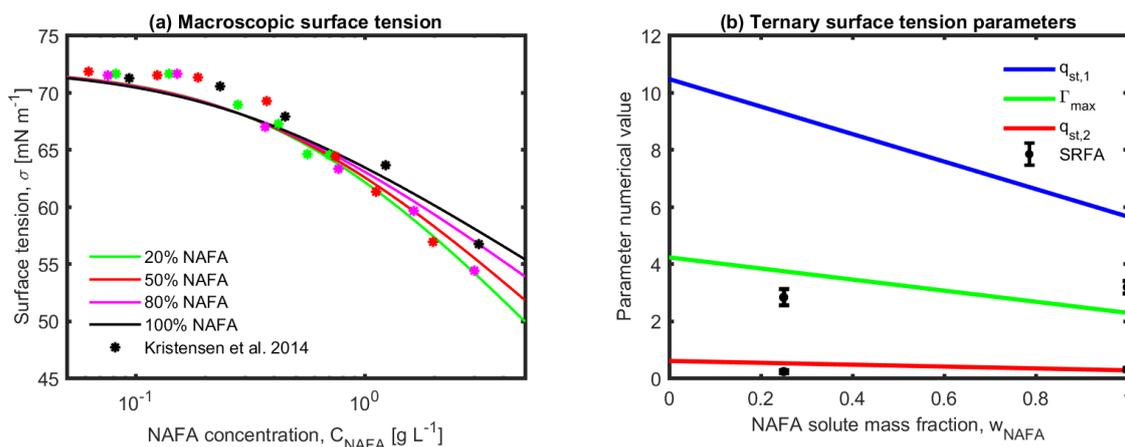
Figure 4. Macroscopic surface tension of aqueous NAFA–NaCl solutions: (a) Surface tension as function of NAFA mass concentration in solutions with different NAFA and NaCl mixing ratios, as predicted with the ternary parametrization in Eq. 4 for 298 K, and compared to data from Kristensen et al. (2014). (b) Variation in the Szyszkowski fitting parameters given in Eqs. 5 and 6 and related maximum surface excess $\Gamma_{\mathrm{NAFA}}^{\mathrm{max}}$ from Eq. 8 with NAFA mass fraction relative to NaCl. Similar data for Suwannee River Fulvic Acid from Aumann et al. (2010) is shown for comparison.

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. 5 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 is included and these results are shown in Fig. 5 merely
5 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} gL^{-1}, the predicted ternary surface tensions are virtually identical to σ_{w}. 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 gL^{-1} of NAFA, and 9.2485, 3.6409, and 2.0446 gL^{-1} of
10 NaCl, 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 surface tension values for solution compositions representative of activating NAFA–NaCl droplets in Fig. 5 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 parametriza-
15 tions 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
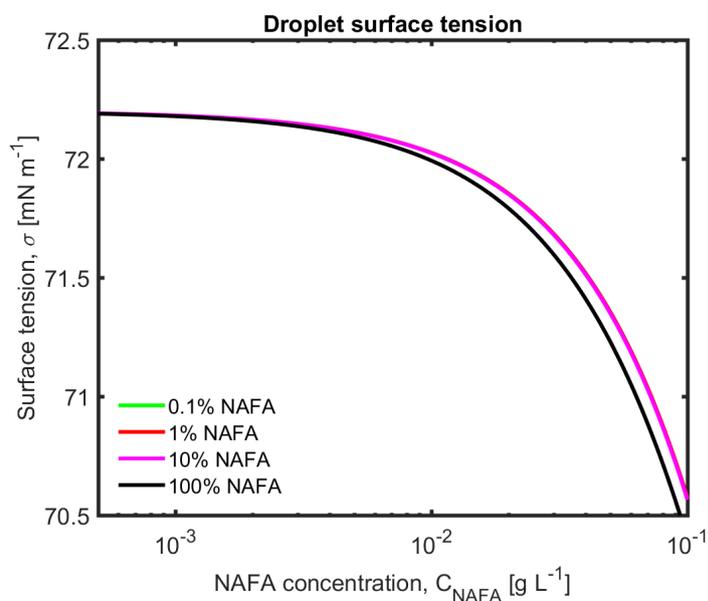
Figure 5. Surface tensions as function of NAFA mass concentration C_{NAFA} predicted with Eq. 4 for aqueous solutions with NAFA solute mass fractions w_{NAFA} of 0.001, 0.01, 0.1, and 1, relative to NaCl.

(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.

3.4.3 Consequences for Köhler modeling

Here, we summarize the key points of the preceding discussion relevant for modeling of CCN activity. The preceding discussion demonstrates how the full partitioning model (P) consistently predicts the vast majority of NAFA solute 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 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 at droplet activation predicted with (P) is barely lowered at all for particles with less than 80% NAFA mass and for still higher NAFA fractions, the surface tension reduction never reaches more than around 10 mN/m 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 very large surface areas compared to the volume 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 good performance of the simple model (S), where contributions from NAFA on both water activity and surface tension reduction effectively are set to zero, with respect to (P).

The very poor performance of model (B) with respect to both data from Kristensen et al. (2014) and predictions of (P), in contrast to the good performance of (S), shows that for the studied NAFA–NaCl mixtures, the most significant surfactant impact on cloud microphysics is on bulk phase depletion from surface partitioning, and notably *not* on surface tension reduction in activating droplets. Therefore, including surface tension effects of surface active organic aerosol without considering the altered bulk–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 measured CCN activity of the mixed NAFA–NaCl particles surprisingly well, even if NAFA is indeed fairly surface active and has significant surfactant strength in bulk aqueous solutions. These conclusions are similar to those of previous studies for mixtures of simple surfactants SDS and FAS with NaCl (Sorjamaa et al., 2004; Prisle et al., 2008, 2010; Forestieri et al., 2018) This may prove to be a signature feature of surface activity impact on CCN activity for relatively strong surfactants.

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 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 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 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 (Prisle et al., 2018) 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 Köhler model of Prisle et al. (2010), including bulk–surface partitioning in growing droplets, for chemically unresolved NAFA and its mixtures with NaCl. This required input of ternary parametrizations of surface tension and water activity as functions of both NAFA and NaCl aqueous mass concentrations. We then calculated CCN activity of

5   particles comprising NAFA and NaCl using the comprehensive framework (P) to benchmark three alternative representations of the effect of NAFA surface activity in cloud droplet activation: (S) the simple 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, (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.

10   Results of our calculations show how 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 describe the previously reported CCN data well. These latter models give mutually similar results for both calculated critical supersaturations, as well as a number of other critical properties of activating droplets. This reflects how the NAFA partitioning equilibrium is strongly shifted toward the surface,

15   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 very large surface-to-volume ratios of sub-micron activating droplets, 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,

20   NAFA has only modest influence on water activity in both macroscopic aqueous solutions and activating droplets alike. In sub-micron droplets, the weak intrinsic impact on water activity is further dampened by surface partitioning of NAFA.

This work demonstrates how, even 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 well-defined molecular properties. We show that also for the complex NAFA mixtures,

25   sub-micron droplet properties can be governed by size-modulated influences of surface activity on both water activity and curvature terms of the Köhler curve. From the early studies of 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; Prisle et al., 2018), 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.

30   Finally, understanding organic aerosol surface activity 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, recently described by Tsui and McNeill (2018). A comprehensive

description of droplet surface composition, including size-dependent surface excess 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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