Comparison of six approaches to predicting droplet activation of surface active aerosol – Part 2: strong surfactants

Sampo Vepsäläinen¹, Silvia M. Calderón², and Nønne L. Prisle³

¹Nano and Molecular Systems Research Unit, University of Oulu, P.O. Box 3000, FI-90014, Oulu, Finland
 ²Finnish Meteorological Institute, P.O. Box 1627, FI-70211, Kuopio, Finland
 ³Center for Atmospheric Research, University of Oulu, P.O. Box 4500, FI-90014, Oulu, Finland

Correspondence: Nønne L.Prisle (nonne.prisle@oulu.fi)

Abstract. Surfactants have been a focus of investigation in atmospheric sciences for decades due to their ability to modify the water uptake and cloud formation potential of aerosols. Surfactants adsorb to the air-solution interface at the surface and can decrease the surface tension , while in of aqueous solutions. In microscopic aqueous droplets simultaneously depleting with finite amounts of solute, surface adsorption may simultaneously deplete the droplet bulk of the surfactant. While this

- 5 mechanism is now broadly accepted, the representation in atmospheric and cloud droplet models is still not well constrained. We compare the predictions of five bulk-surface partitioning models and a general bulk solution model documented in the literature to represent aerosol surface activity in Köhler calculations of cloud droplet activation. The models are applied to a suite of common aerosol particle common aerosol systems, consisting of strong atmospheric surfactants (sodium myristate or myristic acid) and sodium chloride in a wide range of relative mixing ratios. The For the same particles, the partitioning models predict
- 10 comparable similar critical droplet properties at small surfactant mass fractions, but differences between the model predictions for identical particles increase significantly with the surfactant mass fraction in the particles. For the same particles and simulation conditions, the partitioning models also predict Furthermore, significantly different surface compositions and surface tensions tensions are predicted for growing droplets at given ambient conditions along the Köhler curves. The inter-model variation is furthermore different for these particles comprising strongly surface active organics, than for these strong surfactant
- 15 particles is different than previously observed for moderately surface active atmospheric aerosol components. Our results show that experimental validation across a range of atmospherically relevant aerosol compositions, surface active properties, and droplet states is necessary before a given model can be generally applied in atmospheric predictionshighlight the importance of establishing bulk-surface partitioning effects in Köhler calculations for a wide range of conditions and aerosol types relevant to the atmosphere. In particular, conclusions made for a single type of surface active aerosol and surface activity model may
- 20 not be immediately generalized.

1 Introduction

The global climate is affected by atmospheric aerosols both directly through interaction with solar radiation and indirectly through their ability to serve as cloud condensation nuclei (CCN). The indirect effect from cloud–aerosol radiation interactions still remains a large source of one of the largest sources of uncertainty to global radiative forcing estimates (IPCC, 2013,

- 25 2021). Surface active species (surfactants) are commonly found in atmospheric aerosols (e.g., Gérard et al., 2016; Petters and Petters, 2016; Nozière et al., 2017; Kroflič et al., 2018; Gérard et al., 2019). The presence of surfactants in aqueous droplets reduces the surface tension from that of pure water and simultaneously causes mass transfer from the droplet bulk to the surface (e.g., Shulman et al., 1996; Li et al., 1998; Sorjamaa et al., 2004; Prisle et al., 2008, 2010; Nozière et al., 2014; Bzdek et al., 2020), through a process called bulk–surface *partitioning*. In atmospheric aerosols, surfactants potentially Aerosol surface activity
- 30 has been shown to affect the critical point of cloud droplet activation, but a clear consensus has not yet been reached on the magnitude and specific dynamics of the effect extent and specific mechanisms (e.g., Hänel, 1976; Shulman et al., 1996; Facchini et al., 1999; Facchini et al., 2000; Li et al., 1998; Sorjamaa et al., 2004; Prisle et al., 2008, 2010, 2011; Topping, 2010; Raatikainen and Laaksonen, 2011; Ruehl and Wilson, 2014; Nozière et al., 2014; Ruehl et al., 2016; Petters and Petters, 2016; Ovadnevaite et al., 2017; Malila and Prisle, 2018; Lin et al., 2018; Prisle et al., 2019; Davies et al., 2019; Lowe et al., 2019; Lin
- 35 et al., 2020; Bzdek et al., 2020; Prisle, 2021; Vepsäläinen et al., 2022).

Surface tension measurements are commonly performed for macroscopic solutions and have only recently been successfully performed for microscopic droplets (i.e., with diameters in-

Surfactants adsorb at the surface of a solution, resulting in enhanced surface concentrations compared to the interior (bulk) solution. The presence of surfactants in aqueous solutions can significantly reduce the surface tension, compared to

- 40 pure water, which typically decreases with the micrometer range or smaller) and for only a few selected droplet systems. Morris et al. (2015) performed measurements with NaCl, malonic, and glutaric acids, Bzdek et al. (2016) with NaCl and glutaric acid, and Bzdek et al. (2020) with Triton X-100. In microscopic droplets, the partitioning of the surfactant mass between the droplet bulk and surface has been predicted to significantly alter the droplet concentration of surface active compounds (e.g., Wen et al., 2000; Hyvärinen et al., 2006; Vanhanen et al., 2008; Bzdek et al., 2020). The surface tension of
- 45 a solution can be described in terms of either the surface or bulk composition, due to the finite total amount of surfactant contained in such droplets, and therefore affect composition-dependent properties such as the surface tension (e.g., Prisle et al., 2010; Lin et al., 2018, 2020) which are related via the bulk-to-surface concentration gradient for a given surface-active substance. The relation between surface tension and surface composition is typically unknown (Prisle et al., 2012b; Werner et al., 2018), and surface tension is surface-specific composition is often unknown
- 50 (Prisle et al., 2012b; Werner et al., 2014, 2018; Toribio et al., 2018) and experimentally based surface tension relations are therefore typically expressed in terms of the solution bulk composition. In a macroscopic solution with a total composition identical to that of a microscopic droplet, the bulk-phase Measurements of surface tension are commonly performed for macroscopic solutions, where the bulk phase contains a sufficiently large amount of surfactant that bulk-surface partitioning has a solute that adsorption to the surface phase has negligible effect on the solution composition and a relation to the surface
- 55 tension is easily established as the bulk and total compositions are practically identical. For composition of the bulk. The surface tension of a macroscopic solution is therefore readily described in terms of the total solution composition.

In microscopic droplets, the composition change due to surface adsorption of surfactant can significantly alter the bulk composition and therefore the composition-dependent droplet properties, due to the finite total amount of solute comprised in such small droplets (e.g., Prisle et al., 2010; Lin et al., 2018, 2020; Bzdek et al., 2020; Prisle, 2021). The

- 60 distribution of surfactant mass between the surface and bulk phases is referred to as bulk-surface partitioning can be modeled using *bulk-surface partitioning models*. The models calculate the partitioning between the droplet bulk and surface to correct the bulk composition of the droplets to account for the material partitioned to the droplet surface. This allows the use of macroscopic solution properties for microscopic droplets . Recently, Bzdek et al. (2020) *partitioning* (Prisle et al., 2010; Vepsäläinen et al., 2022). Surface tension measurements for microscopic droplets (i.e., with diameters
- 65 in the micrometer range or smaller) have only recently been achieved and for only a few droplet systems, including aqueous sodium chloride (NaCl), aqueous malonic or glutaric acid (Morris et al., 2015), aqueous NaCl or glutaric acid (Bzdek et al., 2016), aqueous mixtures of strong surfactant Triton X-100 with glutaric acid or NaCl (Bzdek et al., 2020). Bzdek et al. (2020) showed that surface tension of aqueous Triton X-100 microscopic droplets (7-9 μ m radius) suspended in air was significantly higher than for a macroscopic solution with identical composition. Their measurements provided the first
- 70 direct experimental evidence of the influence of bulk-phase depletion due to bulk-surface partitioning in microscopic finite sized microscopic droplets(7-9 μ m radius) by experimentally observing the surface tension at the air/solution interface of finite sized dropletscontaining Triton X-100 suspended in air. The droplet surface tension was found to be higher than that of the macroscopic counterpart, indicating a change in the droplet bulk composition due to bulk-surface partitioning.

Several approaches

75 Experimental data for composition dependent properties of microscopic droplets are rare. Therefore, composition–property relations based on macroscopic data are used for estimating microscopic droplet properties, by accounting for the effect of bulk–surface partitioning on bulk composition with a partitioning model

(e.g. Sorjamaa et al., 2004; Prisle et al., 2008, 2010; Malila and Prisle, 2018; Lin et al., 2018, 2020; Bzdek et al., 2020; Prisle, 2021) . Several models have been developed to model surfactant describe surfactant partitioning effects in aqueous droplets of at-

- 80 mospheric relevance, as reviewed by Malila and Prisle (2018). Most approaches. Most models either employ Gibbs surface thermodynamics, where the surface-phase is approximated as a two-dimensional interface (e.g., Sorjamaa et al., 2004; Prisle et al., 2008, 2010; Topping, 2010; Raatikainen and Laaksonen, 2011; Petters and Petters, 2016; McGraw and Wang, 2021; Prisle, 2021), or assume a physical surface layer , in the form of a molecular monolayer (e.g., Malila and Prisle, 2018), liquid–liquid phase separation (LLPS) (e.g., Ovadnevaite et al., 2017), a compressed film , (e.g., Ruehl et al., 2016)(e.g., Ruehl et al., 2016)
- 85 , or complete phase separation (e.g., Prisle et al., 2011; Ovadnevaite et al., 2017). The different approaches each have Each surface partitioning model is based on specific assumptions and requirements for application. A detailed An overview of the history of bulk-surface partitioning is given in the introduction of Vepsäläinen et al. (2022)most widely used partitioning models is given by Malila and Prisle (2018).

Vepsäläinen et al. (2022) investigated six approaches (

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We have previously compared predictions with five bulk–surface partitioning models , developed by Prisle et al. (2010, 2011); Ruehl et al. (2016); Ovadnevaite et al. (2017); Malila and Prisle (2018)-

(Prisle et al., 2010, 2011; Ruehl et al., 2016; Ovadnevaite et al., 2017; Malila and Prisle, 2018) and a general bulk solution approach, for reference) to predict droplet activation for model (Prisle et al., 2010) for droplet activation of moderately surface active organic aerosol. The work showed that the models predict significant differences in the CCN activity, droplet

- 95 surface tension, and degree of bulk-surface partitioning for particles of , comprised of malonic, succinic, or ,-glutaric acid mixed with ammonium sulfate across a range of compositions and the same simulation conditions (Vepsäläinen et al., 2022) . Surfactant strength is here considered in terms of the ability to reduce the surface tension of aqueous solutions at a given concentration. We found that, for the same moderately surface active aerosol, the different models predict significantly different CCN activity, droplet surface tension, and degree of bulk-surface partitioning. However, it is not immediately clear if this
- 100 result can be generalized to other systems or to different simulation conditions. Therefore, in the current work we use the same six approaches to investigate these results cannot be immediately generalized to aerosols with significantly different surface activity. Here, we therefore compare predictions of cloud droplet activation of with different surface activity models for strongly surface active aerosol under common simulation conditions. The strongly surface active aerosol is represented by either a fatty acid sodium salt (sodium myristate) or the fatty acid itself (myristic acid), mixed with sodium chloride (NaCl) in
- 105 a wide range of relative mixing ratios. The surface adsorption properties between strong surfactants and in common conditions. Strong surfactants have different surface adsorption properties than moderately surface active compounds are different. We will investigate whether the same conclusions as those found when the models were applied to common systems of moderate surface active compounds (Vepsäläinen et al., 2022) will also hold for strong surfactants.

Strong surfactants have and a pronounced ability to reduce surface tension in macroscopic solutions

- 110 (e.g. Campbell and Lakshminarayanan, 1965; Wen et al., 2000; Álvarez Silva et al., 2010; Petters and Petters, 2016). The mutual agreement between different surface activity models may therefore also be different than previously observed. Strongly surface active aerosols are here represented by the atmospheric fatty acid myristic acid and its sodium salt (sodium myristate). Fatty acids have been found in atmospheric aerosol samples (e.g., Mochida et al., 2002, 2007; Cheng et al., 2004; Li and Yu, 2005; Kourtchev et al., 2013). Fatty acids and are a major
- 115 component of sea spray aerosol (SSA) (e.g., Mochida et al., 2002, 2007; Wang et al., 2015; Cochran et al., 2016; Kirpes et al., 2019) (e.g., Mochida et al., 2002, 2007; Cheng et al., 2004; Wang et al., 2015; Cochran et al., 2016; Kirpes et al., 2019) and part of particle compositions associated with ice nucleation by SSA (e.g., DeMott et al., 2018; Perkins et al., 2020). Experiments by Wang et al. (2015) indicate that long-chain fatty acids are the dominant contributor to submicron organic SSA (aerodynamic diameter 0.56 1 μm). Cochran et al. (2016) tentatively identified over 280 organic compounds in nascent SSA, including
- 120 saturated and unsaturated fatty acids and derivatives of fatty acids. Kirpes et al. (2019) observed thick organic coatings, consisting of marine saccharides, amino acids, fatty acids, and divalent cations, on Alaskan Arctic winter SSA, where 40 % of the particles containing surfactants matched only long-chain fatty acids, while the rest also contained short-chain fatty acids or saccharides. Fatty acid salts were the first atmospheric surfactants to be investigated in comprehensive experimental and partitioning modeling studies (Prisle et al., 2008, 2010, 2011) and have been subject of several subsequent similar studies
- 125 (e.g. Nguyen et al., 2017; Forestieri et al., 2018).

2 Theory and modeling

We consider the perform Köhler predictions of cloud droplet activation of for surface active aerosol using six different modeling approaches to estimate models to describe possible surfactant effects during droplet growth, including five bulk-surface partitioning models and one bulk solution model. As a reference, we also include a classical Köhler calculations of droplet

- 130 growth. We calculate the model that does not consider any effects of surface activity. In addition, we estimate the relative change in cloud droplet number concentration from Köhler growth curves for particles consisting of sodium myristate (hereafter called NaC14) and NaCl with mass fractions of NaC14 between 0.2 and 0.95 in dry particles of diameter $D_p = 50$ nm. Properties of the individual pure compounds used in the calculations are presented in Table 1. Section S1.1 of the Supplement contains calculations with particles containing myristic acid instead of NaC14 for the models with which we had sufficient preliminary
- 135 information to perform calculations (simple partitioning, compressed film, and partial organic film models). We describe the strength of surfactants in the same way as in Vepsäläinen et al. (2022), by their ability to reduce the surface tension of aqueous solutions at a given concentration. Descriptions of the different model calculations are briefly predictions with the surface activity models in comparison to the classical Köhler model.
- Brief descriptions of the six surface activity models are given in the following sections. For a more detailed description of the calculations, we refer to Vepsäläinen et al. (2022). Table 1. in Vepsäläinen et al. (2022) gives a summary of the surface tension and water activity calculation methods, as well as the different compositions of the droplet bulk and surface phases for the different models. A conceptual figure of the models is shown in Fig. 1 in Vepsäläinen et al. (2022) provides a conceptual figure of the different models of Vepsäläinen et al. (2022). For the most detailed documentation of these models each model, we refer to the presenting publications of each modeloriginal presenting publications.

145 2.1 Köhler theory

Cloud droplet activation in all models is based on is predicted with equilibrium Köhler theory (Köhler, 1936)

$$S \equiv \frac{p_{\rm w}}{p_{\rm w}^0} = a_{\rm w} \exp\left(\frac{4\bar{v}_{\rm w}\sigma}{RTd}\right),\tag{1}$$

where S is the equilibrium water vapor saturation ratio, p_w is the equilibrium partial pressure of water over the solution droplet, p_w^0 is the saturation vapor pressure over a flat surface of pure water, a_w is the droplet solution water activity, $\bar{v}_w = M_w/\rho_w$ is 150 the molar volume of water, σ is the droplet surface tension, R is the universal gas constant, T is the temperature in Kelvin, and d is the spherical droplet diameter. Droplet activation is determined in terms of the critical saturation ratio (S_c), or the critical supersaturation (SS_c , $SS = (S - 1) \cdot 100\%_c = (S_c - 1) \cdot 100\%$), both corresponding to the maximum value of the Köhler curve described by Eq. (1).

We calculate Köhler ealculations are initiated by providing the particle dry size and composition. growth curves for particles comprising surfactants (abbreviated sft) sodium myristate (abbreviated NaC₁₄) or myristic acid mixed with NaCl in mass fractions between $w_{p,sft} = 0.2 - 0.95$ in dry particles with diameter $D_p = 50$ nm. Compound properties used in the calculations are presented in Table 1 for water, NaC₁₄, myristic acid, and NaCl. The total amount of NaCl4 and NaCl molecules surfactant and NaCl in each particle is calculated with the compound from the respective solid-phase densities and relative mass fractions in the particle, also determining which in turn determine the total amount of solute present in the growing aqueous dropletin

- 160 the process. All models assume spherical particles and droplets, as well as additive solid-phase volumes of the different compounds. The droplet solution is a ternary mixture of water—inorganic salt—surfactant where the amount of water in the droplets is calculated in one of two ways. The Gibbs, simple partitioning, compressed film, and partial organic film models assume additive volumes between the dry particle and condensed water. In this case, the dry particle volume is subtracted from the total droplet volume (Hänel, 1976). The monolayer and bulk solution models employ an iterative method based on
- 165 mass conservation in the droplet, making use of a composition-dependent density function to determine the amount of water in the droplet. More details are provided in Vepsäläinen et al. (2022) and its Supplementary material. The. Droplet solutions are described as ternary water-surfactant-inorganic salt mixtures, but the specific treatment of bulk-surface partitioning as well as the corresponding and the resulting droplet water activity and droplet surface tension vary between the different modelsas detailed in the following... Table 2 summarizes the surface tension and water activity calculation methods, as well as
- 170 components considered in the droplet bulk and surface phases, for the different models. For more details on the calculations, we refer to Vepsäläinen et al. (2022).

2.2 Partitioning models

2.3 Gibbs adsorption partitioning model

2.2.1 Gibbs adsorption model

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175 In the Gibbs model of Prisle et al. (2010), the Gibbs adsorption equation (Gibbs, 1878) has been combined with the Gibbs–Duhem equation for the droplet bulk, resulting in-

$$\sum_{j} n_{j}^{\mathrm{T}} k T \frac{d \ln\left(a_{j}^{\mathrm{B}}\right)}{d n_{\mathrm{sft}}^{\mathrm{B}}} + A \frac{d \sigma}{d n_{\mathrm{sft}}^{\mathrm{B}}} = 0, \tag{2}$$

where is solved iteratively for the bulk composition with the boundary condition that the molar ratio of water and NaCl is the same in both the bulk and surface phases. In Eq. (2), n_j^T is the total amount of species *j* in the droplet solution, *k* is the Boltzmann constant, n_{sft}^B is the number of surfactant ions amount of surfactant in the droplet bulkafter dissociation (index "sft" generally referring to the surfactant but the solutes are assumed to be fully dissociated and only the surfactant anions partition to the surface), a_j^B is the activity of *j* in the droplet bulk solution, *A* is the spherical droplet surface area and σ is the droplet surface tension, given as a function of bulk-phase composition. Equation (2) is solved iteratively for the bulk composition with the boundary condition that the molar ratio of water and salt is the same in both the bulk and surface phases, bulk-phase composition. The position of the Gibbs diving surface is selected so that the only adsorbing species is the surfaceant. We assume

volume additivity (such that the droplet diameter is given by the sum of the molar volumes of the individual pure components) bulk-phase volume equals the total equimolar droplet volume and mass conservation $(n_j^{\rm T} = n_j^{\rm S} + n_j^{\rm B})$ of is assumed for all

Table 1. Molar mass (M), densities of the liquid (ρ_1) and solid (ρ_s) phases, and surface tension (σ) of the pure compounds.

Compound	$M_{g} (g mol^{-1})_{g}$	$\rho_{l}(\mathrm{kgm^{-3}})_{\sim}$	$\rho_{\rm S}({\rm kgm^{-3}})_{\sim}$	$\underline{\sigma}(\mathrm{mNm^{-1}})$
Water	18.0	997.0 ^a	\sim	<u>72.0</u> ^b
NaCl	58.4	<u>1977.1</u> ^c	2165^d	<u>169.7</u> ^c
Sodium myristate (NaC14)	250.4	<u>1039.7</u> ^e	1200 ^f	24.2^{g}
Myristic acid	228.4	882.3 ^h	862.2 ^{<i>i</i>}	32.1^{j}

^{*a*} Pátek et al. (2009), ^{*b*} International Association for the Properties of Water and Steam (IAPWS) (2014), ^{*c*} Vanhanen et al. (2008); Janz (1980), ^{*d*} National Toxicology Program (1993), ^{*c*} Extended from binary aqueous density estimated via method of Calderón and Prisle (2021), ^{*f*} Estimate (Prisle et al., 2008), ^{*g*} Value at CMC, ^{*h*} (Noureddini et al., 1992), ^{*i*} At 54 °C (CRC Handbook, 1988), ^{*j*} The method of Zhang et al. (2018), using data from Di Nicola et al. (2016).

components in the droplet (Prisle, 2006). Droplet wateractivity is calculated as a corrected molar fraction, with both NaCland NaC14 having a constant dissociation factor of two(water, surfactant, NaCl).

190 2.3 Simple complete partitioning model

2.2.1 Simple complete partitioning model

The simple partitioning model of Prisle et al. (2011) assumes that surfactants are completely partitioned to the droplet surface all surfactant in the droplet is completely partitioned into an insoluble surface layer of pure surfactant . The surface layer is assumed to not affect the kinetics of water condensation–evaporation equilibrium. The complete partitioning of the surfactant

to the surface means that there is no surfactant present in the droplet bulk, which therefore consists of and the remaining bulk phase is a binary mixture of water and saltNaCl. The surface tension of the droplet solution is assumed to be equal to that of pure water, representing that the coverage is insufficient for large droplet surfaces surface coverage of surfactant is insufficient to form a full monolayer(Prisle et al., 2011; Prisle, 2021). The water activity of the water–NaCl solution is calculated through a fit to AIOMFAC (Zuend et al., 2008, 2011; AIOMFAC-web, 2023) calculations as a function of salt mole fraction. The details
 of the fit can be found in Sect. S2.1 of the Supplement..

2.3 Compressed film surface model

2.2.1 Compressed film surface model

The compressed film model of Ruehl et al. (2016) divides the droplet into an organic surface and a ternary solution droplet bulk of surfactant, inorganic, and water. The droplet water activity water, surfactant, and NaCl. The surface tension is calculated as the

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corrected molar fraction of the droplet bulk solution. The compressed film equation of state defines the relationship between the surface concentration of the surfactant and the surface tension in terms of molecular area (A)

$$\sigma = \min\left(\sigma_{\rm w}, \max\left(\sigma_{\rm w} - (A_0 - A)m_{\sigma}, \sigma_{\rm min}\right)\right) \min\left(\sigma_{\rm w}, \max\left(\sigma_{\rm w} - (A_0 - A_{\rm m})m_{\sigma}, \sigma_{\rm min}\right)\right),\tag{3}$$

where σ_w is the surface tension of water, A_0 is the critical molecular area, $\underline{A_m}$ is the molecular area (Eq. (6)), m_σ accounts for the interaction between surfactants at the interface, and σ_{min} is a lower limit imposed on the surface tension.

210 The isotherm for the equation of state (EoS) of the compressed film model is is

$$\ln\left(\frac{C_{\text{bulk}}}{C_0}\right) = \frac{(A_0^2 - A^2)m_{\sigma}N_A}{2RT}, \frac{(A_0^2 - A_m^2)m_{\sigma}N_A}{2RT},$$
(4)

where C₀ is the bulk solution represents the surfactant bulk concentration at the phase transition, C_{bulk} is the bulk solution concentration represents the surfactant bulk concentration (Eq. (5)), and N_A is Avogadro's number. The bulk concentration of surfactant and molecular area, which is used to calculate the fraction of surfactant partitioned to the surface (f_{surf}). The parameters C_{bulk} and A_m can be expressed as functions of different diameters (salt seed (D_{seed}) the NaCl seed (D_{seed}), dry particle (D_p) and droplet (d) and the fraction of organic molecules partitioned to the surface (diameters, and f_{surf}) as as

$$C_{\rm bulk} = \frac{(1 - f_{\rm surf})(D_{\rm p}^3 - D_{\rm seed}^3)\bar{v}_{\rm w}}{d^3\bar{v}_{\rm sft}}$$
(5)

and

$$A_{\underline{m}} = \frac{6\bar{v}_{\mathrm{sft}}d^2}{f_{\mathrm{surf}}(D_{\mathrm{p}}^3 - D_{\mathrm{seed}}^3)N_{\mathrm{A}}}.$$
(6)

- The values used for the model specific parameters A_0, C_0, m_σ and σ_{\min} are assumed to be compound specific physical constants. The values used for parameters $A_0 = 29.2 \text{ Å}^2$, $\log_{10} C_0 = -7.4$, and $m_\sigma = 1.28 \text{ mJ m}^{-2} \text{ Å}^{-2}$ were obtained from Forestieri et al. (2018) for myristic acid. The minimum surface tension is assumed to be $\sigma_{\min} = 0$, as a conservative estimate, because it could not be determined experimentally (Forestieri et al., 2018). We use the same values for NaC14 parameters for NaC14 due to lack of suitable data to fit the parameters for NaC14. The molar volumes of the acid and its sodium salt are different, as is the dissociation factor. Therefore, an analysis of the differences between the predictions with NaC14 and
- myristic acid as well as a sensitivity analysis of the compressed film model with respect to the molar volume of the surfactant have been provided in Seets. S1.1 and S1.2 of the Supplement. Predictions with myristic acid present in the particles lead to higher predicted critical supersaturations and smaller predicted critical droplet diameters than with particles containing NaC14. Varying the molar volume of myristic acid affects the predictions of the compressed film model more at high surfactant mass
- 230 fractions. Decreasing the molar volume by roughly 25 %, leads to predictions of the critical point similar to those of NaC14 at surfactantmass fraction of $w_{p,sft} = 0.95$ in the particles. The Supplement of Vepsäläinen et al. (2022) contains a more thorough sensitivity analysis of all models with respect to various parameters. The model parameters used here are $A_0 = 29.2$ Å², $\log_{10} C_0 = -7.4$ parameters specifically for NaC₁₄.

2.2.2 Monolayer surface model

235 In the molecular monolayer model of Malila and Prisle (2018), the partitioning between the bulk and surface phases for each compound j is calculated iteratively from the semi-empirical relation

$$\sigma(\mathbf{x}^{\mathrm{B}},T) = \frac{\sum_{j} \sigma_{j} v_{j} x_{j}^{\mathrm{S}}}{\sum_{j} v_{j} x_{j}^{\mathrm{S}}},$$
(7)

where v_j is the liquid phase molecular volume and $x_j^{\rm S}$ is the droplet surface mole fraction of compound j and σ_j is the surface tension of pure j. The vector $\mathbf{x}^{\rm B}$ contains the bulk mole fractions $x_j^{\rm B}$ for water, surfactant, $m_{\sigma} = 1.28$ mJ m⁻² Å⁻². The

240 minimum surface tension model parameter σ_{\min} was assigned a value of zero as a conservative estimate because it could not be determined experimentally (Forestieri et al., 2018). These model specific parameters A_0, C_0, m_σ and σ_{\min} are assumed to be compound specific physical constants and therefore not sensitive to seed or coated particle diameters or the droplet dilution state, such that they can be applied across a range of particle sizes and compositions and NaCl. The thickness of the surface monolayer is calculated as

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$$\delta = \left(\frac{6}{\pi} \sum_{j} v_j x_j^{\rm S}\right)^{1/3} \tag{8}$$

and the condition of mass conservation $(n_j^{\rm T} = n_j^{\rm S} + n_j^{\rm B})$ is imposed for each compound j.

2.3 Partial organic film model

2.2.1 Partial organic film model

In the partial organic film model of Ovadnevaite et al. (2017), all organic content resides in a salt surfactant is assumed to reside 250 in a NaCl- and water-free surface filmthat, similar to the simple partitioning model of Prisle et al. (2011). The surface film is assumed to completely coat the droplet bulk until a minimum surface thickness is reached (δ_{sft})and, where the surface film breaks, resulting in partial coverage of the droplet. The water activity effective surface tension of the droplet bulk consisting only of salt and water is calculated through a fit to AIOMFAC (Zuend et al., 2008, 2011; AIOMFAC-web, 2023) calculations as a function of salt mole fraction in a range relevant to the calculations. See Sect. S2.1 of the Supplement for details.

255 The surface tension of an individual liquid phase is calculated as a volume fraction-weighted is calculated as the surface-area-weighted mean of the pure-component surface tension values (σ_j). For the droplet bulk surface tensions from the surface and bulk phases as

$$\sigma_{-}^{\mathrm{B}} = \sum_{j} \varphi_{j} \underbrace{(1 - c_{\mathrm{S}})\sigma^{\mathrm{B}} + c_{\mathrm{S}}}_{j} \sigma_{j}^{\mathrm{S}}, \tag{9}$$

where $\varphi_j^{\rm B}$ is the volume fraction of the component *j* in the bulk-phase ($\sum_j \varphi_j^{\rm B} = 1$). The parameter that describes the surface coverage $c_{\rm S}$ is defined as-

$$\underline{c_{\rm S} = \min\left(\frac{V^{\rm S}}{V^{\delta}}, 1\right)}.$$

The organic film covers the droplet bulk completely $(e_{\rm S} = 1)$ or partially $(e_{\rm S} < 1)$.

$$c_{\rm S} = \min\left(\frac{V^{\rm S}}{V^{\delta}}, 1\right) \tag{10}$$

is the surface coverage, $V^{\rm S}$ is the volume of the surface-phase at droplet diameter d, and V^{δ} is the corresponding volume of

- 265 a spherical shell of thickness δ_{sft} , which is the minimum surface thickness before the organic surface film breaks. The surface thickness -. Here, the surface thickness δ_{sft} is set equal to the surface thickness values calculated by the monolayer model of Malila and Prisle (2018) for the same test system. Originally, Ovadnevaite et al. (2017) assumed a single constant value of the surface thickness, but since the monolayer model already explicitly calculates surface thickness, here we use these values to improve the consistency between the results of the different models. Sect. S1.3 of the Supplement contains a corresponding
- 270 values calculated with Eq. (8) of the monolayer model of Malila and Prisle (2018). A comparison between using a constant value as δ_{sft} , and using vs. the values calculated with the monolayer model is presented in Sect. S1.3 of the Supplement. The surface tensions of individual liquid bulk (σ^{B}) and surface (σ^{S}) phases are calculated as volume fraction-weighted means of the pure-component surface tensions (Table 1).

The effective surface tension of the droplet is calculated as the surface–area–weighted mean of the surface tensions from 275 both phases as-

$$\sigma = (1 - c_{\rm S})\sigma^{\rm B} + c_{\rm S}\sigma^{\rm S}.$$

2.3 Monolayer model

In molecular monolayer model of Malila and Prisle (2018) the partitioning between the bulk and surface phases for each compound *j* is calculated iteratively from an extension of the Laaksonen–Kulmala equation (Laaksonen and Kulmala, 1991)

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$$\sigma(x^{\rm B},T) = \frac{\sum_j \sigma_j v_j x_j^{\rm S}}{\sum_j v_j x_j^{\rm S}}$$

where v_j is the liquid phase molecular volume, σ_j the surface tension, while $x_j^{\rm S}$ and $x_j^{\rm B}$ are the droplet surface and bulk mole fractions of compound *j* respectively. The condition of mass conservation $(n_j^{\rm T} = n_j^{\rm S} + n_j^{\rm B})$ is imposed on the calculation of each compound *j*. The droplet water activity is calculated as the corrected molar fraction using the composition of the droplet bulk after the bulk–surface partitioning. The thickness of the surface monolayer is calculated as-

$$285 \quad \delta = \left(\frac{6}{\pi} \sum_{j} v_j x_j^{\rm S}\right)^{1/3}$$

2.3 The bulk solution Bulk surface activity model

The results of the different bulk-surface partitioning models are compared with a In the bulk solution model where the (e.g. Prisle et al., 2010; Prisle, 2021), droplet properties are assumed to be equivalent to those for a macroscopic solution with the same total composition. In particular, bulk-surface partitioning does not affect the concentration of surfactants in

290 the droplet bulk solution. The droplet bulk is equivalent in volume to the whole droplet , and no separate surface-phase exists. The The droplet bulk-phase composition is determined directly as the total composition of the droplet and the droplet surface tension is estimated as a function of composition through a fit made into the ternary data of Wen et al. (2000) for mixtures of **Table 2.** Methods of calculating the droplet water activity (a_w) and surface tension (σ) , and the composition of the droplet surface and bulk phases used with the different models. For more details on the calculations, we refer to Vepsäläinen et al. (2022).

Model	\widetilde{a}_w	$\overset{\sigma}{\sim}$	Surface	Bulk
Gibbs	Corrected mole fraction ^a	<u>Fit to data^b</u>	water, NaC ₁₄ , NaCl ^c	water, NaC14, NaCl
Simple partitioning	$\underbrace{\text{AIOMFAC}^d}_{}$	σ_w	NaC_{14}	water, NaCl
Compressed film	$\underbrace{\text{Corrected mole fraction}^a}_{a}$	Eq. (3)	NaC_{14}	$\underbrace{\text{water, NaC}_{14}}^{e}, \underbrace{\text{NaCl}}_{e}$
Partial organic film	$\underbrace{\text{AIOMFAC}^d}_{}$	Eq. (9)	NaC_{14}	water, NaCl
Monolayer	$\underbrace{\text{Corrected mole fraction}^a}_{a}$	$\underbrace{\text{Fit to data}^b}$	water, NaC14, NaCl	water, NaC14, NaCl
Bulk solution	$\underbrace{\text{Corrected mole fraction}^a}_{a}$	$\underbrace{\text{Fit to data}^b}$	\sim	water, NaC14, NaCl
Classical Köhler	$\underbrace{\text{Corrected mole fraction}^a}_{a}$	$\underbrace{\sigma_w}{\sim}$	\sim	water, NaC14, NaCl

^{*a*} Corresponding to the bulk phase composition. See Sect. S2.1 of the Supplement. For the bulk solution and classical Köhler models this calculated from the total composition of the droplet. ^{*b*} Fit into the data of Wen et al. (2000) (Sect. S2.2 of the supplement). ^{*c*} NaCl and water depletion from the surface balance the surfactant partitioning. ^{*d*} Fit into AlOMFAC-web (2023) calculations (Zuend et al., 2008, 2011). See Sect. S2.1 of the Supplement. ^{*c*} Typically all surfactant has partitioned to the surface at activation.

NaCl, NaCl4, and water. The surface tension above the CMC is a constant value. The details of the fit are presented in from a macroscopic ternary solution surface tension parametrization (Sect. S2.2 of the Supplement. Water activity is calculated as a corrected molar fraction, assuming that the critical micelle concentration (CMC) limits the maximum amount of surfactant dissolved in the bulk. Any additional surfacetant) using this composition.

2.4 Classical Köhler model

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In the classical Köhler model (e.g. Prisle et al., 2010; Prisle, 2021), surface active aerosol components are treated as regular soluble solutes and specific effects of surface activity are not considered. The droplet surface tension is assumed to be undissolved and has no impact on the calculation constant and equal to that of pure water.

2.5 Critical micelle concentration

Above the so-called critical micelle concentration (CMC), some surfactants can self-aggregate to form structures here collectively referred to as *micelles*. The micellization process is highly dependent on the surfactant species - (Langevin, 1992)

- In this work, the critical micelle concentration in the droplet bulk is assumed equal to that of the binary solution of 305 water–NaC14 determined graphically from the digitized surface tension measurements of Wen et al. (2000). More information is available in Sect. S2.4 of the Supplement. The surface tension after the CMC is reached is assumed to be constant, and is determined by the binary organic surface tension fit to be $\sigma_{\rm CMC} = 24.2$. We are aware that in ternary solutions of water-surfactant-inorganic salt (Langevin, 1992). In ternary water–surfactant–inorganic salt solutions, both the CMC and the surfactant CMC and solution surface tension at the CMC vary depending on the can vary with inorganic salt concentra-
- 310 tion . These variations also depend on the chemical nature of the inorganic salt (i.e., whatever inorganic salt and the ionie

surfactant share the surfactant counterion as a common ion). However, accounting and may be further affected for ionic surfactants that share a common counterion with the inorganic salt. Accounting for these effects requires the use of complex modeling frameworks (e.g., Kralchevsky et al., 1999) with parameters that must be retrieved from experiments that are scarce or nonexistent for these ternary systems complex modeling (e.g., Kralchevsky et al., 1999; Calderón et al., 2020) with parameters

315 obtained from experiments. The surfactant CMC often decreases with increasing inorganic salt concentration, compared to a binary water–surfactant solution (Calderón and Prisle, 2021). However, for most ternary surfactant solutions, and in particular for atmospheric surfactants, the relevant interaction parameters are not known or readily accessible with existing experimental techniques.

Due to lack of available data on the actual pure compound surface tension (in a hypothetical supercooled liquid state), the

- 320 binary surface tension at the CMC is assumed to be equal to the surface tension of pure NaC14 when such a value is needed (in the monolayer and partial organic film models). The CMC is In this work, the CMC of NaC₁₄ is estimated from binary water–NaC₁₄ surface tension data (Wen et al., 2000) and taken into account in the composition-dependent ternary surface tension function (Supplement Sect. S2.2) used for the monolayer, Gibbs , Gibbs (Sect. 2.2.1), monolayer (Sect. 2.2.2), and bulk solution models, ensuring that (Sect. 2.3) models. The surface tension at this concentration, $\sigma_{CMC} = 24.2$ mN m⁻¹, is set as
- 325 a lower limit for the droplet surface tension does not assume values smaller than the value at the CMC (and assumed to be constant, such that NaCl has no effect on σ_{CMC}). After the main calculations of the monolayer model are performed, a check is made such that if the predicted surface tension is equal to. For calculations with the Gibbs and monolayer models, the value at the CMC, the droplet bulk and surface compositions are assumed to be unknown. The comparison is made with the assumption that the salt has no effect on predicted droplet surface tension must be larger than σ_{CMC} for the Köhler curves to be calculated,
- 330 because neither model explicitly treats micelle formation. With the bulk solution model, the CMC limits the maximum amount of surfactant dissolved in the bulk when the droplet surface tension is equal to σ_{CMC} . Any additional surfactant present in the droplets, as micelles or undissolved, is assumed to have negligible impact on the droplet volume and solution state. For the monolayer and partial organic film models, the surface tension value at the CMC. This method is different from what was originally described in Malila and Prisle (2018) where the surfactant surface mole fraction equal to unity was assumed, when
- 335 the bulk surfactant concentration was above the CMC value. We employed a similar check for the Gibbs model, setting the droplet composition to unknown if the predicted droplet surface tension value is that at the CMC. The water activity calculated with of pure NaC₁₄ (in a hypothetical supercooled liquid state) is assumed to be equal to σ_{CMC} , due to lack of available data (Malila and Prisle, 2018). More information is given in Sect. S2.4 of the Supplement.

2.6 Relative change in the cloud droplet number concentration

340 We estimate the relative change in cloud droplet number concentration caused by the differences in critical supersaturation (SS_c) predicted for the different partitioning models, as well as the bulk solution modelalso employs this check with the predicted droplet surface tension to determine if surfactant concentration in the droplet is above the CMC. The maximum amount of surfactant dissolved in the bulk is limited by the CMC., with respect to the classical Köhler model (SS⁰_c), using the method outlined by Bzdek et al. (2020). The cloud droplet number concentration N is assumed to depend on the supersaturation SS as

$$\frac{\Delta N}{N} = \frac{(\mathrm{SS}_{\mathrm{c}}^{0})^{k} - (\mathrm{SS}_{\mathrm{c}})^{k}}{(\mathrm{SS}_{\mathrm{c}})^{k}}.$$
(11)

3 Results and discussion

- In the following sections, we present the results of the simulations performed Köhler calculations with the different models
 detailed described above for common particle systems containing NaC14 and NaCl. Section aerosol systems with dry diameters of D_p = 50 nm and comprising NaC₁₄ and NaCl in various mixing ratios. Results for particles comprising myristic acid are presented in Sect. S1.1 of the Supplementpresents analogous results for particles containing myristic acid... Furthermore, critical supersaturations and droplet diameters predicted for particles across the size range D_p = 50 200 nm are presented in Section S1.4 of the Supplement. With a given mass fraction of NaC₁₄, the inter-model variation between the different particioning models is similar for particles of all sizes. The absolute differences in predicted SS_c between the models are larger for small
- particles, and therefore we here focus on the results for $D_{\rm p} = 50$ nm.

3.1 Köhler curves and droplet activation

- Figure 1 shows the Köhler curves predicted with the different models in terms of supersaturation (SS) for dry particles with as a function of droplet size for particles with initial dry diameter $D_{\rm p} = 50$ nm and at NaC14 NaC₁₄ mass fractions $(w_{p,sft})$ of 0.2, 0.5, 0.8, and 0.95 relative to NaCl. The critical points (d_c, SS_c) are shown corresponding to the Köhler 360 curves in Fig. 1 are given in Table 3and are determined as the maximum SS value of each curve with the corresponding droplet diameter. Fig. 1 immediately highlights that the different models can predict significantly different eritical points Köhler growth curves and activation properties for the same dry particle systems. Of the partitioning models, the particles. The differences in both SS_c and d_c predicted with the different bulk-surface partitioning models increase with $w_{\rm p,sft}$. The 365 simple partitioning and compressed film models consistently predict the highest SS_c values and the smallest d_c values. The Gibbs modelpredicts larger for all $w_{\rm p,sft}$. For the Gibbs model, predicted $d_{\rm c}$ values than are larger and SS_c are lower than for the other partitioning modelsand SS_c values between the extremes of the predictions. The monolayer model and the and partial organic film model predictions agree well across all NaC14 mass fractions, and the predictions of the critical point with the two models are always between the maximum and minimum predictions of the six models. As seen in numerous 370 previous studies (e.g., Sorjamaa et al., 2004; Prisle et al., 2008, 2010; Topping, 2010; Prisle et al., 2019; Prisle, 2021), there is
- also a large difference between the predictions models agree well and the predicted critical points are between the extremes for all models at each $w_{p,sft}$. There are generally large differences between the SS_c of the partitioning models and the bulk solution model, especially in terms of supersaturation. The predictions of the critical droplet properties with the different bulk–surface partitioning models begin to show more significant differences in both SS_c and d_c as the NaC14 mass fraction in the particles
- 375 increases. Furthermore, in Fig. 1(d) for particles containing NaC14 ($w_{p,sft} = 0.95$), none of the model predictions match the

 $\frac{SS_c}{S_c}$ value fitted to experimental data (Prisle et al., 2008) whereas the critical points of the classical Köhler model fall between the extremes of the different surface activity models.

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3.1.1 Critical supersaturations

380 For particles with w_{p,sft} = 0.2 in Fig. 1(a)with w_{p,sft} = 0.2, the different, the Köhler curves and SS_c values predicted by of the different models are comparable, apart from the predictions of the except for the bulk solution model. The SS_c predicted with the monolayer and partial organic film models predict very similar SS_c even as the NaC14 mass fraction increases (Fig. 1and Table 3) agree even as w_{p,sft} increases in Figs. 1(b) - 1(d). We used the surface thickness (δ) predicted by the monolayer model (δ_{ML}) as input for the partial organic film model calculations, but this contributes only a small enhancement to the similarities between the predictions of only slightly enhances the similarities of results from the two models. Using a constant surface thickness of 0.5 nm with (δ_{0.5}) for the partial organic film model does not drastically change the SSpredictions SS_c(a maximum of 4 % calculated from SS^{δ_{ML}/SS^{δ_{0.5}}. The largest differences were seen for w_{p,sft} = 0.5 and 0.8). See-, where}

 $SS_{ML}^{\delta_{ML}}/SS_{ML}^{\delta_{0.5}} = 0.96$. A detailed comparison is provided in Sect. S1.3 of the Supplement for the full comparison.

The Gibbs model predicts lower SSc values comparable to than the monolayer and partial organic film models for all

- 390 particle compositions $w_{p,sft}$ in Fig. 1, but the critical point predicted with. However, the critical points for the Gibbs model is always correspond to droplet sizes immediately after the dilution state of the growing droplet is sufficient to overcome the droplet surface tension increases from the minimum value at the NaC₁₄ CMC (see Fig. 2), suggesting that predictions could be sensitive to the assumed value of the CMC. This could be due to a numerical artifact of the Gibbs model caused by the CMCconstraint imposed on the simulation. As none of the models employed accounts for the CMC variation with NaCl content
- 395 in the droplet solution, nor for the explicit effect of micelles in the thermodynamic expression for the adsorption equilibrium, any explanation given to the Gibbs model response is speculativeExperimentally determined CMC values can vary significantly for a given solution, depending on the measurement technique used (Álvarez Silva et al., 2010).

The <u>SSc</u> of the simple partitioning and compressed film predictions of <u>SSc</u> increase considerably more with the <u>NaC14 mass</u> fraction than models increase more with $w_{p,sft}$ than for the other models (Table 3). In For particles with $w_{p,sft} = 0.2 - 0.8$ in

- 400 Figs. 1(a) 1(c), the <u>SS_c is only slightly higher for the</u> simple partitioning model always predicts slightly higher SS_c. In than for the compressed film model but the difference between models increases for $w_{p,sft} = 0.95$ in Fig. 1(d), the difference between the predicted. Köhler calculations for myristic acid with the simple partitioning, compressed film, and partial film models acid (Sect. S1.1 of the Supplement) predict higher SS_c and smaller d_c than for NaC₁₄, but the inter-model comparison between the three models for myristic acid is similar as for NaC₁₄ in Fig. 1. We assessed the sensitivity of the compressed film
- 405 model predictions to the assumed molar volume of myristic acid, and found that the critical point is only significantly affected at $w_{p,sft} = 0.95$ (Sect. S1.2 of the Supplement).

In Fig. 1, the SS_c values of the two models are compressed with particles containing a strong surfactant, of the classical Köhler model are lower than for the simple and compressed film models, but larger than for the monolayer, Gibbs, and partial film models. The bulk solution model predicts significantly lower SS_c values than any of than the partitioning models, as has

- 410 been extensively observed in previous work analogously to several previous results for strong surfactants (e.g., Sorjamaa et al., 2004; Prisle et al., 2008, 2010; Topping, 2010; Prisle et al., 2019; Prisle, 2021). The bulk solution model For moderately surface active malonic, succinic, or glutaric acid and ammonium sulfate particles, we previously did not predict significantly lower SS_c values compared to the with the bulk solution model than with the bulk–surface particioning models for particles containing malonic, succinic, or glutaric acid and ammonium sulfate due to the moderately surface active nature of the three
- 415 acids (Vepsäläinen et al., 2022) (Vepsäläinen et al., 2022). Due to the moderate surface activity of these di- and poly-carboxylic acids, the monolayer and Gibbs partitioning models predicted only moderate extent of surface partitioning and consequently droplet bulk-phase compositions, surface tensions, and Köhler curves similar to the bulk solution model. The mutual agreement between the different models and in particular the significance of bulk–surface partitioning can therefore vary significantly with the surface active properties of the investigated aerosol.
- 420 The SSFor comparison, a critical supersaturation of $SS_{c}^{exp} = 0.965$ % calculated from a fit to experimental SS_{c} predictions for particles containing NaC14 ranges from 0.08 % to 1.63 % (see Table 3). data of Prisle et al. (2008) for $w_{p,sft} = 1$ and $D_{p} = 50$ nm is included in Fig. 1(d). The simple partitioning and compressed film model predict larger SS_{c} and the monolayer, Gibbs, partial organic film, bulk solution, and classical Köhler model smaller SS_{c} than this experimental value. For $w_{p,sft} = 1$, the SS_{c} is higher than with $w_{p,sft} = 0.95$, but the difference is minor compared to the difference between the SS_{c} for the
- 425 monolayer, Gibbs, and partial organic film models and SS_{α}^{exp} in Fig. 1(d). The simple model has previously been observed to overestimate SS_{α} at high $w_{p,sft}$ and for less surface active aerosols (Prisle et al., 2011; Vepsäläinen et al., 2022).
 - Average supersaturations in low-level clouds range from 0.1 % to 0.4 % (e.g. Politovich and Cooper, 1988) . Higher values but higher supersaturations of 0.7 % to 1.3 % can be reached during strong convection (e.g. Siebert and Shaw, 2017; Yang et al., 2019) turbulent fluctuations of temperature and water vapor concentration
- 430 (e.g. Siebert and Shaw, 2017). Only the simple partitioningand compressed filmmodels predict values , compressed film, and classical Köhler models predict SS_c above 0.7 % at high surfactant mass fractions $w_{p,sft}$, while the other models predict considerably lower SS_c values feasible for low-level (Table 3). Therefore, the inter-model variation for the strongly surface active aerosol studied here is sufficiently pronounced to affect predictions of activation for the ambient conditions in low level clouds. The absolute differences between the highest and lowest calculated values for SS_c in Fig. 1 are Δ SS_c = 0.27, 0.42, 0.73,
- 435 and 1.49 $_{c} = 0.27, 0.41, 0.69, and 1.30 \%$ for $w_{p,sft} = 0.2, 0.5, 0.8, and 0.95$, respectively. However, excluding the bulk solution modelis an outlier in most cases. Among the, maximum differences in SS_c between the bulk-surface partitioning models, then the maximum differences between the predicted critical supersaturation values partitioning models are $\Delta SS_{c} = 0.10, 0.24, 0.54, and 1.28 \%$ for $w_{p,sft} = 0.2, 0.5, 0.8, and 0.95$, respectively.

An experimentally derived This range of ΔSS_c value from Prisle et al. (2008) for pure NaC14 particles ($SS_c^{exp} = 0.9655\%$)

440 is included in Fig. 1(d). The for strongly surface active NaC₁₄ particles is similar to predictions for malonic acid by Vepsäläinen et al. (2022). The large differences between the SS^{exp} value for pure NaC14 particles of $D_p = 50$ nm falls between the extremes of the different model predictions. The simple partitioning and compressed film model predictions of SS_c are larger, while the monolayer, Gibbs, partial organic film, and bulk solution model predictions are smaller than SS^{exp}. None of the different model predictions matches the experimental value, even when considering that the comparison is between

- 445 $w_{p,sft} = 1$ and $w_{p,sft} = 0.95$. Simulations with pure NaC14 particles have a somewhat higher SS_c than with $w_{p,sft} = 0.95$, but the difference is minor for the predictions of the monolayer, Gibbs, and partial organic film models compared to the large discrepancy between the model predictions and SS_c^{exp} shown in Fig. 1(d). Predictions of the simple model have been observed to overestimate SS_c at high surfactant mass fractions in the past (Prisle et al., 2011; Vepsäläinen et al., 2022). The droplet surface tension parametrization used for this work is based on a different data set for an aqueous system containing
- 450 NaC14 and NaCl (Wen et al., 2000) than the one employed by Prisle et al. (2008) for aqueous solutions of NaC14 during their simulations (Campbell and Lakshminarayanan, 1965). The disparity in the predicted droplet surface tension based on the two different fits explains the difference in the predictions between the Gibbs model employed in Prisle et al. (2008) and the predictions with the Gibbs model in the present workmodels for both strongly and moderately surface active aerosol means that representation of surface activity during Köhler calculations could cause significant changes in predictions of cloud droplet
- 455 number concentrations (Fig. 4), with corresponding uncertainty in estimations of the cloud radiative effect. The critical diameter

3.1.2 Critical droplet diameters

In Fig. 1, the critical droplet diameters (d_c) values predicted with the different models in Fig. 1 decrease mainly as the NaC14 mass fraction in the particles increases, excluding the predictions of the Gibbs model in Figs. 1(a) and (b) where the situation

- 460 is reversed and generally decrease as $w_{p,sft}$ increases, except for the Gibbs model where d_c increases with $w_{p,sft}$ between $w_{p,sft} = 0.2$ and 0.5. The Gibbs model predicts the largest d_c values out of all of the bulk-surface partitioning models in Fig. 1, and generally even when including the predictions of the, and also larger d_c that for the bulk solution modeloutside of Fig. 1(a). However, except for particles with $w_{p,sft} = 0.2$. However, as the critical point for of cloud droplet activation predicted with the Gibbs model is directly related occurs close to the droplet size where dilution overcomes the CMC, these values predicted with
- 465 a constant CMC limit may not be reliable.

The predictions of the monolayer, compressed film, and partial film models of d_c are closely grouped the surface tension increases from the minimum value σ_{CMC} (Fig. 2), predictions may vary depending on the value used for the CMC of aqueous sodium myristate. For $w_{p,sft} = 0.2$ in Fig. 1(a)but the, the d_c agree fairly well between the different bulk–surface partitioning models, except the Gibbs model. The monolayer and partial film model predict similar d_c for all particle compositions (models

- 470 furthermore agree well for each $w_{p,sft}$ in Fig. 1, (see also Table 3). The difference in d_c between using the surface thickness predicted by the monolayer model and a constant value of 0.5 nm with the partial film model is a maximum of 8 % for $w_{p,sft} = 0.95$. The full comparison is presented in Sect. S1.3 of the Supplement. The simple partitioning and compressed film models predict similar d_c values that decrease as the NaC14 mass fraction in the particles increases, only , only showing a significant difference for $w_{p,sft} = 0.95$ in Fig. 1(d)showing a significant difference. The curve predicted by
- 475 The Köhler curves predicted with the bulk solution model has have a distinct shape in the form of with two local maximain Fig. 1, because the predicted droplet surface tension is at a constant CMC value before eventually starting to increase due to the dilution of the droplet solution constant equal to σ_{CMC} for the concentrated small droplet sizes before eventually increasing as the droplet grows and dilutes beyond the myristate CMC (Fig. 2). The bulk solution model For $w_{p,sft} = 0.2$ in Fig. 1(a)predicts

considerably larger d_c than the other models, corresponding to predictions where, the critical point is reached at a surface

480 tension other than the value at the CMC. the maximum corresponding to the larger droplet size, where surface tension is higher than σ_{CMC} . For the classical Köhler model, predicted d_c are lower than for the monolayer and partial film models, but higher than the simple and compressed film models.

The absolute differences between the largest and smallest calculated values for d_c in Fig. 1 are $\Delta d_c = 947.84, 479.56, 509.86$, and 518.29 nm % for $\Delta d_c = 952, 477, 508$, and 518 nm for particle compositions $w_{p,sft} = 0.2, 0.5, 0.8$, and 0.95, respectively. Excluding the d_c predictions of the bulk solution model only affects the maximum difference in Fig. 1(a), where $\Delta d_c = 337.09$

mm for $w_{\rm p,sft} = 0.2$ between only Differences between the bulk-surface partitioning models -

The inter-model comparison of predicted Köhler curves in Fig. 1 for particles containing NaC14 does not follow the same pattern as previously observed for malonic, succinic, or glutaric acid (Vepsäläinen et al., 2022). In are however smaller, $\Delta d_c = 334$ nm, for $w_{p,sft} = 0.2$. The size of activating droplets will affect their liquid water content, and in turn the optical properties of droplets and cloud albedo (Twohy et al., 2013). Variations in d_c between the different models may therefore

contribute to the uncertainty of estimations for radiative properties of clouds.

3.1.3 Inter-model variation

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For particles containing strong surfactant NaC₁₄ with NaCl in Fig. 1, the simple partitioning and the compressed film models predict the highest SS_c at high mass fractions of NaC14, the surfactant fractions $w_{p,sft}$. The monolayer and partial film models

- 495 agree well for the entire range of particle compositions, while the Gibbs model predicts comparable SS_c. For In previous Köhler calculations for particles containing moderately surface active malonic, succinic, and glutaric acids, the simple partitioning and partial film models predicted the or glutaric acid with ammonium sulphate (Vepsäläinen et al., 2022), the highest SS_c, were predicted with the simple partitioning model, while the Gibbs, monolayer, and bulk solution models predicted similar droplet properties, while the compressed film model predicted comparable agreed well, and predicted similar SS_c. The Gibbs
- 500 model predictions depend strongly on the CMC for droplets containing NaC14, which is a significant change from malonic, succinic, and glutaric acids, as the three acids are not known to form micelles. Predictions of the partial organic film model at $w_{p,sft} = 0.8$ and 0.95 for NaC14 also do not show the same reduction in d_c as with malonic, succinic, and glutaric acids. This is a result of the critical point in Figs. 1(e) and 1(d) being reached only after the organic surface film has broken and covers the droplet bulk only partially. The droplet size where the organic film breaks is not clearly visible in Fig. 1, but we
- 505 assume there is no change in the relative location of the critical point even if the smallest droplet sizes could be plotted based on Fig. S1 of the Supplement, where the simulation with a constant surface thickness of 0.5 nm for particles containing NaC14 is displayed, and no change in the relative location of to the critical point is observed compressed film and partial film models for most $w_{p,sft}$. The inter-comparison of surface activity and partitioning models therefore show several differences between strongly and moderately surface active aerosols. This suggests that effects of aerosol surface activity on cloud droplet formation
- 510 captured by the different partitioning models cannot be robustly understood based on any single model or a few aerosol systems with similar surface activity. Therefore, assessments of bulk–surface partitioning effects in Köhler calculations should be based on predictions for a wide range of conditions and types of surface active aerosol relevant to the atmosphere.



Figure 1. Köhler curves calculated with the different models for dry $\frac{NaC14 - NaC1}{NaC14 - NaC1}$ particles with $D_p = 50$ nm. Each panel shows curves for particles droplets with different NaC14 NaC14 mass fractions ($w_{p,sft}$) in the particles. Critical points are also marked on each curve, and the experimental critical supersaturation reported by Prisle et al. (2008) corresponding to $w_{p,sfk} = 1$ is included in panel (d)corresponding to $w_{p,sft} = 1$. Note that the vertical-axis scaling changes between the panels.

3.2 **Droplet surface tension**

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Figure 2 shows the droplet surface tensions along the predicted along the corresponding Köhler curves ealeulated with the different models for initial dry particles of $D_{\rm p} = 50$ nm and at NaC14 mass fractions ($w_{\rm p,sft}$) of 0.2, 0.5, 0.8 and 0.95. Table 3 contains the droplet surface tensions at the critical point of cloud droplet activation predicted with the different models for each particle system. In Fig. 2, all panels show similar characteristics in the overall structures of the predicted droplet surface tension eurvesin Fig. 1. The simple partitioning model assumes and classical Köhler models both assume a constant surface tension value equal to that of water. Predictions of the droplet surface tension pure water ($\sigma_{\rm w}$). The surface tensions predicted during

520 droplet growth vary significantly between the different models. Surface tension depression is significant at small droplet sizes for most predictions of the bulk-surface partitioning models, except for the compressed film model in Fig. 2(a). At the point of droplet activation, the predicted degree of surface tension depression varies other models, but the surface tension curves for each model show similar characteristics between different $w_{\rm p,sft}$.

Surface tensions at the critical point of cloud droplet activation (σ_c) predicted with the different models for each $w_{\rm p,sft}$ are 525 given in Table 3. The σ_c differ significantly between the different models and different particle compositions. Differences in the predicted surface tension at activation increase together with models and the NaC14 mass fraction differences increase with surfactant fraction $w_{p,sft}$ in the particles. In For $w_{p,sft} = 0.95$ in Fig. 2(d)the predicted surface tension at droplet activation varies from the CMC value to the surface tension of water, σ_c span the extremes from σ_{CMC} to σ_w between the different models. In Fig. 2, the The monolayer and partial organic film models predict a degree of surface tension depression that increases with

- 530 σ_c that significantly decrease with $w_{p,sft}$, while σ_c for the NaC14 mass fraction in the particles, while the Gibbs model only predicts a small depression from the surface tension of water. The are close to σ_w . For the compressed film modelpredicts the surface tension of water at the point of cloud droplet activation for all particle compositions. The predictions of the $\sigma_c = \sigma_w$ for the investigated $w_{p,sft}$. The bulk solution model are equal to the surface tension at the CMC in all panels of Fig. 2 except (a), but the predicted surface tension depression is still the largest of the models predicts $\sigma_c = \sigma_{CMC}$ for $w_{p,sft} = 0.5 - 0.95$
- 535 and also the lowest σ_c among the models for $w_{p,sft} = 0.2$.

The surface tension Droplet surface tensions predicted with the Gibbs model has show a step increase from the surface tension at CMC to a surface tension near that of water for all panels of σ_{CMC} to values near σ_w for each $w_{p,sft}$ in Fig 2. The droplet diameter at the step increase (or immediately afterit)) the step increase corresponds to the critical point for all panels of Fig. 2, as mentioned above during the discussion on the predicted, as discussed in connection with the Köhler curves. The

- step increases in Fig. 2 are visible for the benefit of the reader, as the droplet composition is assigned to be unknown when the droplet surface tension is equal to the surface tension at CMC. The surface tension curves predicted with surface tension curves of the monolayer and partial organic film models are similar for all panels of $w_{p,sft}$ in Fig. 2. The partial organic film model calculations were also tested performed with a constant surface thickness $\delta = 0.5$ nm, but the predictions with a constant surface thickness show only minor changes compared to the curves presented here. Detailed results of the differences are presented in
- 545 <u>changes to the results were minor (Sect. S1.3 of the Supplement. The breaking of the surface organic film in the predictions of</u> the partial organic film model is not visible in the figures presented, aside from Fig. 2(a)where the film breaks near the smallest visible droplet sizes).

The surface tension predictions of droplet surface tension curves for the compressed film model behave differently for NaC₁₄ particles in Fig. 2 generally display behavior different from previous studies featuring the model than for previous applications to other surface active aerosol systems (e.g., Ruehl et al., 2016; Forestieri et al., 2018; Vepsäläinen et al., 2022). The compressed film model predicts no visible surface tension depression in Fig. 2(a). Surface tension depression before from σ_w before droplet activation is visible in Figs. 2(b) - (d), but the critical point is at the same droplet size as the point when the surface tension reaches that of water only only for the highest NaC₁₄ fractions in Fig. 2(d) is d_c close to droplet size where the surface tension reaches σ_w , as was the typical behavior in Ruehl et al. (2016) observation by Ruehl et al. (2016) for dicarboxylic acids. Vepsäläinen et al. (2022) observed an occurrence of that the critical point and surface tension becoming that of water at different points with earboxylic reaching σ_w occurred at different droplet sizes for particles with $D_p = 50$ nm comprising moderately surface active di- and tri-carboxylic acids and ammonium sulfate particles at $w_{p.org} = 0.2$ at $w_{p.stt} = 0.2$. Forestieri et al. (2018) made analogous observations as Vepsäläinen et al. (2022) for $D_p = 50$ nm.

- Forestieri et al. (2018) observed the same for 80 nm NaCl particles coated with strongly surface active oleic acid at an organic
- 560 volume fraction of 0.8. We interpret the difference in observed behavior of the surface tension predictions between Fig. 2 and

past works to indicate that the model specific parameters used in this work do not adequately capture the solution properties of the aqueous droplet solution containing NaC14 and NaCl. This is not surprising as the parameters used in this work were fitted for particles containing myristic acid by Forestieri et al. (2018), not NaC14. Simulations comparing the predictions between NaC14 and myristic acid in Predictions for myristic acid–NaCl particles (Sect. S1.1 of the Supplementreveal) show that the

- 565 critical point and the surface tension reaching that of water σ_{w} do not happen at the same droplet size even for myristic acid. Forestieri et al. (2018) fitted the model parameters for similar droplet sizes at all $w_{p,sft}$. Forestieri et al. (2018) used the same compressed film model parameters fitted for myristic acid as used here for both NaC₁₄ and myristic acid, at organic volume fraction range of 0.40 – 0.98 for $D_{seed} = 180,200$ fractions of 0.40 – 0.98 for $D_{seed} = 180$ and 200 nm and RHrange of 99.83–99.93 %. This suggests that the = 99.83 – 99.93 %. The compressed film model parameters are fitted assuming
- 570 pseudo-ideal droplet solutions, but aqueous fatty acids and their sodium salts can show significant deviation from an ideal solution (Michailoudi et al., 2020; Calderón et al., 2020). The present results suggest that the compressed film model is sensitive to the specific fitting conditions of the model parameters, and the. The underlying assumption that the model parameters are compound specific compound-specific physical constants across varying NaC14 surfactant mass fractions and dry particle sizes may not hold true for real non-ideal droplet solutions. The fitting of the model parameters of the compressed film model assumes
- 575 that the droplet solution is pseudo-ideal, but systems of fatty acids or sodium salts of fatty acids can show significant deviation from an ideal solution (Michailoudi et al., 2020; Calderón et al., 2020). In Fig. 2, the droplet surface tension predicted with the compressed film model is always above the surface tension at the CMC of the binary mixture of NaC14–water that has been used to denote the physical lower limit of the droplet surface tension. The lowest predictions of droplet surface tension during droplet growth for malonic, succinic, or glutaric acids with the compressed filmmodel were lower than the surface tension of the pure compound due to the model parameter σ_{min} (Vepsäläinen et al., 2022).
 - -In-

The σ_c predicted for the monolayer, Gibbs, partial organic film, and bulk solution models in Fig. 2, generally the predicted surface tension values at the critical point of cloud droplet activation (σ_c) decrease as the NaC14 mass fraction in the particles (decrease with increasing w_{p,sft}) increases. At w_{p,sft} = 0.2 in Fig. 2(a), the minimum σ_c value predicted between the. For the monolayer, Gibbs, compressed film and partial organic film models is 67.27 (Table 3), the mutual variations of σ_c are within 4.7, 11.8, 20.4, and 26.9 mNm⁻¹ of surface tension of water. In Fig. 2(b), the maximum difference increases to 11.95, in Fig. 2(c) 20.47 and in Fig. 2(d)26.86. This large depression is only observable with the predictions of the of σ_w for particles with w_{p,sft} = 0.2, 0.5, 0.8, and 0.95, respectively (Table 3). For the monolayer and partial organic film models, σ_c show large depressions from σ_w, in agreement with previous applications of the models (Ovadnevaite et al., 2017; Malila and Prisle, 2018; Lin et al., 2018, 2020; Vepsäläinen et al., 2022). The simple partitioning and compressed film models predict σ_c equal to the surface tension of water for all particle compositions. The For sodium myristate particles in Fig. 2, the Gibbs model predicts σ_c to be very close to that of water in all eases, but predicts a small degree of close to σ_w and σ_c = σ_w for w_{p,sft} = 0.2, 0.95 with the simple partitioning, compressed

595 and compressed film model predictions of a small degree of surface tension depression or no surface tension depression are

film, and classical Köhler models. The small or absent surface tension depression (Table 3). The predicted with the Gibbs

models for NaC₁₄ is in agreement with past works other surface active aerosols (Prisle et al., 2008, 2010; Ruehl et al., 2016; Forestieri et al., 2018; Lin et al., 2018; Prisle, 2021; Vepsäläinen et al., 2022). The Gibbs model has been observed to predict higher surface tension values significantly higher σ_c than the monolayer model to a significant degree for SDS-NaCl and ragweed-ammonium sulfate particles, as well as somewhat lower surface tension for strongly surface active SDS–NaCl and

- moderately surface active ragweed pollenkitt-ammonium sulfate aerosol, and somewhat lower σ_c than the monolayer model for succinic acid-NaCl particles even more moderately surface active succinic acid-NaCl aerosol (Lin et al., 2018). The droplet σ_c for the bulk solution model predicts very low σ_c values for all particle compositions. In shows a 27.8 mNm⁻¹ reduction from σ_w for w_{p.sft} = 0.2 in Fig. 2(a), the predictions of the bulk solution model reach the critical point after the dilution is sufficiently strong to move away from the surface tension value at the CMC, but the reduction of the surface tension of water is
 still 27.96 and a 47.7 mNm⁻¹. In reduction from σ_w for w_{p.sft} = 0.5 0.95 in Figs. 2(b) 2(d), the critical points are reached
 - when the surface tension is at the value of the CMC surface tension for where $\sigma_{c} = \sigma_{CMC}$. Droplet surface tension impacts the conditions for growth and activation via the Kelvin term of the bulk solution model predictions, a 47.72 reduction from the surface tension of water.

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The predicted droplet Köhler equation (1). The importance of surface tension in Fig. 2 for particles containing NaC14 are significantly different from the curves for droplets containing malonic, succinic, or glutaric acid in Vepsäläinen et al. (2022).

- In Fig. 2 the monolayer, Gibbs, cloud droplet formation has been a topic of debate for decades (e.g. Li et al. (1998); Sorjamaa et al. (2004); Booth et al. (2009); Prisle et al. (2008, 2010); Nozière et al. (2014); Gérard et al. (2016) Ruehl et al. (2016); Ovadnevaite et al. (2017); Davies et al. (2019); Lowe et al. (2019); Bzdek et al. (2020)). Here, we observe that different models predict diverging droplet surface tensions for strongly surface active aerosol, similarly to
- 615 predictions for moderately surface active aerosol by Vepsäläinen et al. (2022). The σ_c of the monolayer and bulk solution models predict different surface tensions, although they use the same surface tension function. The three models predicted similar surface tensions for malonic, succinic, and glutaric acids (Vepsäläinen et al., 2022). The step increase in surface tension observed in Fig. 2 with the Gibbs model predictions is a direct consequence of the CMC, as is the extremely low surface tension predicted with the bulk solution model for a significant portion of the droplet growth. This is in clear contrast to
- 620 Vepsäläinen et al. (2022), as malonic, succinic, and glutaric acids are not known to form micelles. Generally, the predictions for σ_c for particles containing NaC14 are much lower than those for particles containing malonic, succinic, or glutaric acid with the models where surface tension depression is possible and with the exception of the partial organic film model, which predicts similar droplet surface tension values for both strong surfactant and moderately surface active organics for strongly surface active aerosol are significantly lower than for moderately surface active aerosol, while the other partitioning models
- 625 predict similar σ_c for both strongly and moderately surface active aerosol. The predicted droplet surface tensions reflect the underlying assumptions of the different models (Table 2), which do not account for all surfactant properties to the same degree. This suggests that varying conclusions about the importance of surface tension in cloud droplet activation could be partly due to differences between the various surface activity models applied. These model differences show that caution should be taken when interpreting the role of surface tension based on the predictions of any given model.



Figure 2. Surface Droplet surface tensions of droplets along the Köhler curves, calculated predicted with the different models for dry particles of $D_p = 50 \text{ nm}$ at different NaC14 with varying NaC₁₄ mass fractions ($w_{p,sft}$). The critical points evaluated for the Köhler curves in Fig. 1 are also marked. The surface tension for at the CMC (σ_{CMC}) for NaC₁₄ in binary mixture of water - NaC14 has been aqueous solution was estimated from the measurements of Wen et al. (2000) - and is indicated as a physical lower limit for the droplet surface tension.

630 3.3 Surfactant bulk-surface Bulk-surface partitioning of surfactant

Figure 3 shows the surface partitioning factors, in terms of the fraction of NaC14 in the droplets, calculated as the fraction of NaC14 molecules present in the droplet surface compared to the total amount of NaC14 in the droplet NaC₁₄ which is partitioned to the surface $(n_{sft}^{S}/n_{sft}^{T})$, with the different models for NaC14-NaCl dry particles of $D_{p} = 50$ nm and at NaC14 mass fractions $(w_{p,sft})$ of 0.2, 0.5, 0.8 for growing droplets along the Köhler curves in Fig. 1. Both the simple partitioning and 0.95. The simple partitioning model and the partial organic film model calculations are performed with the assumption that all organic-models assume that all surfactant content is partitioned to the droplet surface during the entirety of the droplet growth the partitioning factor is equal to unitythroughout the droplet growth, such that $n_{sft}^{S}/n_{sft}^{T} = 1$. The bulk solution model has no and classical Köhler models do not consider bulk-surface partitioning, and the partitioning factor is zero. Because of this, these eonstant values of the simple partitioning , partial film, and bulk solution model partitioning factors therefore $n_{sft}^{S}/n_{sft}^{T} = 0$.

640 The constant partitioning factors for these models are not shown in Fig. 3.

Figure 3 shows that the different partitioning models predict very different compositions of surfaces for growing droplets formed on the same aerosol systems. The predicted compressed film model predicts the strongest bulk–surface partitioning

of NaC14 is strongest with the compressed film modelNaC14 in growing droplets, followed by the Gibbs and monolayer models, respectively. The predicted partitioning factor value is near or equal to unity with the three models throughout the

- 645 droplet growth, meaning majority or all NaC14 content is residing in the droplet surface. The partitioning factors predicted with the monolayer and Gibbs models decrease slightly as the droplet grows. Fig. 3 shows the partitioning factors predicted with the Gibbs model only after the droplet has grown sufficiently to have a composition where micelles no longer form. For NaC14, the degree of NaC14 partitioning is similar between the Gibbs, compressed film, and monolayer models predictions, . For these models, the predicted partitioning factors are close, or equal, to unity throughout the respective Köhler curves, but
- 650 the predicted <u>droplet</u> activation properties can vary significantly <u>between the models</u> (Table 3). For <u>moderately surface active</u> malonic, succinic, and glutaric <u>acids</u>, <u>acid particles</u>, we previously found that the compressed film model predicted considerably larger partitioning factors , and there was some variation between the Gibbs and monolayer model predictions but than the monolayer and Gibbs models, whereas the different models could still predict similar droplet activation properties (Vepsäläinen et al., 2022). The monolayer and Gibbs models predict significantly higher partitioning factors for NaC14 compared
- 655 to succinic acid or SDS, both mixed with NaCl, in Lin et al. (2018). In the same work, the Gibbs model did predict high partitioning for Nordic aquatic fulvic acid (NAFA) and ragweed mixed with NaCl and ammonium sulfate, respectively. The monolayer model did also predict high partitioning factor for ragweed but the factor decreased significantly as the surfactant mass fraction in the particles approached unity. The Gibbs model also predicted generally higher partitioning factors compared to the monolayer model in Lin et al. (2018). Lin et al. (2020) used a Gibbs model and a monolayer to predict bulk-surface
- 660 partitioning of NAFA-NaCl particles, but the partitioning factor with the Gibbs model was defined differently from Fig. 3 and direct comparison is not possible. Lin et al. (2020) used the monolayer model to predict moderate to high partitioning factors (roughly 0.3-0.9) in a range of particle sizes ($D_p = 50 150$ nm) and compositions ($w_{p,org} = 0.02 1$) while accounting for surface tension time evolution. Comparing the predictions of the compressed film model partitioning factor for NaCl4 with those of Ruehl et al. (2016) for carboxylic acids, the minimum partitioning factors during dropletgrowth predicted for
- 665 NaC14 are equal to unity, while those predicted in Ruchl et al. (2016) generally only increase to unity at the critical point of cloud dropletactivation. strong partitioning predicted (or assumed) with the different partitioning models for NaC₁₄ means that inter-model differences in predicted droplet activation in Fig. 1 are mainly caused by differences in the droplet surface tension (Fig. 2). Surface activity could also have important implications for a variety of processes related to cloud microphysics, including aqueous droplet chemistry (Prisle, 2021). Chemical reactions in aqueous aerosols can be accelerated relative to
- 670 macroscopic solutions (Marsh et al., 2019). Strong partitioning of surface-active species and the simultaneous depletion of the droplet bulk phase can affect the chemical environment in the droplet, in particular in the submicron range (Prisle et al., 2010), changing possible reaction pathways and rates in the surface (Prisle et al., 2012b; Öhrwall et al., 2015; Werner et al., 2018) and bulk (Prisle, 2021) phases of the droplet. Interfacial reactivity could be pronounced due to the large surface-area-to-volume ratios of finite volume droplets (Prisle et al., 2012b; Bzdek et al., 2020; Prisle, 2021).
- 675 3.4 Relative change in the cloud droplet number concentration



Figure 3. NaC14-Surface partitioning factors $(n_{sft}^{S}/n_{sft}^{T})$ predicted with the monolayer, Gibbs, and compressed film <u>bulk-surface partitioning</u> models along the Köhler curves for <u>dry-NaC₁₄</u> particles with $D_{p} = 50$ nm at different <u>NaC14-NaC₁₄</u> mass fractions ($w_{p,sft}$). The critical points of the corresponding Köhler curves in Fig. 1 are also marked.

Figure 4 shows the relative change in cloud droplet number concentration predicted with the different bulk-surface partitioning models and the bulk solution model to account for aerosol surface activity, with respect to predictions of the classical Köhler model (ΔNN^{-1} , Eq. (11)), for NaC₁₄ particles in the size range $D_{\rm p} = 50 - 200$ nm. Implementations corresponding to the classical Köhler model are used in most larger-scale simulations, with a few exceptions (e.g., Prisle et al., 2012a; Lowe et al., 2019). The magnitude of ΔNN^{-1} therefore highlights how variations in critical supersaturations predicted with the different surface activity models may translate into uncertainty in estimates of atmospheric cloud droplet number concentrations based on Köhler theory.

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In Fig. 4, the monolayer, simple partitioning, compressed film, and partial film models all show very little variation in ΔNN^{-1} with particle size D_p for each $w_{p,sft}$. The differences in ΔNN^{-1} between the surface activity model predictions increase with $w_{p,sft}$, as also seen with the SS_c in Fig. 1. For $w_{p,sft} = 0.2$, the monolayer, simple partitioning, compressed film, and partial film models each yield ΔNN^{-1} within ± 5 %. For $w_{p,sft} = 0.95$, we predict 29 % and 28 % more cloud droplets with the monolayer and partial film models, respectively, than with the classical Köhler model, on average over the investigated particle size range. This is in reasonable agreement with results of Lowe et al. (2019), who used a partial film partitioning model combined with a cloud parcel model to predict an increase of 13 % in cloud droplet number concentrations

690 for marine and an increase of 26 % for continental boreal aerosol populations, compared to classical Köhler predictions. For

Table 3. The critical Critical droplet diameters (d_c), supersaturations (SS_c) and surface tensions (σ_c) for predicted with the different models for simulations NaC₁₄-NaCl particles with NaC14 at 298.15 K for $D_p = 50$ nm at 298.15 K. The simple partitioning, compressed film, and classical Köhler models all predict that $\sigma_c = \sigma_w = 72.0 \text{ mN m}^{-1}$ for each $w_{p,sft}$, and are not shown in the table.

Parameter	$d_{\rm c}$ (nm)	$\mathrm{SS}_{\mathrm{c}}\left(\% ight)$	$\sigma_{\rm c}~({\rm mNm^{-1}})$	$d_{\rm c}~({\rm nm})$	SS_{c} (%)	$\sigma_{\rm c}~({\rm mNm^{-1}})$	$d_{\rm c}~({\rm nm})$	$\mathrm{SS}_{\mathrm{c}}\left(\% ight)$	$\sigma_{\rm c}({\rm mNm^{-1}})$
$w_{ m p,sft}$	Monolayer		Gibbs			Bulk solution			
0.2	451	0.31	67.7	726	0.26	<u>71.8</u>	1345	0.09	44.2
0.5	394	0.35	60.6	761	0.26	71.7	504	0.09	24.2
0.8	334	0.4	<u>52.1</u>	677	0.3	<u>71.5</u>	295	0.15	24.2
0.95	293	0.43	<u>45.6</u>	612	0.34	71.3	148	0.33	24.2
Parameter	$d_{\rm c}$ (nm)	SS _c (%)	$\sigma_{\rm c}({\rm mNm^{-1}})$	$d_{\rm c}$ (nm)	SS _c (%)	$d_{c_{\rm c}}({\rm nm})$	<u>SSc (%)</u>	$d_{c}(\underline{nm})$	SS_{c} (%)
Parameter $w_{\rm p,sft}$	$d_{\rm c} ({\rm nm})$	SS _c (%) Partial organ	$\sigma_{\rm c} ({\rm mN}{\rm m}^{-1})$	$d_{\rm c} ({\rm nm})$	$SS_{c}(\%)$		SSc.(%)	$\frac{d_{c}(nm)}{Class}$	SS _c .(%)
Parameter w _{p,sft}	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	SS _c (%) Partial organ 0.32	$\frac{\sigma_{\rm c} ({\rm mNm^{-1}})}{{\rm hic film}}$	$\frac{d_{\rm c} ({\rm nm})}{\underset{392}{\text{Sin}}}$	$\frac{\text{SS}_{c} (\%)}{0.36}$	$\frac{d_{c}(nm)}{Compresse}$ $\frac{406}{2}$	$\frac{SS_{c}(\%)}{d \text{ film}}$ 0.34	$\begin{array}{ } \underbrace{d_{c}(nm)} \\ \underbrace{Class} \\ 4\underline{18} \end{array}$	$\frac{SS_{\varepsilon}(\%)}{\text{ical K\"öhler}}$ 0.34
Parameter $w_{\rm p,sft}$ 0.2 0.5	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$SS_{c} (\%)$ Partial organ 0.32 0.36	$\sigma_{\rm c} ({\rm mN}{\rm m}^{-1})$ $\frac{\rm dc}{\rm film}$ 67.3 60.2	$\begin{array}{c} d_{\rm c} \text{ (nm)} \\ \\ \underline{Sin} \\ 392 \\ \underline{392} \\ \underline{284} \\ \end{array}$	$SS_{c} (\%)$ $nple$ 0.36 0.5	$\frac{d_{c.}(nm)}{Compressee}$ $\frac{406}{293}$	$\frac{\text{SS}_{c}(\%)}{\text{d film}}$ 0.34 0.48	$\begin{array}{ } \underline{d_{\varepsilon}(nm)} \\ \underline{Class} \\ 418 \\ 326 \end{array}$	$\frac{SS_{c}(\%)}{\frac{1}{1000}}$
Parameter $w_{p,sft}$ 0.2 0.5 0.8	$ \begin{array}{c c} d_{c} (nm) \\ \hline 435 \\ 385 \\ 330 \\ \end{array} $	SS _c (%) Partial organ 0.32 0.36 0.41	$\sigma_{\rm c} (\rm mN m^{-1})$ $ic film$ 67.3 60.2 51.6	$\begin{array}{c} d_{\rm c} (\rm nm) \\ \\ \underline{Sin} \\ 392 \\ 284 \\ 169 \end{array}$	$ SS_{c} (\%) $ nple 0.36 0.5 0.84	$\frac{d_{c}(nm)}{Compressed}$ $\frac{406}{293}$ $\frac{174}{74}$	$\frac{\text{SS}_{c}(\%)}{\text{d film}}$ 0.34 0.48 0.81	$\begin{array}{ } \underline{d_{c}}(nm) \\ \underline{Class} \\ 418 \\ 326 \\ 239 \\ \end{array}$	$\frac{\sum \sum_{c} (\%)}{\text{ical K\"ohler}}$ 0.34 0.43 0.59

 $w_{p,sft} = 0.95$, we however predict a 28 % decrease in cloud droplet number concentrations with the compressed film model and a decrease of 35 % with the simple model, compared to the classical Köhler model. This shows that, for these strongly surface active particles, even the direction of the effects of surface activity as significant positive or negative ΔNN^{-1} can vary with the choice of partitioning model.

- 695 With the Gibbs model, we here predict ΔNN^{-1} of 2-21 % averaged over the particle size range for the surfactant fractions $w_{p,sft} = 0.2 0.95$. The bulk solution model predicts the lowest SS_c for the cases studied, resulting in the largest positive ΔNN^{-1} of all the surface activity models. This is similar to the results of Prisle et al. (2012a), who implemented surfactant effects in the global circulation model (GCM) ECHAM5.5–HAM2. The bulk solution model here yields ΔNN^{-1} which both decrease (for $w_{p,sft} = 0.2$ and 0.5), increase (for $w_{p,sft} = 0.95$), or change non-monotonically (for $w_{p,sft} = 0.8$) with
- increasing D_p . This variation is due to the constraint on the droplet water activity imposed by the CMC, as well as the critical point of droplet activation moving between the two maxima of the Köhler curve, located at droplet sizes before and after the droplet surface tension increases from the minimum value σ_{CMC} (see Figs. 1 and 2). On overage over the investigated particle size range, the bulk solution model predicts ΔNN^{-1} of 55 – 99 % for particles with different surfactant mass fractions. However, these very large ΔNN^{-1} should be considered with some caution, as large relative changes in SS_c may conflict with
- 705 the assumption of simple exponential dependence in Eq. (11). The bulk–surface partitioning models are considered to give more comprehensive and realistic representations of the droplet activation behavior, whereas the bulk solution model has been included in this comparison mainly for reference.



Figure 4. Relative change in cloud droplet number concentration (ΔNN^{-1}) predicted the different surface activity models, for $D_{\rm p} = 50 - 200$ nm at different NaC₁₄ mass fractions ($w_{\rm p,sft}$) in the particles. The relative change is calculated with respect to predictions of the classical Köhler model.

Results in Fig. 4 support previous estimates, showing that the surface activity of organic aerosol and its representation in calculations of cloud droplet activation have the potential to significantly influence global-scale predictions, at least for

- 710 specific regions (Prisle et al., 2012a). Increased cloud droplet number concentrations would ultimately have a negative radiative effect and, therefore, a cooling effect on the climate. Decreased cloud droplet number concentrations would conversely lead to a warming effect. Facchini et al. (1999) estimated that a 20 % increase in the cloud droplet number concentration from consideration of aerosol surface activity would correspond to a change in cloud radiative forcing of -1 Wm⁻², in good agreement with the later full GCM predictions of Prisle et al. (2012a) for similar conditions. In the present work, the variation in
- 715 ΔNN^{-1} between the different model predictions for particles with high NaC₁₄ mass fractions suggests that the representation of surfactant effects could translate to significant uncertainty in larger-scale predictions of cloud radiative effects for regions where strongly surface active aerosol are prevalent. Consideration of surface activity could result in both significant warming or cooling effects, compared to the conventional predictions of a classical Köhler model, depending on the specific partitioning model used. Therefore, conclusions regarding bulk–surface partitioning effects on cloud droplet number concentrations and
- 720 aerosol-cloud-climate effects based on any one model should be considered and extrapolated with caution.

4 Conclusions

We have <u>used applied</u> five bulk–surface partitioning models (Prisle et al., 2010, 2011; Ruehl et al., 2016; Ovadnevaite et al., 2017; Malila and Prisle, 2018) and currently in use in the atmospheric aerosol research community, together with a general bulk solution model and a classical Köhler model, in predictive Köhler modeling of growing aqueous solution droplets for

725 identical particles consisting of a strong surfactant droplet growth and activation for particles comprising strong surfactants sodium myristate or myristic acid mixed with NaCl across a range of particle compositions.

The different models can predict significantly different properties of the activating droplets droplet activation properties (SS_c, d_c , and σ_c) for identical particles. The differences between the the same strongly surface active particles. Differences between the predictions of the bulk–surface partitioning models increase with the surfactant mass fraction in the particles.

- 730 All bulk-surface partitioning models predict or assume a high degree of bulk-surface partitioning of NaC14Each partitioning model predicts or assumes strong partitioning of surfactant to the droplet surface, leading to the Raoult effect having only a small effect a small overall Raoult effect and small variations in the droplet bulk water activity between the different predictions. The partitioning model predictions. Predicted differences in the predicted critical droplet properties result mainly for the investigated strongly surface active aerosols mainly stem from the droplet surface tension (the Kelvin effect). The predictions
- 735 with particles containing strong surfactant depend on the modeling method and emphasize the need for validation of the different bulk-surface partitioning models across a wide range of particle mixtures and conditions. Uncertainty in predicting the critical properties of activating droplets creates uncertainty in generalizations for atmospheric processes such as estimating the number of cloud droplets, cloud albedo, and radiative forcing and ensuing Kelvin effect. Our results further show that cloud droplet number concentrations predicted for strongly surface active aerosol can vary significantly between the different
- 740 models. Relative changes in cloud droplet number concentrations with respect to a classical Köhler model range from -35 % to 29 % between the five partitioning models, corresponding to both considerable warming and cooling climate effects. These differences represent a significant uncertainty in estimating the cloud radiative effects for regions where strongly surface active aerosol are prevalent. Therefore, conclusions regarding aerosol–cloud–climate effects of aerosol surface activity and bulk-surface partitioning based on any one surface activity model should not immediately be generalized.
- 745 The <u>Comparison of inter-model variation for common aerosol systems comprising NaC14 and analogous predictions for</u> particles containing malonic, succinic, or glutaric acid (Vepsäläinen et al., 2022) differ. In all cases investigated so far, the differences between the predictions of the different models increase with the mass fraction of the surface active compound in the particles. The predictions of cloud droplet activation for a given aerosol system containing either moderately surface active compounds or strong surfactants depend on the modeling method. Details of which models mutually agree or disagree in
- 750 predictions of critical droplet properties for identical initial particles vary between the strong and moderate surfactants studied. This highlights how models must be validated strongly and moderately (Vepsäläinen et al., 2022) surface active aerosol shows how the mutual agreement between the different surface activity and partitioning models varies with aerosol surface activity. Therefore, conclusions about the robustness of our understanding of the effects of aerosol surface activity, as captured by the inter-model variation, do not immediately translate between different surface active aerosol systems. This emphasizes the

755 need to validate aerosol surface activity models for a range of surface active aerosol systems and surfactant properties, as well as atmospheric-types and ambient conditions, before establishing their broad applicability for atmospheric modelingean be established. Otherwise significant errors could be introduced in modeling larger scale atmospheric processes through the generalization in atmospheric modeling. Generalization of Köhler predictions created for only a given few systems or conditions few surface active aerosol systems and conditions could introduce significant bias in modeling larger-scale atmospheric 760 processes.

Author contributions. SV performed the simulations and the analysis of model results with assistance from SMC and NLP. SV and NLP wrote the original and revised manuscript drafts, response to reviewers, and made the visualizations, with assistance from SMC. NLP conceived the project and methodology, was responsible for supervision and project management, and secured funding for the work.

Competing interests. There are no conflicts to declare.

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