**Atmospheric
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A simple representation of surface active organic aerosol in cloud droplet formation

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Abstract

Atmospheric aerosols often contain surface active organics. Surface activity can affect cloud droplet formation through both surface partitioning and surface tension reduction in activating droplets. However, a comprehensive thermodynamic account for these effects in Köhler modeling is computationally demanding and requires knowledge of both droplet composition and component molecular properties, which is generally unavailable. Here, a simple representation of activation properties for surface active organics is introduced and compared against detailed model predictions and laboratory measurements of CCN activity for mixed surfactant-salt particles from the literature. This simple organic representation is seen to work well for aerosol organic-inorganic composition ranges typically found in the atmosphere, and agreement with both experiments and detailed model predictions increases with surfactant strength. The simple representation does not require resolution of the organic aerosol composition and relies solely on properties of the organic fraction that can be measured directly with available techniques. Thus, it has high potential for application to complex and ambient aerosol. It is not computationally demanding, and therefore also has potential for implementation to atmospheric models accounting for cloud microphysics.

1 Introduction

The indirect climate effect of atmospheric aerosol particles via cloud formation and properties still constitutes the single largest uncertainty in assessing the anthropogenic contribution to global climate change (IPCC, 2007). The cloud condensation nuclei (CCN) properties of aerosol particles are determined by both size and chemical composition. Presence of surface active molecules (surfactants) has been demonstrated in bulk samples of atmospheric cloud and fog waters (Facchini et al., 1999, 2000) as well as in aerosol samples (Yassaa et al., 2001; Mochida et al., 2003; Cheng et al., 2004) and aqueous extracts thereof (Oros and Simoneit, 2000; Mochida et al., 2002;

Kiss et al., 2005; Dinar et al., 2006; Asa-Awuku et al., 2008) from marine, and rural and urban/polluted continental environments. A number of the identified surface active organic molecules have been observed in laboratory experiments to be CCN active at atmospheric conditions and surface activity can significantly affect CCN properties of these compounds (Prisle et al., 2010, 2008). Comparison to detailed model predictions from thermodynamically consistent relations suggests that surface activity influences cloud droplet activation via both surface partitioning and surface tension effects. However, the combined effect of these mechanisms is not readily anticipated in each case (Prisle et al., 2010, 2008, and references therein).

To improve estimates of the aerosol indirect climate effect and predictions of future climate, a correct description of organic aerosol properties, such as surface activity, in atmospheric models accounting for cloud microphysics is therefore essential. In previous work, the surface partitioning equilibrium and surface tension of activating droplets were determined from numerical solutions to thermodynamic relations (Prisle et al., 2010, and references therein). Such calculations are however computationally too demanding for implementation into atmospheric models (Kokkola et al., 2006). Furthermore, the use of thermodynamically consistent relations requires knowledge of droplet composition, and composition-dependent properties, in terms of aqueous solution water activity and surface tension, that is generally not available for aerosol compositions such as those found in the atmosphere. Finally, the detailed model cannot be applied in its current form to aerosol systems with more than three components (Prisle et al., 2010, 2008; Sorjamaa et al., 2004). Recent works by Topping (2010) and Raatikainen and Laaksonen (2010) address in particular the first point and present approximate analytical solutions to the partitioning equilibrium that do not require iterative procedures. Nevertheless, both solutions still require knowledge of particle compositions and component properties.

In this work, we apply a different approach and introduce a simple representation for the activation properties for surface active organics, based on insights to the behavior of organic surfactants in cloud droplet activation gained from model predictions

employing detailed thermodynamic relations. Köhler predictions using this simple representation are compared to laboratory measurements and detailed model calculations of CCN activity for mixed organic surfactant–inorganic salt particles of atmospheric relevance from the literature.

2 Theory and modeling

2.1 Köhler theory

Cloud droplets form in the atmosphere when water vapor condenses on the surfaces of aerosol particles. As the aqueous phase forms, particle constituents may dissolve into solution droplets. The equilibrium growth and activation of such an aqueous solution droplet is described by the Köhler equation (Köhler, 1936), relating the equilibrium water vapor supersaturation (SS) over a spherical droplet to its diameter (d):

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

Here, 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, v_w is the partial molar volume of water in solution, σ is the droplet surface tension, R is the universal gas constant, and T is the temperature (in Kelvins).

The water activity describes the suppression by dissolved solutes of the equilibrium partial pressure of water over an aqueous solution, compared to the pure water saturation vapor pressure, according to the generalized Raoult's Law:

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

Here, x_w is the water mole fraction in solution and γ_w is the corresponding mole-fraction based activity coefficient of water. The exponential term in Eq. (1) is equivalently called the Kelvin term and describes the enhancement of vapor pressure over a concave

curved droplet surface, compared to a flat liquid surface, by the Kelvin effect. These two opposing effects on equilibrium water partial pressure define a maximum equilibrium supersaturation for growing droplet sizes, or a critical supersaturation (SS_c), with corresponding critical droplet diameter (d_c), that must be surpassed for droplets to activate and grow into full-sized cloud drops.

The Kelvin term depends explicitly on droplet surface tension. Any reduction in surface tension by dissolved surfactants will decrease the vapor pressure enhancement at a given droplet size and corresponding surface curvature, and therefore also decrease the maximum value of the Köhler curve, the critical supersaturation, for the droplet.

2.2   Surface partitioning

Surfactants preferentially accumulate at the air-water interface of aqueous solutions. In Gibbs adsorption theory (Gibbs et al., 1928), this is described by the partitioning of surfactant molecules within a solution between an isotropic bulk phase (superscript B in the following), and an anisotropic surface phase (superscript S) with a steep surfactant radial density gradient, separated by an infinitely thin dividing surface. The relative distribution of surfactant solute between these distinct solution phases is referred to as the (bulk-)surface partitioning and depends on the intrinsic propensity of surfactant molecules for the surface, as well as the relative dimensions of the solution bulk and surface phases, described by the surface-area-to-bulk-volume ratio (Prisle et al., 2010, and references therein). For spherical droplets, the latter is given by the diameter as:

$$\frac{A}{V} = \frac{6}{d}. \tag{3}$$

As surfactant molecules partition to the solution surface, their concentration in the bulk phase is simultaneously depleted. Solution droplets involved in cloud droplet formation typically have sub-micrometer diameters and thus $A/V \gg 0\,\mu\text{m}^{-1}$, whereas for a macroscopic solution $A/V \rightarrow 0\,\mu\text{m}^{-1}$. In small droplets, surface partitioning and the resulting bulk-phase depletion of surfactant molecules can significantly affect solution properties

(Seidl and Hanel, 1983; Bianco and Marmur, 1992; Laaksonen, 1993). Droplet bulk-phase depletion will result in a relatively larger water activity (a diminished water partial pressure suppression) and a larger surface tension (a diminished solution surface tension reduction) from a given total (superscript T) concentration of dissolved surfactant within the droplet phase. Surface partitioning may thus be anticipated to affect cloud droplet activation through both water activity and Kelvin effects.

Analogously to Prisle et al. (2010), surfactant strength is here quantified as the surface tension reduction from the pure water value attained at a given surfactant bulk phase concentration (c_{SFT}^B) in solution

$$\text{Surfactant strength} = \Delta\sigma\left(c_{SFT}^B\right) = \sigma_w - \sigma\left(c_{SFT}^B\right). \tag{4}$$

The strength of a surfactant is this way determined by both the nature of molecular interactions and the concentration gradient in the anisotropic surface, as given from an appropriate adsorption isotherm, for example the Langmuir-based Szyskowski equation (Szyskowski, 1908). In macroscopic solutions, a strong surfactant can yield a large reduction in surface tension, compared to pure water, at a given concentration by being strongly partitioned to the surface and/or displaying molecular interactions to enable efficient reduction in the solution surface tension. Inorganic salts can influence individual surfactant properties (Lin et al., 2005; Tuckermann, 2007; Vanhanen et al., 2008; Prisle et al., 2010) by enhancing surfactant activity in solution through both solute-solute non-ideal interactions and common ions increasing the surfactant solubility product. Surfactant strength, as defined in Eq. (4), is therefore affected by the mixing state of solutes within an aqueous solution.

In microscopic activating droplets, the surface tension reduction attained from a given strong surfactant is not immediately evident. From simple Köhler theory, it is predicted that spherical dry particles with larger diameters (D_p) activate with critical droplet sizes corresponding to larger diameter growth factors (GF=d_c/D_p), and thus with more dilute total solute concentrations within the droplets ($c^T \propto GF^{-3}$). However, the larger critical droplets also have smaller surface-area-to-bulk-volume ratios ($A/V \propto d_c^{-1}$) and

are thus subject to relatively less bulk-depletion from surface partitioning at a given total droplet composition. In addition to potentially influencing surfactant molecular properties, the presence of inorganic solutes directly affects critical droplet sizes and thus total surfactant concentrations, as well as surface-area-to-bulk-volume ratios, of
5 activating droplets. The CCN properties of a given surfactant are therefore intricately linked to both dry particle composition and size.

An example of these effects is shown in Fig. 1, for dry particles with diameters in the range 15–150 nm and comprising 80% by mass of surfactant (sodium dodecanoate, C12Na) mixed with sodium chloride (NaCl). The values presented are calculated with
10 a detailed thermodynamic model accounting for the surface partitioning equilibrium within the activating droplets and have been adapted from the results presented in Figs. 6 and 7 of Prisle et al. (2009, and references therein). Droplet surface tension is here evaluated as a function of surfactant and salt bulk molal concentrations (m_{SFT}^B and m_{NaCl}^B) from a ternary parametrization based on the Szyskowski equation (Prisle
15 et al., 2009, and references therein):

$$\sigma = \sigma_w + \left(\frac{d\sigma_{NaCl}}{dm_{NaCl}^B} \right) m_{NaCl}^B - a\ln(1 + m_{C12Na}^B/b), \qquad (5)$$

$$a = 48.98 - 0.88w_{C12Na}^B, \qquad (6)$$

$$b = 0.004 + 0.004w_{C12Na}^B. \qquad (7)$$

Here, parameters a and b depend on the relative C12Na and NaCl solute mass-
20 fractions in the solution bulk, where $w_{C12Na}^B + w_{NaCl}^B = 1$, and $\sigma_w = 72.2$ mN m^{-1} is the pure water surface tension at 296.65 K. The surface tension gradient for aqueous NaCl is $(\frac{d\sigma_{NaCl}}{dm_{NaCl}^B}) = 1.61$ [mN m^{-1}/mol kg^{-1}] and accounts for the slight increase in solution surface tension arising directly from the inorganic salt.

Individual panels in Fig. 1 show values predicted at the point of activation for (a)
25 droplet GF and A/V, (b) surfactant depletion from the droplet bulk in terms of the

molar fraction of surfactant left in the bulk (n^B_{C12Na}/n^T_{C12Na}) and the molar fraction of solute remaining in the bulk that is surfactant ($n^B_{C12Na}/[n^B_{C12Na}+n^B_{NaCl}]$), (c) bulk-phase water mole fraction (x^B_w) and water mole fraction with respect to only NaCl solute ($x^B_{w,NaCl}$), and (d) droplet surface tension, all as functions of dry particle diameter (D_p). Figure 1 illustrates how the majority of surfactant molecules are depleted from the droplet bulk at the point of activation, due to partitioning to the surface phase ($n^B_{C12Na}/n^T_{C12Na}\sim0.05$). Even with the rather high surfactant mass fraction in the dry particles of the present example, the majority of solute left in the droplet bulk at activation is NaCl ($n^B_{C12Na}/[n^B_{C12Na}+n^B_{NaCl}]\sim0.05$). The effects on activating droplet solution properties are that both water activity and surface tension are significantly less affected by the organic solute than would be anticipated from its total concentration in the droplet phase. Similar results were obtained for other surfactants and dry particle component mixing ratios studied (Prisle et al., 2009).

2.3 Critical supersaturation

In the Köhler calculations, critical supersaturations (SS_c) are determined for activating droplets formed on dry particles of given compositions and sizes, by iterating the respective maxima of the Köhler curves described by Eq. (1). Dry particles are assumed to be spherical and the particle volume is obtained from the diameter (D_p) as:

$$V_p = \frac{\pi}{6}D_p^3. \tag{8}$$

Particle compositions are given by the relative dry mass fractions ($W_{p,i}$) of organic surfactant ($i=$SFT) and inorganic salt ($i=$s), where $W_{p,SFT}+W_{p,s}=1$. Assuming volume additivity of the individual dry particle components, the total molar amounts (n^T_i) of each solute ($i=$SFT,s) available in the droplets are then:

$$n^T_i = \frac{W_{p,i}}{M_i}\frac{\pi}{6}D_p^3\left(\frac{W_{p,SFT}}{\rho_{SFT}} + \frac{W_{p,s}}{\rho_s}\right)^{-1}. \tag{9}$$

Here, ρ_{SFT} and ρ_{s} are the respective mass densities of pure solid organic surfactant and inorganic salt, and M_i is the molar mass of each component.

Complete dissolution of each dry particle component, and volume additivity of water and all solutes, is assumed within the aqueous droplets formed. The increasing total molar amount of water (n_{w}^{T}) in a growing droplet is then calculated as a function of the diameter (d) according to:

$$n_{\text{w}}^{\text{T}} = \frac{\rho_{\text{w}}}{M_{\text{w}}} \frac{\pi}{6}\left(d^3 - D_{\text{p}}^3\right). \tag{10}$$

Both water activity and surface tension are determined from the droplet solution bulk-phase composition, such that $a_{\text{w}}=a_{\text{w}}^{\text{B}}(n_i^{\text{B}}, n_{\text{w}}^{\text{B}})$ and $\sigma=\sigma^{\text{B}}(n_i^{\text{B}}, n_{\text{w}}^{\text{B}})$.

In the detailed model accounting for the surfactant partitioning equilibrium (Prisle et al., 2010, and references therein), droplet bulk-phase molar composition (n_i^{B}, n_{w}^{B}) is determined for each droplet size and corresponding total composition (n_i^{T}, n_{w}^{T}) by solving the partitioning equilibrium numerically. The droplet bulk-phase water activity is subsequently set equal to the corresponding water mole-fraction concentration ($a_{\text{w}}^{\text{B}}=x_{\text{w}}^{\text{B}}$), equivalent to assuming ideal water mixing properties in solution (unit water activity coefficient, $\gamma_{\text{w}}^{\text{B}}=1$), and the droplet surface tension is evaluated from concentration-dependent parametrizations for ternary aqueous solutions analogous to the one given in Eq. (5). This information is generally not available for complex aerosol mixtures, let alone for particles of unresolved composition, just as the method of solving the partitioning equilibrium numerically cannot be applied in its current form to droplets with more than three components. The detailed model is therefore currently not applicable to more realistic particle systems, such as smog-chamber generated secondary organic aerosol (SOA) or ambient aerosol, with unresolved organic composition and molecular properties in solution.

2.4 Simple organic representation

Motivated by knowledge of the behavior of organic surfactants in activating solution droplets gained from the detailed thermodynamic model (as illustrated in Fig. 1), we here introduce a very simple representation to account for the cloud droplet activation properties of such surface active organic aerosols. This simple representation (abbreviated "rep1" in the following) just assumes all the surface active organic is partitioned to the droplet surface, and thus has no net effect on either water activity or surface tension of the droplet solution, at the point of activation. Specifically, the molar amount of surfactant in the droplet bulk-phase is

$$n_{SFT}^{B} = 0. \tag{11}$$

It is implied that the division of the bulk and surface phases is such that neither the inorganic nor water partition to the droplet surface, whence

$$n_{s}^{B} = n_{s}^{T}, \tag{12}$$

$$n_{w}^{B} = n_{w}^{T}. \tag{13}$$

The bulk-phase water mole fraction is then

$$x_{w}^{B} \equiv \frac{n_{w}^{B}}{n_{w}^{B} + n_{s}^{B} + n_{SFT}^{B}} = \frac{n_{w}^{B}}{n_{w}^{B} + n_{s}^{B}} = \frac{n_{w}^{T}}{n_{w}^{T} + n_{s}^{T}} \equiv x_{w,s}^{T}, \tag{14}$$

where $x_{w,s}$ is the water mole fraction with respect to only inorganic solute. The corresponding droplet water activity is then

$$a_{w} = a_{w}\left(x_{w,s}^{T}\right) \tag{15}$$

and the surface tension is simply that of pure water at the given activation temperature

$$\sigma = \sigma_{w} \tag{16}$$

The assumption of complete organic surface partitioning is essentially just the simplest parametrization conceivable of a solution to the partitioning equilibrium. The implications for Köhler calculations are analogous to treating the entire organic particle fraction as an insoluble, fully wettable core within the activating droplet; however, the view of complete partitioning to the droplet surface is clearly thermodynamically more consistent in the case of a surface active organic displaying some finite water solubility. Although it may seem contradictory that a soluble and surface active solute in effect has no influence on either water activity or surface tension of the droplets, properties approaching those described by Eqs. (15) and (16) are exactly the implications of the detailed model predictions, as seen in Fig. 1. Notably, the expected consequences for surface active organic CCN properties have been demonstrated experimentally for a number of compounds (Prisle et al., 2008, 2010; Sorjamaa et al., 2004).

The complete surface partitioning of surfactant molecules is a consequence of the large surface-area-to-bulk-volume ratios (A/V) of the microscopic activating droplets, compared to macroscopic solutions. The equilibrium concentration gradient in the anisotropic surface leaves essentially no surfactant solute in the isotropic droplet bulk, as explained in more detail by Prisle et al. (2010). The solution surface tension is fundamentally determined by molecular interactions within the surface phase, but is typically parametrized as a function of the bulk phase composition, as must be valid at equilibrium between the two phases. A surface tension equal to that of pure water (neglecting any direct influence on surface tension from the inorganic salt) then follows immediately from substituting the vanishing bulk concentration of surfactant resulting from Eq. (15) into an appropriate concentration-dependent parametrization, analogous to that given in Eq. (5). Owing to the large A/V of activating droplets, the surfactant density in the surface phase is still insufficient to enable molecular interactions that significantly reduce solution surface tension, compared to pure water, even when the surfactant molecules are essentially completely partitioned to the surface.

Using this simple organic representation, the droplet bulk-phase composition and properties are here obtained directly from the total composition, according to Eqs. (11)–

(16) above, without iterations of a numerical solution to the surface partitioning equilibrium. This makes the Köhler calculations computationally much less demanding. Furthermore, using the simple representation only requires knowledge of the total organic aerosol mass fraction, as well as the average density of this fraction (for use in Eq. (9) when $i=s$). Both of these quantities can in principle be measured for aerosols of unresolved organic composition with available techniques. In particular, the simple representation does not require the identity and properties of the organic molecular components to be known (since these are assumed to not affect the properties of the activating droplets), making this representation potentially applicable to organic aerosol of unresolved composition.

3   Results and discussion

The CCN activity of particles comprising one of the surfactants sodium octanoate ($CH_3(CH_2)_6COONa$; C8Na), sodium decanoate ($CH_3(CH_2)_8COONa$; C10Na), sodium dodecanoate ($CH_3(CH_2)_{10}COONa$; C12Na), or sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$, SDS), mixed with NaCl, was studied in laboratory experiments and modeled from Köhler theory accounting for the surface partitioning equilibrium by Prisle et al. (2010). For comparison with these results, Köhler calculations using the simple organic representation (rep1) were here made assuming ideal water mixing properties in the droplet solutions (unit water activity coefficient, $\gamma_w^B=1$), such that

$$a_w = x_{w,s}^T = \frac{n_w^T}{n_w^T + \delta_{NaCl} n_{NaCl}^T} \,. \tag{17}$$

NaCl was assumed to be fully dissociated by using a constant dissociation factor $\delta_{NaCl}=2$ in Eq. (17). The partial molar volume of water (v_w) was approximated with the molar volume of pure water, given by the water molar mass and mass density as $v_w^0 = M_w/\rho_w$, according to the assumption of ideal mixing volume for water within the droplets. Mass densities used for the organics were $\rho_{C8Na}=\rho_{C10Na}=\rho_{C12Na}=1.2\,\mathrm{g\,cm^{-3}}$

and ρ_{SDS}=1.176 g cm^{-3}, and for the salt ρ_{NaCl}=2.165 g cm^{-3}. The temperature was T=296.65 K.

Results are shown in Figs. 2, 3, 4, and 5, for particles comprising C8Na, C10Na, C12Na, and SDS, respectively, mixed with NaCl. In each figure, panel (a) shows critical supersaturations (SS_c) as functions of dry particle diameter (D_p), for particles with dry surfactant mass fractions of 0% (blue), 20% (green), 50% (red), and 80% (purple), and in panel (b), critical supersaturations are shown as functions of dry particle surfactant mass fraction ($W_{p,SFT}$) for particle diameters of 40 and 100 nm. Calculations with rep1 are shown as solid lines, and the results of Prisle et al. (2010) from experiments and calculations using the detailed partitioning model (σ,p) are shown as points and dashed lines, respectively. Overall, very good agreement between critical supersaturations calculated using the simple organic representation and both experimental values and detailed model predictions are seen for particles with up to at least 50% by mass of surfactant, and for particles comprising C10Na, C12Na and SDS even up to at least 80% surfactant.

Surfactant strength, as defined in Eq. (4) above, for the C8Na–C12Na fatty acid salts and SDS increases in the order of increasing molar mass, $M_{C8Na} < M_{C10Na} < M_{C12Na} < M_{SDS}$ (Prisle et al., 2010, 2008, and references therein). The agreement of predictions using rep1 with both experiments and the detailed model increases with the surfactant strength, as expected; the stronger surfactants are relatively more partitioned to the droplet surface, yet the effect on droplet activation of the surface tension reduction attained evidently cannot overcome that of increased water activity due to bulk-depletion of surfactant solute (Prisle et al., 2010). As the strength of these surfactants increases, their surfactant properties are described still better by Eq. (11), yet still poorer by Eq. (16); however, the combined effect on surfactant CCN properties is dominated by the first, rather than the latter. For particles comprising the stronger surfactants C12Na and SDS, the agreement of rep1 with experiments and the detailed model is very good over the full range of surfactant–salt mixing ratios shown in Figs. 4a and 5a.

With the weaker surfactant C8Na, using the simple representation overpredicts critical supersaturations for particles with 80% surfactant. Likely, C8Na is not sufficiently surface active for the majority of these molecules to be effectively partitioned to the droplet surface at the concentrations attained for activating droplets formed on particles with this high surfactant dry mass fraction. In general, the simple organic representation is *not* expected to work for weak surfactants; these organics will only be partially partitioned to the solution surface and some effect of the resulting finite organic bulk concentrations on droplet water activity ($x_w^B < x_{w,s}^T$), and possibly even a slight surface tension reduction ($\sigma < \sigma_w$), may therefore be anticipated in activating droplets containing these molecules. This emphasizes that the simple representation proposed here is not intended to replace analytical solutions to the partitioning equilibrium derived from thermodynamic relations. The simple representation rather presents an alternative to such approaches with potential for application to complex aerosol systems, for which the properties required for analytical solutions are not yet available.

For increasing surfactant mass fractions in the dry particles, the simple organic representation eventually overpredicts critical supersaturations, as is clearly seen in Figs. 2b, 3b, 4b, and 5b. A number of surface active organics have been demonstrated in previous experimental and theoretical works to act as efficient CCN in single-component particles under atmospherically relevant conditions (Prisle et al., 2008; Sorjamaa et al., 2004). As dry particle surfactant mass fractions increase, critical supersaturations generally increase, and activating droplets become smaller and more concentrated. Eventually, the position of the partitioning equilibrium does leave some surfactant solute in the bulk at droplet activation, thus resulting in some reduction in droplet surface tension and/or water activity. For aerosol consisting purely of water soluble surfactant, some of this solute may likewise be expected to remain dissolved in the droplet bulk. These situations are innately not captured by the simple representation, effectively treating the organic as an insoluble but wettable core/surface; the simple organic representation is therefore not expected to be applicable to pure organic particles of water soluble surfactants. In the context of atmospheric modeling, however, such particle compositions

are unlikely to be representative of ambient aerosol, which are generally found to be mixtures of both organic and inorganic species (Murphy et al., 2006; O'Dowd et al., 2004). The surfactant-salt particles that are seen here to be well described by the simple organic representation cover the range of organic-inorganic mixing ratios typically seen in the atmosphere (Zhang et al., 2007).

The errors in predicted critical supersaturations (SS_c), relative to the experimental values (SS_c^{exp}) measured by Prisle et al. (2010),

$$SS_c \text{ relative error } = \frac{SS_c - SS_c^{exp}}{SS_c^{exp}}, \tag{18}$$

are shown in Fig. 6. Individual panels show results as functions of dry particle diameter (D_p) for particles comprising (a) C8Na, (b) C10Na, (c) C12Na, and (d) SDS. Open symbols correspond to predictions made with the detailed thermodynamic model (σ,p) and filled symbols are for predictions with the simple organic representation (rep1). Dry particle surfactant mass fractions are indicated by the symbol colors as 0% (blue), 20% (green), 50% (red), and 80% (purple).

Figure 6 emphasizes the results in Figs. 2, 3, 4, and 5, in terms of the performance of the simple organic representation, compared to the detailed thermodynamic model accounting for the partitioning equilibrium. The detailed model generally describes experimental observations better than the simple representation, as expected. Nevertheless, predictions of the latter are comparable to those of the detailed model, for all but the weakest of the four surfactants (C8Na), and dry particles with the very highest organic mass fractions (80%) shown. The applicability of the simple representation to surfactants with different strength and particles with increasing organic mass fraction needs to be investigated in more detail in future work. Currently, the availability of both laboratory data and detailed model predictions of CCN activity for mixed surfactant– salt particle systems is however still limited. Contrary to the detailed thermodynamic model, the simple organic representation presented here does not require composition and molecular properties of the organic particle fraction to be known; specifically, only

the magnitude and mass density of this organic fraction is required, both of which can be measured directly with available techniques. The simple representation is therefore promising for application to complex and realistic aerosol systems, such as the before-mentioned smog-chamber generated SOA, and ambient aerosol. Moreover, calculations using the simple representation are computationally much less demanding than the detailed partitioning model and should therefore be as applicable to cloud modeling as the analytical solutions presented by Topping (2010) and Raatikainen and Laaksonen (2010).

4   Conclusions

A simple representation for the cloud droplet activation properties of surface active organics is introduced and applied in Köhler predictions for mixed organic–inorganic aerosol particles. Results of these calculations are compared against laboratory measurements, as well as model predictions based on detailed thermodynamic relations, of the CCN activity for mixed surfactant–salt aerosols from the literature. The simple organic representation is seen to work well for particle composition ranges corresponding to those typically found in the atmosphere. As expected, the agreement with both experiments and detailed model predictions increases with surfactant strength. For all but the weakest surfactant and highest organic aerosol fractions, the simple representation closely follows the performance of the detailed thermodynamic model in capturing observed droplet activation for the studied particle mixtures. Contrary to the detailed model, the proposed simple organic representation does not require knowledge of either composition or composition-dependent molecular properties for the organic aerosol fraction and consequently has high potential for application to complex and realistic aerosols. The simple representation is not computationally demanding and therefore also has potential for implementation to atmospheric models accounting for cloud microphysics.

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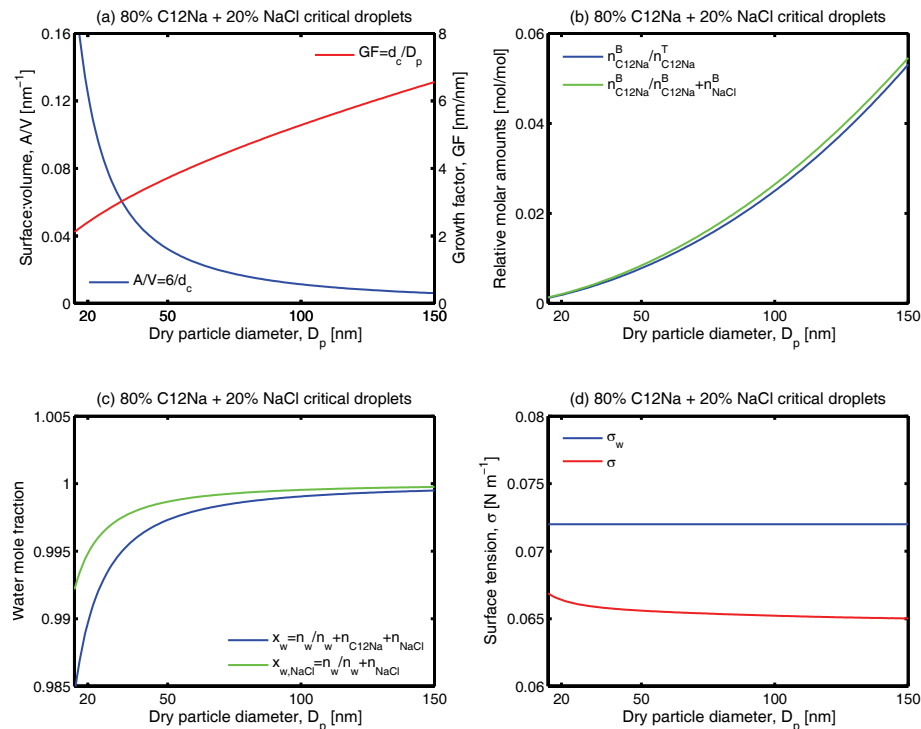
Fig. 1. Selected properties predicted at the point of droplet activation **(b)** molar fraction of surfactant left in the droplet bulk ($n_{C12Na}^{B}/n_{C12Na}^{T}$) mixed with sodium chloride (NaCl): **(a)** diameter growth factor (GF) and droplet surface-area-to-bulk-volume ratio (A/V), **(b)** molar fraction surfactant left in the droplet bulk ($n_{C12Na}^{B}/n_{C12Na}^{T}$) and molar fraction of total solute in the droplet bulk that is surfactant ($n_{C12Na}^{B}/[n_{C12Na}^{B}+n_{NaCl}^{B}]$), **(c)** bulk-phase water mole fraction (x_{w}^{B}) and water mole fraction with respect to only NaCl solute ($x_{w,NaCl}^{B}$), **(d)** droplet surface tension (σ), together with the surface tension of pure water (σ_{w}). Values are presented as functions of dry particle diameter (D_{p}) and have been adapted from Prisle et al. (2009).
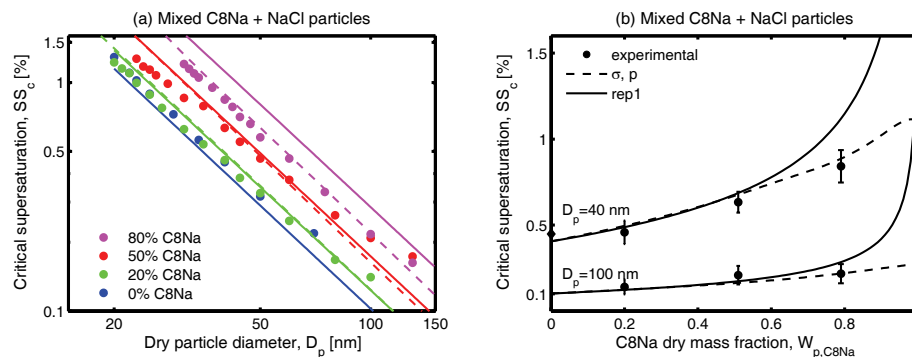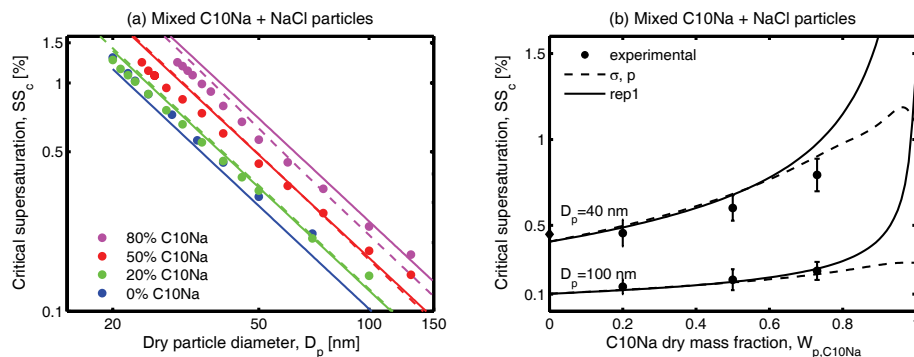
Fig. 2. Critical supersaturations (SS_c [%]) for particles comprising sodium octanoate (C8Na) mixed with sodium chloride (NaCl), as functions of **(a)** dry particle diameter (D_p [nm]), and **(b)** dry particle surfactant mass fraction ($W_{p,C8Na}$). Results are shown particles with selected dry surfactant mass fractions in panel (a), and for dry particle sizes of D_p=40 nm (upper curves and data points) and D_p=100 nm (lower curves and data points) in panel (b). In both figures, points are experimental values, dashed lines are calculated with the detailed thermodynamic model (σ,p), both adapted from Prisle et al. (2010), and solid lines are calculated with the simple organic representation (rep1).
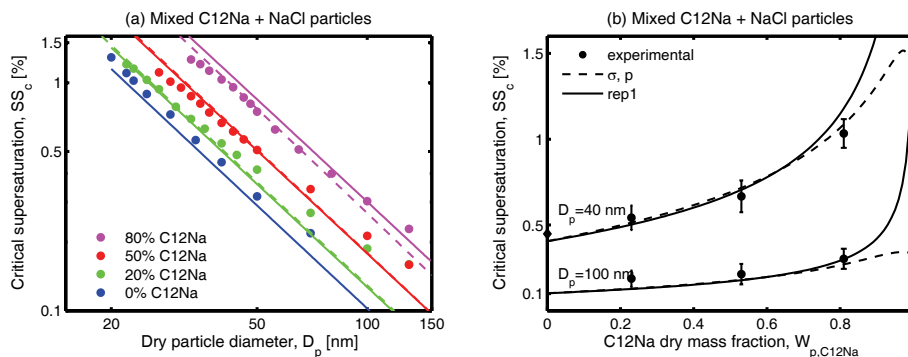
Fig. 3. Critical supersaturations (SS_c [%]) for particles comprising sodium decanoate (C10Na) mixed with sodium chloride (NaCl), as functions of **(a)** dry particle diameter (D_p [nm]), and **(b)** dry particle surfactant mass fraction ($W_{p,C10Na}$). Results are shown particles with selected dry surfactant mass fractions in panel (a), and for dry particle sizes of D_p=40 nm (upper curves and data points) and D_p=100 nm (lower curves and data points) in panel (b). In both figures, points are experimental values, dashed lines are calculated with the detailed thermodynamic model (σ,p), both adapted from Prisle et al. (2010), and solid lines are calculated with the simple organic representation (rep1).

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Fig. 4. Critical supersaturations (SS_c [%]) for particles comprising sodium dodecanoate (C12Na) mixed with sodium chloride (NaCl), as functions of **(a)** dry particle diameter (D_p [nm]), and **(b)** dry particle surfactant mass fraction ($W_{p,C12Na}$). Results are shown particles with selected dry surfactant mass fractions in panel (a), and for dry particle sizes of D_p=40 nm (upper curves and data points) and D_p=100 nm (lower curves and data points) in panel (b). In both figures, points are experimental values, dashed lines are calculated with the detailed thermodynamic model (σ,p), both adapted from Prisle et al. (2010), and solid lines are calculated with the simple organic representation (rep1).
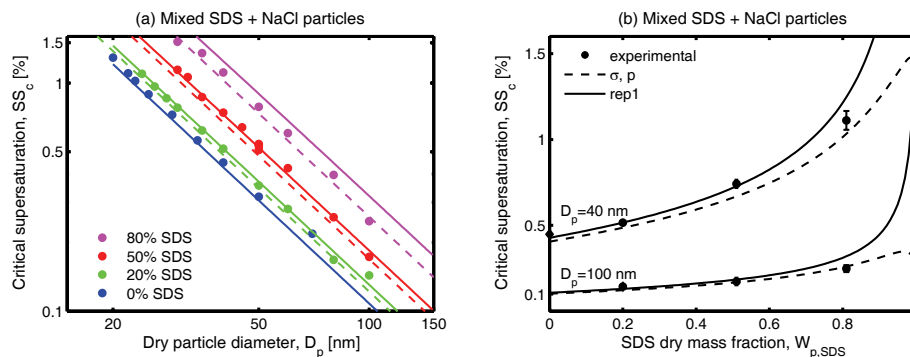
Fig. 5. Critical supersaturations (SS_c [%]) for particles comprising sodium dodecyl sulfate (SDS) mixed with sodium chloride (NaCl), as functions of **(a)** dry particle diameter (D_p [nm]), and **(b)** dry particle surfactant mass fraction ($W_{p,SDS}$). Results are shown particles with selected dry surfactant mass fractions in panel (a), and for dry particle sizes of D_p=40 nm (upper curves and data points) and D_p=100 nm (lower curves and data points) in panel (b). In both figures, points are experimental values, dashed lines are calculated with the detailed thermodynamic model (σ,p), both adapted from Prisle et al. (2010), and solid lines are calculated with the simple organic representation (rep1).

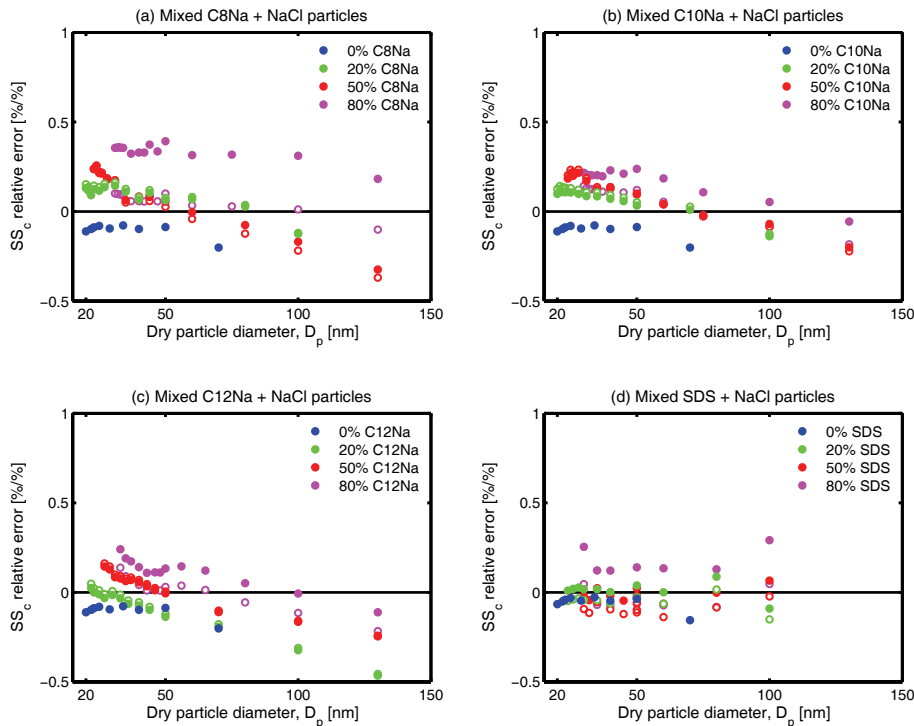**Fig. 6.** Relative errors in predicted critical supersaturations ($SS_c - SS_c^{exp}$)/SS_c^{exp} [%/%]) with the detailed thermodynamic model (σ,p, open symbols) and the simple organic representation (rep1, filled symbols) as functions of dry particle diameter (D_p [nm]) for particles comprising **(a)** sodium octanoate (C8Na), **(b)** sodium decanoate (C10Na), **(c)** sodium dodecanoate (C12Na), and **(d)** sodium dodecyl sulfate (SDS). Dry particle surfactant mass fractions are indicated by the color of symbols as 0% (blue), 20% (green), 50% (red), and 80% (purple). Results correspond to those shown in Figs. 2, 3, 4, and 5.

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