

# A simplified treatment of surfactant effects on cloud drop activation

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**Abstract.** Dissolved surface active species, or surfactants, have a tendency to partition to solution surface and thereby decrease solution surface tension. Activating cloud droplets have large surface-to-volume ratios, and the amount of surfactant molecules in them is limited. Therefore, unlike with macroscopic solutions, partitioning to the surface can effectively deplete the droplet interior of surfactant molecules.

Surfactant partitioning equilibrium for activating cloud droplets has so far been solved numerically from a group of non-linear equations containing the Gibbs adsorption equation coupled with a surface tension model and an optional activity coefficient model. This can be a problem when surfactant effects are examined by using large-scale cloud models. Namely, computing time increases significantly due to the partitioning calculations done in the lowest levels of nested iterations.

Our purpose is to reduce the group of non-linear equations to simple polynomial equations with well known analytical solutions. In order to do that, we describe surface tension lowering using the Szyskowski equation, and ignore all droplet solution non-idealities. It is assumed that there is only one surfactant exhibiting bulk-surface partitioning, but the number of non-surfactant solutes is unlimited. It is shown that the simplifications cause only minor errors to predicted bulk solution concentrations and cloud droplet activation. In addition, computing time is decreased at least by an order of magnitude when using the analytical solutions.

## 1 Introduction

The aerosol effect on cloud albedo and thereby on the radiation balance of the Earth constitutes the largest single scientific uncertainty in the assessment of the current radiative forcing (IPCC: Solomon et al., 2007). Among the reasons for the large uncertainty are various chemical effects (Charlson et al., 2001; Topping et al., 2007; Wex et al., 2008) such as surface tension reduction of activating cloud droplets. By preferentially partitioning to the droplet solution surface, surface active species can cause a clear decrease of the surface tension of aqueous solutions (Li et al., 1998; Sorjamaa et al., 2004). Decreased surface tension is often taken into account in aerosol and cloud modelling, but the effect of droplet size-dependent surface partitioning on solution concentrations is often ignored (e.g. Shulman et al., 1996; Facchini et al., 1999; Mircea et al., 2002; Broekhuizen et al., 2004). The reason for this is probably that the partitioning has no effect on bulk concentrations in large systems, such as laboratory samples from which the surface tensions are measured. However, the influence of partitioning on droplet bulk concentrations does become relevant for micron-sized or smaller droplets having large surface area to volume ratios (Laaksonen, 1993; Sorjamaa et al., 2004; Prisle et al., 2010).

The effect of surfactant partitioning on cloud droplet activation has been studied both experimentally using CCN counters and theoretically relying on the Köhler theory (Li et al., 1998; Sorjamaa et al., 2004; Prisle et al., 2008, 2010). Briefly, three common modelling approaches have been used: (1) accounting for surface tension decrease and for the effect of partitioning on bulk solution concentrations, (2) accounting for surface tension decrease but not for surfactant partitioning, and (3) ignoring both surface tension and partitioning effects. Models accounting for surface



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tension decrease but not for surfactant partitioning are predicting clearly too high cloud forming activity. On the other hand, predictions which either account for or ignore both the surface tension and partitioning effects are generally quite similar and also in reasonable agreement with experimental measurements of critical supersaturations. However, even if the predicted critical supersaturations are similar, predicted critical droplet sizes and droplet bulk solution concentrations in general are clearly different. These affect solution thermodynamics (e.g. solubility), vapour-liquid equilibrium, and droplet growth dynamics (Kokkola et al., 2006).

A special problem in the surface partitioning calculations is that droplet concentrations are determined by numerically solving a set of non-linear equations including the Gibbs adsorption equation coupled with a surface tension model and an optional activity coefficient model, which is often too time-consuming in large-scale model calculations. Our purpose is to reduce these partitioning equations to simple polynomial equations with well known analytical solutions, which are more practical for large-scale applications. Some approximations and limitations are needed for the polynomial equations. For example, droplet solution non-idealities are ignored and it is assumed that there is only one surfactant exhibiting bulk-surface partitioning. The validity of the simplified solutions is confirmed by comparing predictions with those of iteratively solving the partitioning equilibrium.

## 2 Theory

Surfactant partitioning effects are greatest with small and dilute droplets. With very large droplets, accounting for surfactant mass balance has a minor effect on the bulk concentration as the concentration change due to partitioning to surface is roughly proportional to the inverse of radius. With most surfactants, the strongest surface tension decrease as a function of concentration (which influences the partitioning) takes place at very low concentrations. Both conditions, i.e. small droplet size and low concentrations, are usually fulfilled at the cloud droplet activation.

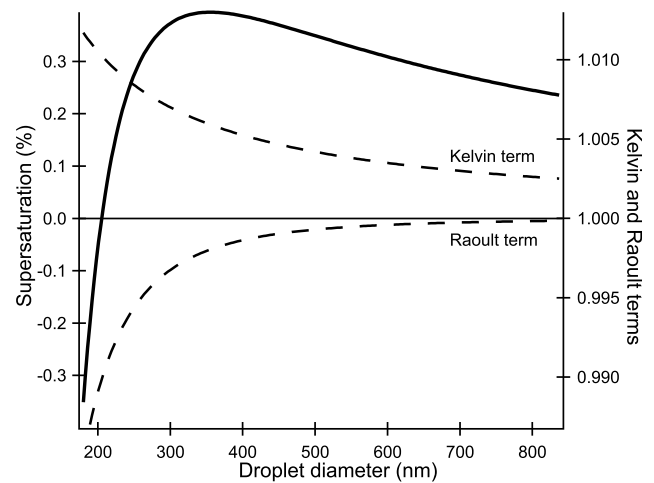
Here the term bulk refers to droplet's homogeneous liquid interior, which is the phase defining droplet properties such as equilibrium vapour pressures. Droplet surface is assumed to be in thermodynamic equilibrium with the bulk solution.

### 2.1 Cloud droplet activation

The equilibrium saturation ratio of water ( $S$ ) over droplet surface can be calculated from the well known Köhler equation (Köhler, 1936):

$$S = \gamma_w x_w \exp\left(\frac{4v_w \sigma}{RT D_{aq}}\right) \quad (1)$$

The Raoult term gives water activity as a product of activity



**Fig. 1.** Water supersaturation as a function of droplet size for a 40 nm dry particle. Kelvin and Raoult terms are shown with the dashed line in the right hand side scale.

coefficient  $\gamma_w$  and mole fraction  $x_w$ . Increased vapour pressure due to droplet curvature is taken into account by the exponential Kelvin term. In addition to partial molar volume of water  $v_w$  ( $\text{m}^3 \text{mol}^{-1}$ ) (which we approximate by the molar volume of pure water), ideal gas constant  $R$  ( $\text{J}(\text{mol K})^{-1}$ ) and temperature  $T$  (K), the Kelvin term depends on droplet solution surface tension  $\sigma$  ( $\text{N m}^{-1}$ ) and droplet diameter  $D_{aq}$  (m).

Total numbers of moles of solutes can be calculated from the known dry particle composition (dry size  $D_{dry}$  and e.g. dry particle volume fractions of solutes). Assuming volume additivity ( $V_{dry} + V_w = V_{aq}$ ), the total (superscript T) number of moles of water can be calculated from

$$n_w^T = \frac{\pi}{6} (D_{aq}^3 - D_{dry}^3) / v_w. \quad (2)$$

When suitable water activity coefficient and surface tension parameterizations are available, total numbers of moles of droplet water and solutes can be used in calculating the equilibrium saturation ratio  $S$ . An example of a Köhler curve showing equilibrium supersaturation  $SS = (S - 1) \cdot 100\%$  as a function of droplet size, is shown in Fig. 1.

When an initially dry particle is exposed to water vapour and relative humidity (RH) is increased above the deliquescence point, a droplet is formed. When RH is further increased, the droplet grows by condensation of water vapour until equilibrium given by Eq. (1) is reached, thus the droplet equilibrium growth follows the Köhler curve. However, when water supersaturation exceeds the maximum value of the Köhler curve, condensation of water can not lead to equilibrium any more, thus the droplet grows to cloud droplet sizes. Equilibrium theory is no longer valid for this non-equilibrium growth, which depends on the availability of water vapour. As the non-equilibrium growth is initiated at the maximum of the Köhler curve, the droplet

size and supersaturation corresponding to the maximum are called critical droplet diameter and supersaturation needed for cloud droplet formation.

As described above, the total numbers of moles of droplet water and solutes can be calculated from the given dry particle composition and droplet size. These can be used in calculating water activity and solution surface tension needed in the Köhler equation (Eq. 1). However, some chemical and physical effects such as limited solubility and partial dissociation can have an effect on droplet bulk liquid phase concentrations. Of course, if e.g. some fraction of a solute is undissolved, bulk concentrations used in calculating water activity and surface tension should be determined from the dissolved fraction. Analogously, surfactant bulk-surface partitioning changes bulk solution concentrations. Here we are ignoring these other effects and focus on the surfactant partitioning.

## 2.2 Bulk-surface partitioning of surfactants

The effect that the partitioning to a surface layer has on bulk solution concentrations depends greatly on the system size. For example, saturation surface excess ( $\Gamma^\infty$ ) values, giving the maximum number of surfactant molecules per unit surface area, are on the order of  $1 \mu\text{mol m}^{-2}$  (e.g. Tuckermann, 2007). For  $1 \mu\text{m}$  and  $1 \text{mm}$  droplets with  $1 \text{mM}$  surfactant bulk concentration, the saturation surface to bulk mole ratios are then roughly 6 and 0.006, respectively. The partitioning is thus not important for  $1 \text{mm}$  droplets as it has a negligible effect on the bulk concentration. However, in the case of  $1 \mu\text{m}$  and smaller droplets, the majority of the surfactant molecules can partition to surface, causing the bulk concentration to decrease strongly.

Surface and bulk solution concentrations can be solved from the Gibbs adsorption isotherm (Gibbs, 1928):

$$\sum n_i^S d \ln(\gamma_i^B c_i^B) + \frac{A}{RT} d\sigma^B = 0 \quad (3)$$

where  $n_i^S$  (mol) is surface (excess) concentration,  $\gamma_i^B$  is activity coefficient and  $c_i^B$  is concentration of liquid phase component  $i$ ,  $A$  ( $\text{m}^2$ ) is droplet surface area, and  $\sigma^B$  ( $\text{N m}^{-1}$ ) is droplet surface tension. Mole fractions are commonly used, but any concentration scale is possible especially when activity coefficients are included. With a reasonable approximation, the simplified equations can be derived without fixing the concentration scale even if the activity coefficients are ignored. Superscripts B and S refer to bulk and surface solutions, respectively, and subscript  $i$  includes all liquid phase species such as molecular solutes, ions and water. We assume a closed system, thus  $n_i^T = n_i^B + n_i^S$ . In addition, the ions of an electrolyte can not partition independently as the phases can not have a net charge.

In order to simplify the calculation of the surface concentrations, we are limited to single surfactant solutions. This is a common limitation also for the numerical methods.

Even if there is only one surfactant in the droplet, water and non-surfactant solutes may have non-zero surface concentrations as long as these depend on that of the surfactant. Commonly, only the surfactant is expected to partition, i.e.  $n_i^S = 0$  for other than surfactant species. Alternatively, it can be assumed that the partitioning of the surfactant (subscript s) is compensated by depletion of water from the surface, i.e. volume of the surface  $V^S = n_w^S v_w + n_s^S v_s = 0$ , which is in agreement with the definition of flat surface in the adsorption equation. In the case of multicomponent solutions, water and non-surfactant solutes (subscript  $j$ ) can be assumed to behave as a pseudobinary solution so that the equalities  $n_w^T/n_w^B = n_j^T/n_j^B$  and  $V^S = \sum n_i^S v_i = 0$ , where  $i$  includes all droplet species, connect all concentrations to that of the surfactant (Sorjamaa et al., 2004; Prisle et al., 2010).

With any of the three above mentioned assumptions for  $n_i^S$ , the adsorption equation contains only one unknown and it can be solved numerically. Unfortunately, the numerical solution may be too slow for large-scale models, where bulk concentrations are needed in the lowest levels of nested iterations. Our purpose is to derive, making reasonable approximations, an analytical solution for Eq. (3), and to show that the results do not differ significantly from the numerical solution of Eq. (3).

### 2.2.1 Analytical solution for surfactant partitioning

Some approximations and limitations are needed to simplify the adsorption equation (Eq. 3) so that the analytical solution can be found. It is clear that activity coefficients must be ignored and the derivation will be based on a chosen surface tension model. Furthermore, there can be only one independent variable, which limits the number of species exhibiting bulk-surface partitioning to one. The approximations are detailed below.

When solving Eq. (3) analytically, it is not only the number of surfactants but especially the number of species having non-zero surface concentrations that needs to be reduced. Therefore, the first approximation is that only the surfactant exhibits bulk-surface partitioning, i.e.  $n_i^S = 0$  for all other species. Because surface depletion of water and non-surfactant solutes is not allowed, the surface volume defined as  $V^S = \sum n_i^S v_i$  is not generally zero. When this is the case, it can be shown that surface tension depends on droplet size and bulk solution volume differs from the given droplet volume (Laaksonen et al., 1999). However, it will be shown below that the non-zero surface volume has a negligible effect on predictions of cloud droplet activation.

The second approximation we make is that activity coefficients are set to unity or alternatively considered as constants, which means that the activity coefficients vanish from the adsorption equation. This approximation is needed, because there are no simple and generally valid activity coefficient equations for surfactant solutions. According to

the definition of the infinite dilution reference state, both solute and water activity coefficients approach unity and can be treated as constants at the infinite dilution. Because activating droplets are very dilute, unit or constant activity coefficients is a fair approximation. It will be shown that activity coefficients have only a small effect on surfactant partitioning.

Our third approximation is that bulk solution concentrations are linearly dependent on the corresponding numbers of moles:  $c_i^B = n_i^B/c_i^0$ , where  $c_i^0$  is a constant based on total numbers of moles of the droplet species. For example, it is total mass of droplet water (kg), volume of the liquid phase (L) and total number of moles of liquid phase species for molality, molarity and mole fraction scales, respectively. The approximation is usually very good for dilute solutions, because the value of  $c_i^0$  depends mainly on the total number of moles of water. In fact,  $c^0$  is actually constant for the molality and molarity scales. In addition to simplifying the concentration derivative terms in the adsorption equation, this approximation makes the result largely independent of the concentration scale used in the surface tension model.

There are a number of functional forms available in the literature that describes the surface tension lowering of aqueous surfactant solutions. We apply the well known Szyskowski equation (Szyskowski, 1908):

$$\sigma^B = \sigma_w - R T \Gamma^\infty \ln\left(1 + \frac{c^B}{\beta}\right) \quad (4)$$

where  $\sigma_w$  is surface tension of pure water, and saturation surface excess  $\Gamma^\infty$  ( $\text{mol m}^{-2}$ ) and  $\beta$  (same unit with the surfactant bulk concentration  $c^B$ ) are experimentally determined parameters. Note that we have dropped the subscript from the surfactant concentration, because it is the only species in this equation. Common concentration scales include molarity ( $\text{mol L}^{-1}$  or just M), molality ( $\text{mol kg}^{-1}$ ) as well as dimensionless mole and mass fractions. With the above mentioned approximation,  $c^B = n^B/c^0$ , surface tension gradient can be calculated as:

$$\frac{d\sigma^B}{d\ln n^B} = \frac{d\sigma^B}{d\ln c^B} = -\frac{R T \Gamma^\infty c^B}{\beta + c^B} = -\frac{R T \Gamma^\infty n^B}{\beta c^0 + n^B} \quad (5)$$

The last form of the equation is the most useful one, because our goal is to solve the bulk number of moles of surfactant ( $n^B$ ).

With the three approximations described above, the sum term of the adsorption equation (Eq. 3) can be simplified greatly. When assuming constant or unit activity coefficients, we have  $d\ln(\gamma_i^B c_i^B) = d\ln(c_i^B)$ . This can be further simplified with the the third approximation:  $d\ln(c_i^B) = d\ln(n_i^B)$ . At this point the sum term of the adsorption equation is:

$$\sum n_i^S d\ln(\gamma_i^B c_i^B) = \sum n_i^S d\ln(n_i^B) \quad (6)$$

Because there is only one surfactant with a non-zero surface concentration, the subscript  $i$  includes either ions resulting from the dissociation of the surfactant or just the molecular surfactant. In the case of dissociating surfactant, ion concentrations at the surface are obtained just by multiplying concentration of the undissociated species by the dissociation factors  $\nu_i$ , which give the numbers of ions (cations and anions) from the dissociation. When assuming unit dissociation factors for non-dissociating surfactants, surface concentrations can be expressed in general form as  $n_i^S = \nu_i n^S$  or  $n_i^S = \nu_i (n^T - n^B)$  in the case of a closed system. The sum term is now:

$$\sum n_i^S d\ln(\gamma_i^B c_i^B) = (n^T - n^B) \sum \nu_i d\ln(n_i^B) \quad (7)$$

Here and from now on, any concentration including the numbers of moles of species expressed without a subscript refer to the undissociated surfactant salt or molecule; the subscripted ones are for dissolved surfactant species including either molecules or ions. It should be noted that non-surfactant solutes can have a contribution to the  $n_i^B$  above. This is the case when the non-surfactant solutes and the surfactant have a common ion. When the derivatives in the adsorption equation are taken with respect to  $\ln(n^B)$ , the surface tension term is given in Eq. (5). With the approximations above, we have:

$$(n^T - n^B) \frac{\sum \nu_i d\ln(n_i^B)}{d\ln n^B} = \frac{A \Gamma^\infty n^B}{\beta c^0 + n^B} \quad (8)$$

As mentioned above, subscript  $i$  refers to either undissociated surfactant or surfactant cations and anions resulting from dissociation. The numbers of moles without a subscript refer to the undissociated surfactant salt or molecule. In the case of molecular surfactants and in the absence of common ions, the solution is simple. Therefore, cases with and without common ions are considered separately below.

*Surfactant without common ions.* In the absence of common ions, the activity gradient term  $\sum \nu_i d\ln(n_i^B)$  is just  $\nu d\ln(n^B)$ , where  $\nu = \nu_+ + \nu_-$  is the total number of cations ( $\nu_+$ ) and anions ( $\nu_-$ ) resulting from the surfactant dissociation. If the surfactant is not dissociating,  $\nu$  is just one. Then Eq. (8) simplifies to

$$\nu (n^T - n^B) = \frac{A \Gamma^\infty n^B}{\beta c^0 + n^B} \quad (9)$$

This leads to a quadratic equation with number of moles of surfactant in bulk solution ( $n^B$ ) as the unknown:

$$n^T \beta c^0 + (n^T - \beta c^0 - A \Gamma^\infty / \nu) n^B - (n^B)^2 = 0 \quad (10)$$

The quadratic equation has one positive and one negative root at least when  $\beta$  is positive. Because bulk solution concentrations are always non-negative, the positive root is

chosen:

$$n^B = \frac{n^T - \beta c^0 - A\Gamma^\infty / \nu + \sqrt{(n^T - \beta c^0 - A\Gamma^\infty / \nu)^2 + 4n^T \beta c^0}}{2}. \quad (11)$$

From the modelling point of view, this single-line solution for the partitioning equilibrium is very efficient and also reliable as negative or complex values are not possible for realistic input parameters. In addition, there are no obvious risks for having divide by zero errors.

*Surfactant with common ions.* Common ions, e.g.  $\text{Na}^+$  in aqueous sodium dodecyl sulfate (SDS)-NaCl solution, have an effect on the activity gradient term. For simplicity, we assume that the surfactant is composed of  $\nu_+$  cations and  $\nu_-$  anions, and the numbers of moles of common ions from the other solutes are  $n^+$  and  $n^-$  for cations and anions, respectively. Of course, there can not be both common cations and anions, which would be equal to the dissociated surfactant, so either  $n^+$  or  $n^-$  is zero. Then the activity term is

$$\sum v_i d \ln(n_i^B) = \nu_+ d \ln(\nu_+ n^B + n^+) + \nu_- d \ln(\nu_- n^B + n^-) \quad (12)$$

The gradient is

$$\frac{\sum v_i d \ln(n_i^B)}{d \ln n^B} = \frac{\nu n^B + k_2}{n^B + k_1} \quad (13)$$

where common ion terms are denoted by  $k_1$  and  $k_2$ :

$$k_1 = n^- / \nu_- + n^+ / \nu_+ \quad (14)$$

$$k_2 = \nu_+ / \nu_- n^- + \nu_- / \nu_+ n^+ \quad (15)$$

For example, in the case of aqueous SDS-NaCl ( $\nu_+ = \nu_- = 1$ ,  $\nu = 2$ ,  $n^- = 0$ ,  $n^+ = n_{\text{NaCl}}$ )  $k_1 = k_2 = n_{\text{NaCl}}$ . Note that superscripts T or B are not used for the non-surfactant solutes, because their bulk and total concentrations are equal in the absence of partitioning.

By combining Eqs. (8) and (13) we have

$$(n^T - n^B) \frac{\nu n^B + k_2}{n^B + k_1} = \frac{A\Gamma^\infty n^B}{\beta c^0 + n^B} \quad (16)$$

This can be simplified to a cubic polynomial equation:

$$n^T k_2 \beta c^0 + (n^T k_2 + (\nu n^T - k_2) \beta c^0 - k_1 A\Gamma^\infty) n^B + (\nu n^T - k_2 - \nu \beta c^0 - A\Gamma^\infty) (n^B)^2 - \nu (n^B)^3 = 0 \quad (17)$$

There are several well known analytical solutions for cubic polynomial equations (see e.g. Barbeau, 2003). However, unlike in the case of quadratic equation, there is no single closed-form expression that would give the correct root in all possible cases. Even if the analytical solutions exists (not shown here due to the length of the equations), it is

sometimes easier to use numerical methods for finding the correct root. It will be shown later that cubic root finding algorithms can be computationally effective and robust. Regardless of the method for solving the cubic equation, we will refer to the solutions of the quadratic (Eq. 11) and cubic (Eq. 17) equations as analytical solutions for the partitioning equilibrium.

### 3 Model comparison

Here we compare predictions based on the iterative and analytical solutions of the adsorption equation. Clearly, approximations (only the surfactant exhibits bulk-surface partitioning, ideal droplet solutions, and concentrations can be expressed as  $c_i^B = n_i^B / c_i^0$ , where  $c_i^0$  is a constant) needed for the simplified polynomial equations should not have major effects on the results. In addition, the equations should be valid for slightly different Szyskowski surface tension parameterizations, e.g. with different concentration scales. These approximations are not needed and it is possible to use any kind of available surface tension and activity coefficient parameterizations when the adsorption equation (Eq. 3) is solved numerically. The iterative model, described in Appendix A, was designed so that selected approximations can be applied.

We use models based on the *analytical* and *iterative* solutions of the adsorption equation to predict the critical supersaturation, which is the most important parameter coming out of the Köhler theory, and the only directly detectable parameter in CCN experiments. In practise, the analytical and iterative methods are used for solving the bulk solution concentrations as a part of a main function containing the search algorithm for finding the critical droplet size and supersaturation. A series of test calculations with different mixtures (different number of solutes, with and without common ions) and Szyskowski surface tension parameters showed that when the common ions are ignored or absent, model predictions are practically indistinguishable. Also, the test calculations showed that the differences between model predictions are only weakly dependent on the Szyskowski parameters or the mixture. Therefore, the calculations shown here can be considered as an example of typical differences between the analytical and iterative models. For the calculations, particles are composed of sodium dodecyl sulfate (SDS) and sodium chloride (NaCl), which means that there is a common ion. Because Eq. (11) is not valid for this case, it would be unfair to include it in the comparison. However, it will be included in the comparison of the computing times.

The SDS-NaCl mixture was chosen due to the availability of experimental surface tension data and well known chemical and physical properties (Sorjamaa et al., 2004; Prisle et al., 2010). The surface tension of aqueous SDS-NaCl solution can be described with the Szyskowski

equation (Eq. 4) by using the following parameters from Prisle et al. (2010):  $RT\Gamma^\infty = 13.90 \times 10^{-3} \text{ N m}^{-1}$  and  $\beta = (9.273 \times 10^{-6} \text{ M}^2)/(c_{\text{NaCl}} + 9.733 \times 10^{-3} \text{ M})$ . In addition, the effect of salt on water-NaCl solution surface tension was taken into account by assuming linear dependence on salt concentration ( $c_{\text{NaCl}}$ ) with the slope of  $1.61 \times 10^{-3} \text{ N m}^{-1} \text{ M}^{-1}$  (Prisle et al., 2010; Vanhanen et al., 2008). Note that parameter  $\beta$  depends explicitly on salt concentration, but this is not a problem as it is independent of surfactant concentration. In addition to explicitly accounting for the salt effect on surface tension, a simple parameterization based on the SDS only is used ( $RT\Gamma^\infty = 13.90 \times 10^{-3} \text{ N m}^{-1}$  and  $\beta = 9.527 \times 10^{-4} \text{ M}$ ).

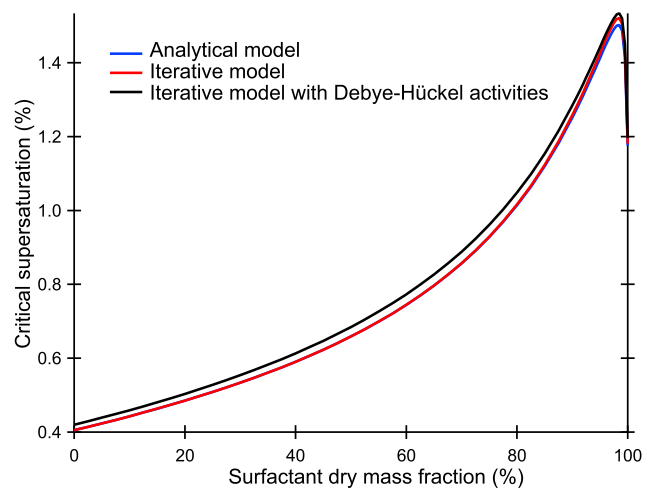
### 3.1 Approximations needed for the polynomial equations

In addition to some obvious considerations (e.g.  $n^T = n^B + n^S$ ), some clear approximations had to be made:

- *Only the surfactant partitions.* This is a fair approximation. Water and salt should have slightly increased bulk concentrations, but their relative concentration would not be changed.
- *Constant/unit activity coefficients.* This approximation had to be done, because activity coefficients are complex functions of solution bulk concentrations.
- *Bulk solution concentration of component  $i$  ( $c_i^B$  in any concentration scale) is directly proportional to the number of moles of the component ( $n_i^B$ ), i.e.  $d\ln(c_i^B) = d\ln(n_i^B)$ .* This depends on the concentration scale, but generally it is a good approximation for dilute droplets.

In the iterative model (Appendix A) it is possible to allow partitioning for all species. Bulk solution concentrations are then connected to that of the surfactant by fixing surface volume to zero ( $\sum n_i^S v_i = 0$ ) and by the pseudobinary approximation ( $n_w^T/n_w^B = n_j^T/n_j^B$ , when  $j$  is not surfactant). The alternative for this is to allow partitioning for the surfactant and water so that surface volume is again zero. The third case is the same as in the analytical solutions i.e. only the surfactant partitions. Activity coefficients can be either calculated from the Debye-Hückel model (Debye and Hückel, 1923; Clegg and Pitzer, 1992) or set to unity. Approximation  $d\ln(c_i^B) = d\ln(n_i^B)$  is not needed for the iterative model, because activity gradients (based on mole fractions) are calculated numerically.

Approximations of the polynomial equations were tested by comparing predictions of the analytical model with those of the iterative model with selected combinations of the approximations (number of species exhibiting bulk-surface partitioning, with and without activity coefficients,



**Fig. 2.** Critical supersaturation for 40 nm SDS-NaCl particles as a function of dry particle surfactant mass fraction. Model predictions are made with the analytical model and iterative model with and without activity coefficients.

and with and without the approximation about linearity of the concentrations). The calculations showed that when activity coefficients are set to unity, predictions for SDS-NaCl particles are practically equal. This indicates that the approximations  $d\ln(c_i^B) = d\ln(n_i^B)$  and zero surface excess for other than the surfactant have negligible effect on model predictions. When Debye-Hückel activities were used in the iterative model, slightly higher critical supersaturations were predicted. However, the main reason for the differences is the water activity coefficient in the Raoult term of the Köhler equation (Eq. 1). The differences in the surfactant bulk concentrations are as small as in the case without activity coefficients. This shows that activity coefficients are not important for the partitioning equilibrium. Figure 2 shows predictions of the analytical model as well as those of the iterative model with and without Debye-Hückel activity coefficients. Model predictions without activity coefficients are practically indistinguishable.

We do not know if the Debye-Hückel model is accurate for the current surfactant-salt mixture, but the effect of non-idealities is not the focus of this paper. It is possible that there are mixtures where unit activity coefficients lead to significant prediction errors. This is also a quite common uncertainty in modelling, because activity coefficients are rarely available for multicomponent mixtures. For simplicity and because of the fact that activity coefficients are much more important for the Raoult term than for the partitioning equilibrium, we use unit activity coefficients in the following calculations.



### 3.2 Effect of surface tension parameterization

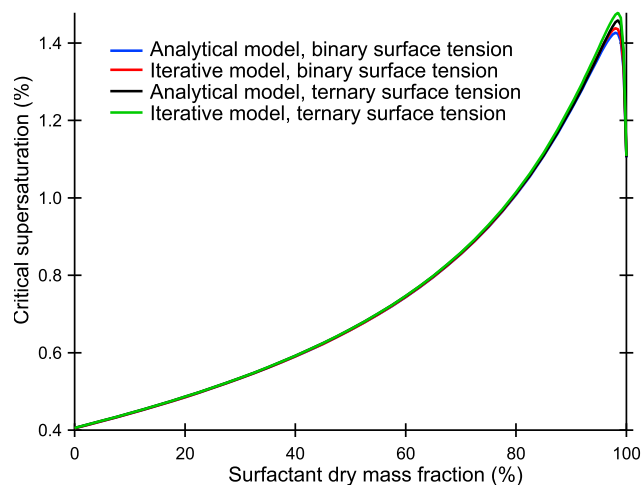
The goodness of the  $d\ln(c_i^B) = d\ln(n_i^B)$  approximation depends somewhat on concentration scale of the surface tension parameterization and if other solutes are accounted for or not. Figure 3 shows predictions from the analytical and iterative models with binary and ternary surface tension fits described in Sect. 3. Again, model predictions are practically equal. Because binary and ternary fits give different surface tensions for other than the pure surfactant case, different model predictions can be expected. This is not seen, so the effect of salt on solution surface tension can be ignored at least in this case. A likely reason is that due to the extensive surfactant partitioning and dilute droplets, surface tension of the critical droplet is always close to that of pure water. In addition, the surface tension gradient, which is important for partitioning equilibrium, is only weakly dependent on salt concentration.

The effect of concentration scale was tested by doing calculations with different binary surface tension fits based on molality, molarity and mole fraction scales. It was seen that predictions from the iterative and analytical models were practically equal (not shown). We can therefore conclude that the analytical solutions are valid for various Szyskowski equation concentration scales.

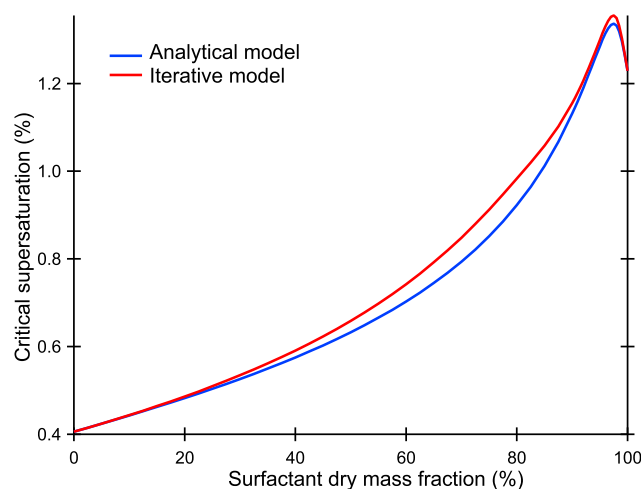
It is possible that concentration dependent Szyskowski surface tension parameters do not fulfil the condition needed for the analytical solution, i.e. being independent of the surfactant bulk concentration. From several possible cases, we choose one in which the Szyskowski parameters depend explicitly on surfactant concentration. The Szyskowski parameters given in Prisle et al. (2010) depend on solute dry mass fraction, which of course changes due to surfactant partitioning. Model calculations based on sodium decanoate-NaCl surface tension parameterization (Prisle et al., 2010) are shown in Fig. 4. Again, model predictions are quite similar, but this finding is not generally valid, because there are numerous expressions for concentration dependent Szyskowski parameters and the outcome depends on the specific case. It seems that in this case NaCl just has quite small effect on surface tension slopes  $\frac{d\sigma^B}{d\ln n^B}$  in Eq. (5), which is important for partitioning.

### 3.3 Computation times

The simplified partitioning expressions are especially suitable for model calculations when short computation times are required. In the calculations above, where we have shown that the approximations needed for the simplified expressions are very reasonable, roughly an order of magnitude difference in computing times was observed. However, these models contain several other operations that may be affecting the computation times. Therefore, the actual comparison of computation times is done by solving the adsorption equation alone both iteratively and with the



**Fig. 3.** Critical supersaturation for 40 nm SDS-NaCl particles as a function of dry particle surfactant mass fraction. Model predictions are made with the analytical and iterative models with both binary and ternary surface tension parameterizations.



**Fig. 4.** Critical supersaturation for 40 nm SDS-NaCl particles as a function of dry particle surfactant mass fraction. Model predictions are made with the analytical and iterative models with sodium decanoate-NaCl surface tension parameterization (Prisle et al., 2010).

analytical expressions. Four modelling approaches were considered: (a) analytical solution of the quadratic (Eq. 10) and (b) cubic (Eq. 17) equations, (c) numerical solution of the cubic equation (Eq. 17), and (d) iterative solution of the adsorption equation (Eq. 3). Matlab<sup>®</sup> function *roots* was the numerical method for finding the roots of the cubic equation. For the iterative method, adsorption equation was first greatly simplified by using the same assumptions with the simplified equations. The solution was found by using Matlab<sup>®</sup> function *fzero*. The analytical solution of the cubic equation was based on the Cardan's method (Barbeau, 2003).

The physical properties of the SDS-NaCl system were again chosen for the calculations. With the exception of the quadratic equation, the common ion effect was properly accounted for. Dry particle diameter (40 nm) and composition (80% SDS, 20% NaCl) were fixed, but both droplet diameter (220–2000 nm) and the Szyskowski parameters ( $\beta$ :  $10^{-4} - 1 \text{ mol L}^{-1}$ ,  $\Gamma^\infty$ :  $10^{-7} - 10^{-4} \text{ mol m}^{-2}$ ) were varied. The effect of NaCl on solution surface tension was ignored. Bulk numbers of moles were calculated 8000 times with a standard laptop PC using the Matlab<sup>®</sup> 6.1 program. The computation times are:

- 0.3 s analytical solution of the quadratic equation,
- 0.9 s analytical solution of the cubic equation,
- 1.5 s numerical solution of the cubic equation,
- 19.6 s iterative solution of the adsorption equation.

Obviously, the shortest computing times are seen when bulk concentrations are calculated from the single-line solution of the quadratic equation. There is a small difference in computing times related to the cubic equation. The analytical solution is about 40% faster here, but the iterative method can be optimized for finding the correct root. In any case, it is clear that the computing time is roughly an order of magnitude longer when surfactant bulk concentrations are solved directly from the adsorption equation. The difference is actually even larger, but in practice it is possible to use specialized algorithms and have better initial values. Therefore, an order of magnitude difference is a fair minimum estimate.

These calculations are for one mixture only, but computing times depend very little on input parameters such as dry particle and droplet sizes, dry particle composition, Szyskowski parameters, temperature and number of other solutes with the exception of the cases with and without common ions. A few additional iterations maybe needed for more difficult cases, but these are not important for the total time. The analytical expressions are even less dependent on the inputs. For example, the time for finding the root of the quadratic equation is totally independent of the values of the polynomial coefficients.

An additional interesting finding from the calculations is that both of the simplified approximations are very reliable for a wide range of solution concentrations and Szyskowski parameter values. All calculated surfactant bulk numbers of moles were between zero and  $n^T$ . In addition, with the exception of the quadratic equation not accounting for the common ion effect, predictions were practically identical. This was expected, because the same assumptions were applied also for the iterative model.

## 4 Conclusions

By making a few approximations, the Gibbs adsorption equation coupled with the Szyskowski surface tension model was reduced to cubic and quadratic polynomial equations for mixtures with and without common ions, respectively. These polynomial equations have well known analytical solutions, which can be used in solving the droplet bulk solution concentrations that account for surfactant bulk-surface partitioning. In addition to the common modelling approximations (e.g. closed system, volume additivity and only single surfactant), we have assumed that only the surfactant exhibits bulk-surface partitioning, activity coefficients can be set to unity, and solution concentrations in any reasonable scale are proportional to the total numbers of moles ( $c_i = \text{constant} \times n_i$ ). Comparison of predictions from the analytical solution and from numerical solution of the original set of equations including the Gibbs adsorption equation coupled with the surface tension model and an optional activity coefficient model showed that the approximations have minimal effects on the predicted bulk solution concentrations. Therefore, models based on the analytical solutions predict critical droplet size, supersaturation and composition accurately. Furthermore, the analytical method is robust, meaning that a solution is always found. It should be stressed that the new equations rely on the Szyskowski equation, so that if for some aqueous-surfactant system the surface tension reduction is given by some other equation, the Szyskowski parameters need to be determined first by a fitting procedure.

Analytical solutions are most useful for large-scale models where cloud microphysics is explicitly accounted for. As bulk concentrations are needed at low-level functions, computation time of the partitioning equilibrium is crucial for total computation time. For example, when calculating critical droplet size (first level iteration) for droplets containing partially soluble solutes (second level iteration), partitioning calculations are in the third level. Use of the new equations reduces the computer time needed for the droplet concentration calculations roughly by an order of magnitude and even more in the absence of common ions.

Current analytical solution for the case without common ions is quite similar to the solution presented in Topping (2010). Although both solutions are based on simultaneous independent work, the assumptions are practically equal. The main difference between the derivations is that the solution presented by Topping (2010) is based on mole fraction scale, but the concentration scale is not fixed in the current solutions. Topping does not consider common ions, but by ignoring surfactant-surfactant interactions the equations are given for mixed surfactant solutions. The result, however, is that the mixed surfactant case is reduced to separate single surfactant cases. With the same approximation, our equations are also valid for mixed



surfactant cases. It is not clear if this approximation is generally valid, so further studies are definitely needed for more complex systems.

Even if the analytical solutions are very accurate in predicting bulk solution concentrations, the approximations may not be valid for predicting equilibrium saturation ratios. For example, as seen in the calculations, water activity coefficient in the Raoult term can be important for the equilibrium saturation ratio even if it can be ignored from the adsorption equation. This is another important question for future studies.

## Appendix A

### Iterative model for single surfactant solutions

The number of independent variables in the adsorption equation is decreased to one by making two assumptions (Sorjamaa et al., 2004; Prisle et al., 2010). First of all, it is assumed that at the Gibbs dividing surface, the following equation holds:

$$V^S = \sum n_i^S v_i = 0 \quad (\text{A1})$$

where  $V^S$  ( $\text{m}^3$ ) is volume of the surface, and  $n_i^S$  (mol) and  $v_i$  ( $\text{m}^3 \text{mol}^{-1}$ ) are number of moles at the surface and molar volume for component  $i$ , respectively. As shown by Laaksonen et al. (1999), Eq. (A1) is consistent with the assumption that the droplet surface tension (when keeping the bulk concentration constant) is not size-dependent. In the case of multicomponent solutions water and non-surfactant solutes (subscript  $j$ ) are assumed to behave as a pseudobinary solution so that their bulk (superscript B) and total (superscript T) concentration ratios remain unchanged:

$$n_w^T/n_w^B = n_j^T/n_j^B \quad (\text{A2})$$

An alternative for the pseudobinary approximation is to ignore partitioning of the non-surfactant solutes. Equation (A1) still holds as water can be depleted from the surface.

Both surface tension and activity gradients are calculated numerically, so any types of equations giving surface tension and activity coefficients can be used. Because our focus is on surface tension and there are no general activity coefficient models for surfactant-salt solutions, activity coefficients are calculated from a Debye-Hückel extension. Our version of the equation is the ideal part of the Pitzer-Simonsen-Clegg model as given by Clegg and Pitzer (1992):

$$\ln \gamma_i = \frac{2A_x I_x^{3/2}}{1 + \rho \sqrt{I_x}} - z_i^2 A_x \left( \frac{2}{\rho} \ln \left( 1 + \rho \sqrt{I_x} \right) + \frac{\sqrt{I_x}}{1 + \rho \sqrt{I_x}} \right) \quad (\text{A3})$$

where  $A_x = 2.917$  (for water at 298.15 K),  $\rho = 13.0$  and mole fraction ( $x$ ) scale ionic strength  $I_x = 0.5 \sum x_i z_i^2$ . Charge  $z_i$  is zero for water.

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