# SENSITIVITIES OF MODELLED HYGROSCOPIC GROWTH AND ACTIVATION ON SURFACE TENSION AND THE AMOUNT OF SOLUBLE SUBSTANCE IN AEROSOL PARTICLES

F. Stratmann[1], H. Wex[1], D. Topping[2], and G. McFiggans[2]

[1]*Leibniz-Institute for Tropospheric Research, Leipzig, Germany*
[2]*Centre for Atmospheric Sciences, University of Manchester, Sackville Street, Manchester, UK*

## 1. INTRODUCTION

The Köhler-equation is widely used to model hygroscopic growth and activation of aerosol particles. In the Köhler equation, the Kelvin term accounts for the effect of the curvature of the droplet surface while the Raoult term (or water activity) describes the influences of soluble material dissolved in the droplet. All together, the important parameters for the prediction of the hygroscopic growth and activation are the number of ions or molecules that are dissolved in the droplet ($N_{ion}$) and the surface tension ($\sigma$).

Here a study regarding the sensitivity of hygroscopic growth and activation on $N_{ion}$ and $\sigma$ will be presented. We will show that $N_{ion}$ is the relevant parameter when determining the hygroscopic growth and $\sigma$ has only negligible influence at relative humidities below 95%. However, when modelling the critical super-saturation needed for activation, both parameters, i.e., $N_{ion}$ and $\sigma$ need to be considered. Interestingly, the sensitivity of the critical super-saturation with respect to $\sigma$ may be a factor of three larger than that regarding $N_{ion}$.

The insensitivity of hygroscopic growth below 95 % relative humidity and the high sensitivity of activation on $\sigma$ control the possibility of achieving closure between hygroscopic growth and activation properties. Furthermore, the strong influence of surface tension needs to be kept in mind when modelling the effect of partitioning on droplet activation (*Sorjamaa and Laaksonen* [2003], *Sorjamaa et al.*, [2004], *Kokkola et al.*, [2006]).

## 2. MODELLING

The Köhler equation can be written as:

$$S_d = \exp(\frac{4M_w\sigma}{RT\rho_w d_d}) \cdot \exp(-\frac{N_{ion}}{n_w})$$

with

$$N_{ion} = \frac{\phi\nu\rho_s V_s}{M_s} = \phi\nu n_s$$

($N_{ion}$ being the number of ions dissolved in the droplet, for the other symbols see nomenclature at the end of this abstract). Two different base cases were examined, one using a value of $N_{ion}$ resulting in a high hygroscopicity (ammonium sulphate), and the other one simulating a less hygroscopic substance (HULIS, HUmic LIke Substance).

While $N_{ion}$ for a particle of a known dry size can be calculated from literature data for ammonium sulphate, $N_{ion}$ for HULIS varies, depending on the HULIS sample. Values for the different parameters were used following those determined in *Wex et al.* [2007].

To obtain accurate values regarding the sensitivity of $S_d$ and $d_d$ on $\sigma$ and $N_{ion}$, calculations were performed for varying values of $\sigma$ and $N_{ion}$ for the two base cases. For a comprehensive description of the derivation of the sensitivities, the readier is referred to *Wex et al.* [2008]. Here, in Figure 1, we directly show the resulting sensitivities for a 1% variation of either $\sigma$ or $N_{ion}$ for the two different substances and for dry particle sizes of 50 and 100nm.

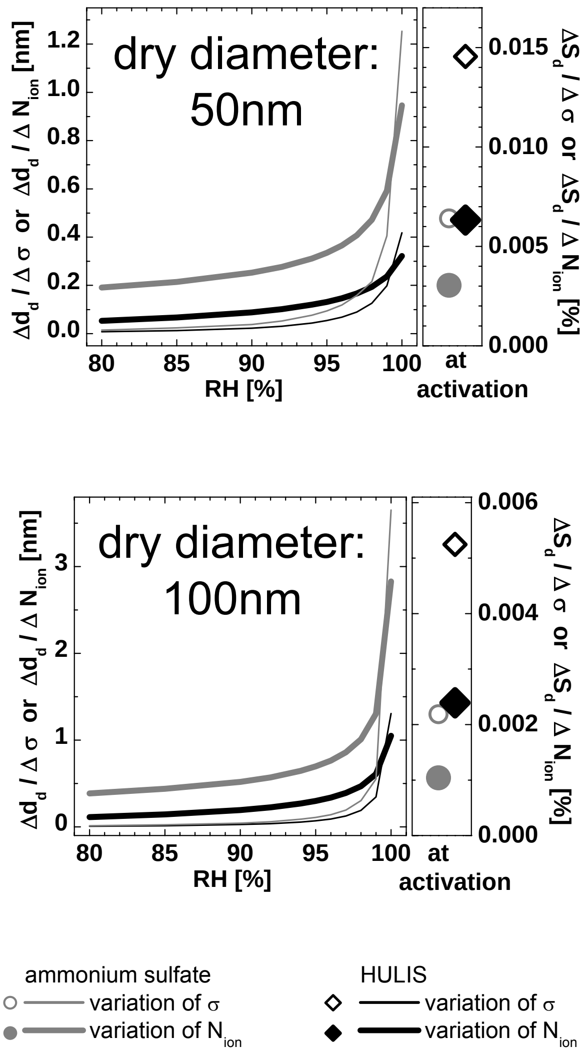

***Fig. 1:*** *Sensitivities of $d_d$ (left parts of each panel) and $S_d$ (right part of each panel) to a 1% variation in $N_{ion}$ (thick lines / filled symbol) or in σ (thin lines / open symbol). Two different dry diameters (50 nm (upper panel) and 100 nm (lower panel)) were examined, for a more and a less hygroscopic substance, i.e. for ammonium sulphate and for HULIS, respectively.*

## 3. RESULTS AND DISCUSSION

**3.1. Sensitivities.** The following important conclusions can be drawn from the sensitivities depicted in Figure 1:

a) The hygroscopic growth regime, i.e., $d_d$, is more sensitive to a 1% variation of $N_{ion}$ than to a 1% variation in σ.

b) The hygroscopic growth below saturations of 0.95 is almost insensitive to σ, but its sensitivity to σ becomes important at larger saturations above 0.95.

c) $S_d$ is more than twice as sensitive to a variation of σ than to a similar variation of $N_{ion}$.

d) In the hygroscopic growth regime the more hygroscopic substance is more sensitive towards changes in both, $N_{ion}$ and σ, than the less hygroscopic one, with an increasing sensitivity towards larger dry diameters.

e) $S_d$ of the less hygroscopic substance is more sensitive towards changes in both, $N_{ion}$ and σ, than that of the more hygroscopic substance, with an increasing sensitivity towards lower dry diameters.

The sensitivities shown in Figure 1 can be used to estimate deviations in $S_d$ or $d_d$ due to uncertainties in $N_{ion}$ and σ assuming

$$\Delta f = \frac{\partial f}{\partial x} \cdot \Delta x \approx \frac{\Delta f}{\Delta x_{1\%}} \cdot \Delta x$$

with $f = S_d \text{ or } d_d$ and $x = N_{ion} \text{ or } \sigma$. For a 50nm HULIS particle

$$\frac{\partial f}{\partial x_{1\%}} \approx \frac{\Delta S_d}{\Delta \sigma} = 0.0145$$

and a $\Delta\sigma$=72.8–50=22.8 mN/m, i.e., a 31% change in surface tension, $\Delta S_d = 0.0145 \cdot 31\% = 0.45\%$ (absolute) can be observed.

The above example was given for an error in σ on purpose, as this value is largely uncertain for atmospheric particles. It can be directly measured only for bulk solutions (or for droplets much larger than freshly activated cloud droplets), and during these measurements, different concentrations and time scales prevail than during activation.

As mentioned among the important implications that can be deduced from Figure 1, the hygroscopic growth regime is insensitive to σ up to high RHs (relative humidities), i.e. information on σ simply can not be drawn from measurements of the hygroscopic growth for RHs below 95%. On the other hand, σ strongly influences the activation. Therefore, deriving $S_d$ from measurements of the hygroscopic growth is only possible, if the examined substance has no influence on σ, i.e. if σ has the value of water, or if the right value of σ can be estimated.

**3.2. Variable surface tension and influence of partitioning.** To complicate the matter further, it has been shown for HULIS, that a concentration dependent σ should be used when describing the activation behaviour [*Ziese et al.*, 2008]. In this context, also partitioning of surface active substances to the droplet surface may play a role. Figure 2 shows Köhler curves for a fulvic acid particle (similar to HULIS, values taken from *Topping et al.* [2007]) with an initial radius of 100 nm, for the partitioning and the non-partitioning case (thick and thin lines, respectively). Also shown, in grey, are the corresponding surface tensions.

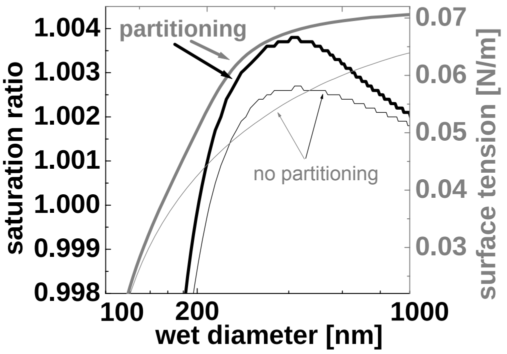

***Fig. 2:*** *Köhler curves for a fulvic acid particle (similar to HULIS, values taken from Topping et al. [2007]) with an initial radius of 100 nm, for a partitioning and a non-partitioning case (thick and thin lines, respectively). Also shown, in grey, are the corresponding surface tensions.*

Figure 2 clearly shows, that consideration of bulk to surface partitioning increases the critical saturation ratio, i.e. $S_d$. This increase in $S_d$ between the partitioning and the non-partitioning case is larger than one that would only originate in a change of σ, because it has to be attributed to both, the increase in σ and, additionally, the change in the amount of soluble substance in solution (+0.11% instead of 0.08% if only σ changed).

Overall, it becomes obvious that the value of σ depends on several factors, as there are the presence of surface active substances, their concentration in the droplet solution that changes during droplet growth, and possible partitioning or additional salting out effects of the surface active material between droplet bulk and surface. These effects aggravate the prediction of the value of σ that is effective during the activation process.

**3.3. Influence on droplet number.** We examine the effect of an erroneous value of σ on the prediction of the droplet number. For this, the change in the number of activated droplets for a 10% change in σ from 72.8 mN/m to 65.5 mN/m is derived. The estimates are based on a measured atmospheric aerosol number size distribution taken from data presented in *Wex et al.*, [2002] and represent an averaged number size distribution measured at an urban location in Germany on August 01, 2002.

For a fixed super-saturation, the critical diameter for the activation was determined, once using σ = 72.8 mN/m and again using σ = 65.5 mN/m. The number of activated droplets was determined as the integral of the measured number size distribution above that diameter. The number of activated droplets was determined, and the relative difference between the cases with different σ was derived. Figure 3 shows the measured particle number concentration and the fraction of the particles that would be activated for the two different values of σ und similar atmospheric super-saturation conditions.

Here $S_d$ was chosen such, that for $\sigma = 72.8$ mN/m the dry particle size for activation was 125 nm. Lowering σ (for a constant $S_d$) caused a lowering of the dry size from 125 nm to 112.5 nm for both ammonium sulphate and HULIS.

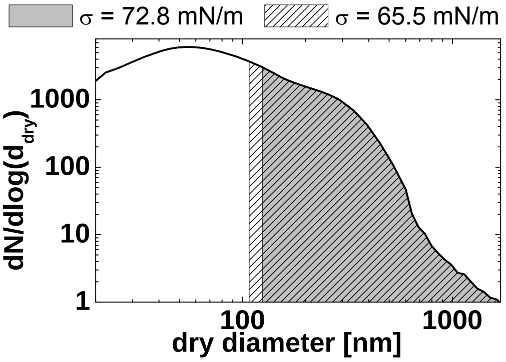

***Fig. 3:*** *Critical diameters and activated particles (highlighted areas) for a constant $S_d$ and two different values of σ, differing by 10%.*

The number of activated droplets associated with the different dry sizes was found to be increased by 20% due to the use of the lower σ. This implies that surface tension effects may have to be accounted for when deriving the correct number of particles activated to become cloud droplets.

## Nomenclature:

| | |
|---|---|
| $d_d$ | droplet diameter |
| $M_s$ | molecular weight of the solute |
| $M_w$ | molecular weight of water |
| $n_s$ | number of moles of the solute |
| $n_w$ | number of moles of water |
| $N_{ion}$ | number of ions or molecules in the droplet |
| R | ideal gas constant |
| $S_d$ | water vapor saturation at the droplet surface |
| T | temperature |
| $V_s$ | Volume of the dry particle |
| Φ | osmotic coefficient |
| ν | number of ions or molecules per molecule in solution |
| $\rho_s$ | density of the solute |
| $\rho_w$ | density of water |
| σ | surface tension |

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