

# CONNECTING HYGROSCOPICITY TO ACTIVATION: HYGROSCOPIC GROWTH AT HIGH RELATIVE HUMIDITIES, SLIGHTLY SOLUBLE SUBSTANCES, AND OTHER EFFECTS

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## 1. INTRODUCTION

In the past, it often has been tried to connect the hygroscopic growth of aerosol particles with their activation to cloud droplets using the Köhler equation (e.g., Covert *et al.* [1998], Brechtel and Kreidenweis [2000], Svenningsson *et al.* [2006]). In these past studies, measurements of the hygroscopic growth were only possible up to 95% relative humidity (RH). In general, connecting the hygroscopic growth of particles to their activation by using the Köhler equation was successful in general when relatively simple substances (e.g., ammonium sulfate) were examined. However, for atmospheric aerosol particles and for mixtures of substances including organic compounds, the number of activated particles predicted from measured hygroscopic growth by the use of a Köhler model often exceeded the measured number (Broekhuizen *et al.*, 2006).

During four measurement campaigns at the ACCENT (Atmospheric Composition Change – the European NeTwork of Excellence) infrastructure site LACIS (Leipzig Aerosol Cloud Interaction Simulator, [Stratmann *et al.*, 2004]), hygroscopic growth up to very high RHs (above 99%) and activation were measured for different types of aerosol particles. This article gives an overview of the results obtained during these campaigns regarding the possibilities to establish connections between hygroscopic growth and activation behavior.

## 2. MEASUREMENTS

The following substances were used as particle material:

- (a) NaCl and three different seawater samples;
- (b) soot particles (generated with a spark-generator) that were coated with either ammonium sulfate or levoglucosan (during the ACCENT campaign LExNo (LACIS Experiment in November));
- (c) two different atmospheric HULIS (HUmic LIke Substances) samples, collected and prepared in Budapest;
- (d) mixtures of succinic acid with ammonium sulfate;
- (e) secondary organic aerosol (SOA).

While particles used in (a), (c) and (d) were generated from a solution, using an atomizer, the SOA particles were generated in the gas phase from  $\alpha$ -pinene and ozone.

LACIS measured hygroscopic growth and activation for the samples given in (a) and (c) and hygroscopic growth for samples examined in (d) and (e). A HH-TDMA (High Humidity Tandem Differential Mobility Analyzer, [Hennig *et al.*, 2005]) and a continuous-flow streamwise thermal-gradient CCNc (Cloud Condensation Nucleus counter [Roberts and Nenes, 2005]) were used to quantify hygroscopic growth and activation during LExNo, i.e. (b), respectively, and a CCNc of the above mentioned type was used to measure the activation for the SOA particles (e). LACIS and the HH-TDMA, measured the hygroscopic growth at high relative humidities (RHs) above 95%, with

the HH-TDMA measuring up to 98% and LACIS up to 99.5% RH.

### 3. MODELING

The modeling was based on the approach described in *Wex et al.* [2007], using a parameter  $\rho_{ion}$  defined as:  $\rho_{ion} = (\Phi v \rho_{sol}) / M_{sol}$  (with the osmotic coefficient  $\Phi$ ,  $v$  being the number of ions the substance dissociates to in solution, the density  $\rho_{sol}$ , and the molecular weight  $M_{sol}$  of the solute). This parameter  $\rho_{ion}$  is included in the water activity term in one of the possible formulations of the Köhler theory. This modeling approach is, in principle, similar to the approach used by Petters and Kreidenweis [2007], in that the hygroscopic growth is described by a single parameter  $\kappa$  in the Raoult (or solubility) term.

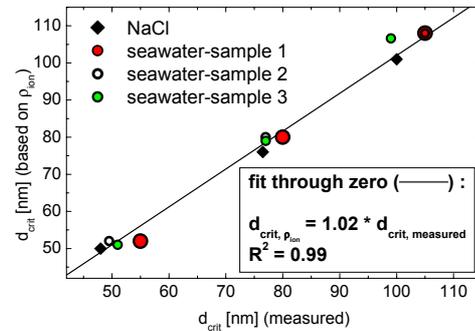
The parameter  $\rho_{ion}$  combines all parameters of the solute influencing the water activity, for which values are not known a priori. With this approach, the number of unknowns in the Köhler equation is reduced to two:  $\rho_{ion}$  in the water activity term and the surface tension  $\sigma$  in the Kelvin term.

In a first step, for the data analysis of the different particle types,  $\rho_{ion}$  was derived from measured hygroscopic growth together with using the surface tension of water ( $\sigma_w = 72.8\text{mN/m}$ ).  $\rho_{ion}$  was adjusted such, that the Köhler equation reproduced the measured particle sizes at the respective RHs. Then, the activation was modeled using the values of  $\rho_{ion}$  derived at RHs above 95%, together with  $\sigma_w$ . The resulting calculated critical super-saturations needed for activation were compared to the measured ones. In this context, for HULIS particles, a better agreement between measured and modeled activation data was found when a surface tension reduction was considered, using a concentration dependent value for the surface tension (see Section 4.2). For SOA particles, the concept of a constant  $\rho_{ion}$  could not be used (Section 4.4).

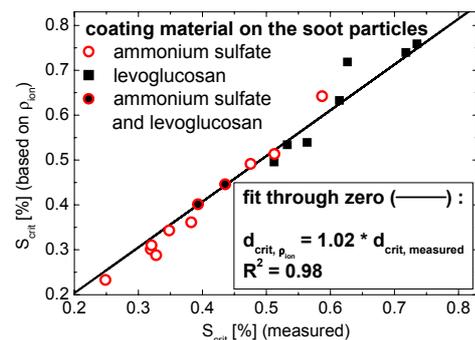
## 4. COMPARISON OF MEASURED AND MODELED ACTIVATION BEHAVIOR

### 4.1. Particles generated from NaCl and seawater and coated soot particles.

For these substances, good agreement between measured and modeled activation behavior was obtained when using the surface tension of water. This was found for both, particles from seawater samples (see Figure 1) and coated soot particles (see Figure 2). The slopes of the fits (which were forced through zero) and the correlation coefficients are also given in Figures 1 and 2. Details on the examination of the seawater samples can be found in *Niedermeier et al.* [2008].

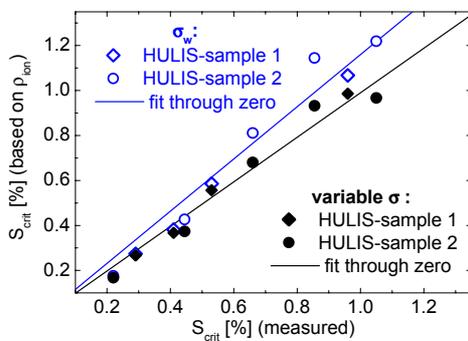


**Fig. 1:** Measured and modeled critical diameters for the NaCl particles and for the particles generated from seawater samples.



**Fig. 2:** Measured and modeled critical super-saturations for the coated soot particles examined during LExNo.

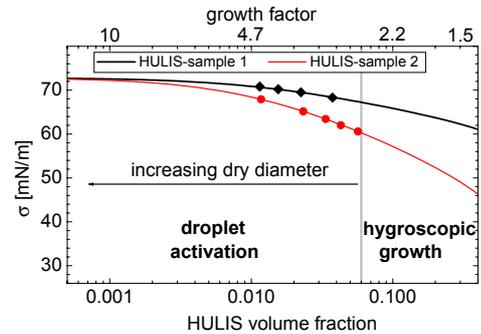
**4.2 HULIS particles.** Two HULIS samples were investigated, both extracted from urban aerosol samples from Budapest. Measurements were performed for dry particle sizes in the range from 40 to 160 nm. HULIS has been described as a surface-active substance in the past [Salma *et al.*, 2006]. When using the surface tension of water, the critical super-saturations ( $S_{crit}$ ) predicted from the hygroscopic growth behavior exceeded the measured values for  $S_{crit}$  above 0.6%, which corresponds to dry particle sizes below 70 nm. This can be seen in Figure 3.



**Fig. 3:** Measured and modeled critical super-saturations for the HULIS particles, for the two approaches, one using  $\sigma_w$  and the other one using a variable  $\sigma$ .

For a fit through zero, a slope of 1.16 is obtained for this dataset. Also shown in Figure 3 are values of  $S_{crit}$  that were obtained using a variable, i.e., concentration-dependent surface tension. This variable  $\sigma$  was determined following Szyszkowski [1908], who suggested a variable  $\sigma$  for solution droplets that contain surface-active substances, depending on the concentration of this substance. Particles with smaller dry diameters have a smaller growth factor at the point of activation. Therefore they are more concentrated and can have a smaller  $\sigma$ . By using a variable  $\sigma$ , the agreement between measured and modeled  $S_{crit}$  was improved, compared to using  $\sigma_w$ , as can be seen in Figure 3. The slope of the fit through zero when using a variable  $\sigma$  is 0.99. Figure 4 shows the derived variable  $\sigma$  for the two

HULIS samples and indicates the values for  $\sigma$  for the droplets activating on the different dry particle sizes. The above analysis shows the need to account for a concentration dependent  $\sigma$  for HULIS particles, and is described in detail in Ziese *et al.* [2008].

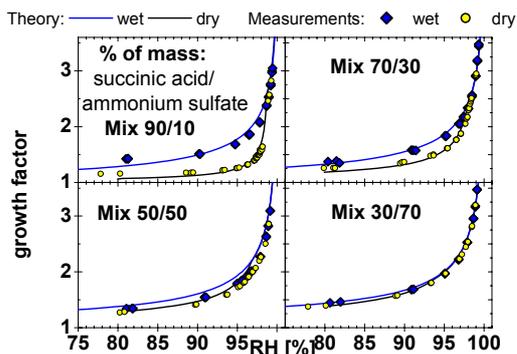


**Fig. 4:** Values for  $\sigma$  varying with concentration for the two different HULIS samples. The straight grey line roughly divides the concentration range in a hygroscopic growth and an activation regime. The symbols indicate the values of  $\sigma$  for the droplets activating on the different dry particle sizes in the range from 40 nm to 160 nm.

**4.3. Hygroscopic growth of slightly soluble substances.** For particles consisting of a mixture of succinic acid and ammonium sulfate, only hygroscopic growth was measured. This was done for particles with different mass fractions of the two substances, which are indicated in Figure 5. Besides measuring, the hygroscopic growth was also modeled for the mixed particles, following the theory given in Laaksonen *et al.* [1999] and Henning *et al.* [2005]. It can be seen in Figure 5, that measurements and theory are in agreement. Particles on the deliquescence branch (denoted “dry” in Figure 5) differ increasingly from those on the efflorescence branch (denoted “wet”) with an increasing mass fraction of succinic acid. The RH at which deliquescence and efflorescence are in agreement, i.e. at which the particle has fully dissolved, also increases with an increasing mass fraction of succinic acid. It is above 98% RH for a succinic acid mass fraction of 90%, and still at 97% RH for particles with a mixture of 50% succinic acid and ammonium sulfate, each.

This shows clearly, that the

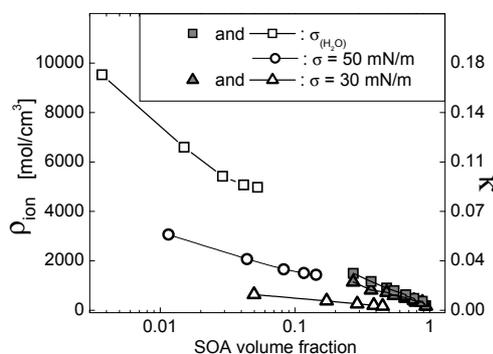
assumption of a constant  $\rho_{ion}$  is not necessarily justified, not even within the range of high RHs above 95%. Values derived for  $\rho_{ion}$  for slightly soluble substances or for mixtures including such substances at RHs below their full deliquescence would lead to an underestimation of  $\rho_{ion}$  and, consequently, an overestimation of  $S_{crit}$ .



**Fig. 5:** Growth factors for particles with a dry diameter of 250 nm, consisting of different mass fractions of succinic acid and ammonium sulfate. Both, deliquescence (“dry”) and efflorescence (“wet”) was measured.

**4.4. SOA particles.** For SOA particles generated from different precursor gases (e.g. monoterpenes) and for both, photo-oxidation as well as oxidation by ozone, OH or other oxidizing species, in general a slight hygroscopic growth is observed [e.g. Virkkula et al., 1999; Varutbangkul et al., 2006], while they are commonly found to be more CCN active than their hygroscopic growth factor would suggest [e.g. VanReken et al., 2005, Prenni et al., 2007]. Assuming a constant  $\rho_{ion}$  derived from measured hygroscopic growth at RHs below 95% implies, that a very low surface tension of about 30 mN/m is needed to explain the measured CCN activity [e.g. Prenni et al., 2007]. Figure 6 shows values of  $\rho_{ion}$  derived from hygroscopic growth and activation measured with LACIS and with the CCNc, respectively. The values were derived assuming different surface tensions, and are given as a function of the SOA volume concentration. Filled symbols originate in measured hygroscopic growth, while open symbols are based on measured activation

diameters. Two things can be seen from Figure 6: 1) The hygroscopicity increases as the particles become more dilute. This change in hygroscopicity becomes clearly obvious only at RHs above 98% and thus could not be observed in the past. This explains the low values of  $\sigma$  that had to be assumed in the past, when a constant hygroscopicity was assumed. 2) A value of  $\sigma$  of 30 mN/m is too low to get a consistent transition from hygroscopic growth to activation data, i.e.  $\sigma$  can reasonably be assumed to be not lower than 50mN/m.



**Fig. 6:** Hygroscopicity of SOA particles derived from LACIS (filled symbols) and CCNc (open symbols) measurements assuming different values for  $\sigma$ , expressed as  $\rho_{ion}$  (or  $\kappa$ ) as a function of the SOA volume fraction.

## 5. CONCLUSIONS

The results gained in the course of the experiments described above clearly indicate that a usage of the surface tension of water in the Köhler equation may result an erroneous prediction of the activation behavior, if surface-active substances are present in the droplet. Also, it was shown that substances (or mixtures of substances) exist for which the assumption of a constant hygroscopicity is not valid. Measurements of hygroscopic growth up to very high RHs, together with measurements of the activation behavior are necessary to gain enough insight to be able to consistently describe the water uptake of particles over the whole range from hygroscopic growth up to activation, and therefore to gain an insight on the importance of the different contributing parameters and processes.

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