Connecting hygroscopic growth at high humidities to cloud activation for different particle types

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Abstract
This work recompiles studies that have been done with respect to hygroscopic growth in the regime of high relative humidities and with respect to activation for different kinds of particle at LACIS (Leipzig Aerosol Cloud Interaction Simulator) during the last few years. The particles examined consisted of a mixture of succinic acid and ammonium sulfate, seawater samples, soot coated with an organic and/or an inorganic substance, and two different atmospheric HULIS (HUmic LIke Substance) samples. An influence of changing non-ideal behavior and of slightly soluble substances on the hygroscopic growth was found in varying degrees in the subsaturation regime. The measured hygroscopic growth was extrapolated towards supersaturation, using a simple form of the Köhler equation, and assuming a constant number of molecules/ions in solution for high relative humidities ($\geqslant$95% or $\geqslant$98%, depending on the particles). When the surface tension of water was used, the modeled critical supersaturations reproduced the measured ones for the seawater samples and for the coated soot particles. To reach agreement between measured and modeled critical supersaturations for the HULIS particles, a concentration-dependent surface tension had to be used, with values of the surface tension that were lower than that of water, but larger than those that had been reported for bulk measurements in the past.

Keywords: hygroscopic growth, activation, surface tension, slight solubility, non-ideal behavior

1. Introduction

Aerosol particles are ubiquitous in the Earth's atmosphere and influence the Earth's climate through several effects that can be distinguished as their direct effect (scattering and absorption of incoming solar radiation) and their indirect effects (different interactions with clouds). As water, too, is ubiquitous in the atmosphere, and as it interacts with atmospheric aerosol particles, the aerosol effects on climate also depend on the aerosol interaction with water and on its availability. Water vapor hydrates the aerosol particles and will eventually let the particles grow into cloud droplets. The equation that is often used to describe both hygroscopic growth of aerosol particles and their activation to cloud droplets is the Köhler equation. It relates the water vapor saturation over the surface of a solution droplet to the droplet diameter, needing the number of molecules/ions in solution and the droplet surface tension as input parameters.

Nevertheless, clouds still cause one of the major uncertainties in our understanding of the Earth's climate (Forster *et al* 2007). Among the open questions related to clouds is the activation of atmospheric aerosol particles to cloud droplets. Attempts to predict the number of cloud droplets based on aerosol number size distributions were already done by Bigg (1986), who reported an overestimation of the measured number of cloud condensation nuclei (CCN), when calculations were based on the assumption that the particles consisted of ammonium sulfate or sodium chloride. As a possible explanation, the presence of a surface active organic compound that suppressed cloud droplet formation was proposed.

A work by Martin *et al* (1994) criticized the very simple parameterization of droplet number concentrations in models that would use one fixed concentration for marine and another one for continental air masses. They say that, as numerical models become more sophisticated, a predictive aerosol parameter will need to be included. However, such a parameterization representing the connection between aerosol and droplet number concentration is still lacking, to date. Medina *et al* (2007) stated that, despite numerous CCN studies, a comprehensive CCN climatology is still lacking, and that there is a strong need for CCN closure studies that cover a wide range of seasons and aerosol types.

Many different CCN closure studies have been performed during the last two decades. They were done either on atmospheric aerosols or in the laboratory. Broekhuizen *et al* (2006), Stroud *et al* (2007), Medina *et al* (2007) all give overviews of closure studies on atmospheric aerosols. In summary, those studies that were able to achieve closure were generally not influenced by strong anthropogenic sources and had low concentrations of organic carbon in the aerosol phase (Broekhuizen *et al* 2006). For studies that did not achieve closure, CCN concentrations were generally overpredicted, and the discrepancy has generally been attributed to an incomplete understanding of the aerosol composition, especially the role of organic species (Stroud *et al* 2007). This is in line with (Chang *et al* 2007), who compared measured CCN number concentrations with those derived with Köhler theory, using aerosol composition obtained from aerosol mass spectrometer measurements as input. They found that during periods when the aerosol organic content is high, the predicted CCN number concentration was significantly lower than the measured one, and they give surface tension and the unknown degree of internal mixing as possible reasons for this.

As laboratory generated particles can be tailored to the subjects one wants to examine, many laboratory studies have also been done to gain information about hygroscopic growth and activation behavior. Among the earlier works were those of Cruz and Pandis (1997, 1998), who found that pure organic compounds and inorganic particles coated with organic compounds activated to cloud droplets more readily than it previously had been assumed, and that, therefore, the role of organic compounds in the activation of atmospheric particles has to be accounted for.

Brechtel and Kreidenweis (2000a, 2000b) described and evaluated a method to extend hygroscopic growth to relative humidities (RHs) above saturation to derive the critical supersaturations for activation. They showed its applicability to simple inorganic substances. The method, however, gave poorer results for ambient particles. Among the possible explanations given for this was the presence of slightly soluble compounds. This was corroborated by Prenni *et al* (2001), who measured that succinic acid particles did not exhibit water uptake up to 93% RH but activated at 0.21% supersaturation, i.e. at a lower supersaturation than would be expected from the hygroscopic growth.

Svenningsson *et al* (2006) examined succinic acid, levoglucosan and fulvic acid and mixtures of these organics with inorganic compounds with respect to hygroscopic growth and activation. For fulvic acid it was stated that the results for the activation were very sensitive to the extrapolation of surface tension data from those concentrations where it was measured to those relevant during activation. Also, concerns were raised again as to the role of slightly soluble substances.

The activation of fulvic acid particles was also studied by Dinar *et al* (2006), together with HULIS (HUmic LIke Substance) particles generated from extracts of atmospheric samples. While a surface tension reduction had to be accounted for for the HULIS particles, this was not so obvious for the fulvic acid particles. Indeed, the question has been raised in the past, how 'humic like' fulvic acids really are (Graber and Rudich 2006).

Another type of substance for which much research was done during recent years is the SOA (secondary organic aerosol), of which HULIS and dicarboxylic acids can be viewed as a subfraction. In laboratory experiments simulating atmospheric SOA, α-pinene, a monoterpene, has often been used as a precursor, from which the SOA is produced by oxidation, either upon reaction with ozone or photochemically. Many groups have observed that an SOA shows only a slight hygroscopic growth (e.g. Virrkula *et al* 1999, Saathoff *et al* 2003, Baltensperger *et al* 2005, Varutbangkul *et al* 2006, Prenni *et al* 2007) but is much more CCN active than the hygroscopic growth would suggest (e.g. VanReken *et al* 2005, Prenni *et al* 2007). Should this discrepancy be explained by a lowering of the surface tension, values as low as 30 mN m^{-1} would have to be assumed (Prenni *et al* 2007), which is highly unlikely and also is lower than measured values reported for substances which can be assumed to be included in the SOA (Huff Hartz *et al* 2006).

The effect of surface tensions on CCN activity were also examined by Asa-Awuku *et al* (2008), who investigated hygrophilic and hydrophobic fractions of water-soluble organics found in fresh biomass burning aerosol. The presence of inorganic species in the hydrophobic fraction caused a surface tension lowering, attributed to salting-out of surface active organic substances to the surface layer, and led to an increased CCN activity for the respective particles.

The studies cited above give an insight into topics that have been examined with respect to hygroscopic growth and activation in the past. In summary, organic material in atmospheric aerosol particles cannot be omitted, but with its existence, effects such as slight solubility or an influence on the surface tension might have to be taken into account when modeling hygroscopic growth and activation.

For both field and laboratory studies, varying degrees of agreement between measured and modeled hygroscopic growth and activation were found. The Köhler equation, which was usually used for modeling, needs the number of molecules/ions present in the solution droplet as an input parameter (in the Raoult term, i.e. water activity), together with the surface tension (in the Kelvin term). Two different approaches were used in the above cited studies. The first one was to use properties of the substances contained in the particles as far as they were known and to estimate those that were not known, and to calculate the hygroscopic growth and/or activation from there. The second approach was to measure the hygroscopic growth, adjust the Raoult term accordingly, and derive the activation based on this adjustment.

The first approach needs information on many different aerosol parameters, as there are the density, molecular weight, degree of dissociation, non-ideal behavior, and mass fraction of the substances contained in the particle, together with the interaction between the different substances. Or, alternatively, the water activity of the examined substances has to be known. These values can be difficult to obtain, even if only a single substance is examined. This is the advantage of the second approach. The hygroscopic growth that is used to adjust the Köhler equation embodies the same process than the activation. But it usually only can be measured up to RHs of 90%, sometimes of 95%.

Some studies have developed a representation of the water activity term in which there is only a single open parameter (Wex *et al* 2007a, Petters and Kreidenweis 2007, Vestin *et al* 2007). It is, however, still in question, whether the use of a constant value for this parameter covering the whole range from hygroscopic growth to activation is justified. If the particles contain slightly soluble substances that dissolve only above the RH for which hygroscopic growth was measured, or if the degree of non-ideal behavior changes above that RH, then erroneous predictions of the activation can result.

A concern for both of the above described approaches is the surface tension. A number of studies have focused on the surface tension of organic compounds and on its influence on hygroscopic growth and activation (e.g. Facchini *et al* 2000, Henning *et al* 2005, Kiss *et al* 2005, Dinar *et al* 2006, Salma *et al* 2006, Svenningsson *et al* 2006, Taraniuk *et al* 2007, Wex *et al* 2007a). It was found, in general, that atmospheric aerosol particles contain substances that have a lower surface tension than that of water (down to below 50 mN m^{-1}, as compared to about 73 mN m^{-1} for water, (Facchini *et al* 2000, Kiss *et al* 2005, Dinar *et al* 2006, Salma *et al* 2006)), and that this has to be accounted for when modeling the activation (Wex *et al* 2008). However, in the past, studies often have used the surface tension of water. How to determine the surface tension of solutions under investigation remains an open question, as up-to-date experimental methods do not measure surface tension at the timescales and solution concentrations that prevail in the atmosphere during the activation process.

This work is meant to give an overview over the studies that have been conducted at the ACCENT (Atmospheric Composition Change—the European NeTwork of Excellence) infrastructure site LACIS (Leipzig Aerosol Cloud Interaction Simulator, (Stratmann *et al* 2004)) after it was built in 2005. The advantage of LACIS and the HH-TDMA (high humidity tandem differential mobility analyzer (Hennig *et al* 2005)), that was also used during some of these studies, is that hygroscopic growth can be measured up to very large RHs, with LACIS measuring up to 99.5% (Wex *et al* 2005) and the HH-TDMA up to 98%. Measured hygroscopic growth was extrapolated to yield critical supersaturations or critical diameters for activation, and these modeled activation parameters were compared to measured ones. The diminished influence of slightly soluble substances and of non-ideal behavior at the high RHs made it easier to test a possible influence of surface tension on hygroscopic growth and activation.

We will combine the results gained for four different types of particle. Those are particles that are mixtures of succinic acid and ammonium sulfate, for which only hygroscopic growth was measured, and three further particle types, for which both the hygroscopic growth and activation were measured. Results for the latter three have been published (Niedermeier *et al* 2008, Wex *et al* 2007a, Ziese *et al* 2008) or will be published soon (Stratmann *et al* 2008). The aim of this work is to reexamine and reinterpret the existing data with respect to the interaction between hygroscopic growth at very high RHs and activation.

2. Particle types and measurements

This study examines different kinds of aerosol particles that were generated in the laboratory: (a) particles consisting of a mixture of succinic acid (SA) and ammonium sulfate (AS) with a mass fraction of 89.3% SA and 10.7% AS; (b) particles consisting of either sodium chloride (NaCl) or one of three different seawater samples (Niedermeier *et al* 2008); (c) soot particles with an inorganic and/or an organic coating (during the ACCENT campaign LExNo (LACIS Experiment in November)) (Stratmann *et al* 2008); (d) two different HULIS (HUmic Like Substance) samples, collected and prepared in Budapest and examined during two separate measurement periods (Wex *et al* 2007a, Ziese *et al* 2008).

Particles consisting of the SA–AS-mixture were generated by atomizing a solution of the two substances in double deionized water. The particles were subsequently dried in a diffusion dryer, and a dry size of 250 nm was selected with a DMA (differential mobility analyzer, type 'Vienna medium'). The hygroscopic growth of the particles was then measured in LACIS. For these particles, the deliquescence and efflorescence branches of the hygroscopic growth curve were measured, following the methods described in Wex *et al* (2007b). NaCl, seawater and HULIS particles were also generated by atomizing the respective solution, while soot particles were produced in a spark generator and subsequently coated in a furnace with either ammonium sulfate and/or levoglucosan. For all particle types, a DMA was used to select dry particle sizes. For more details, the reader is referred to the respective publications given above. Table 1 gives an overview of the different instruments used for the measurements of the different particle types. DMT-CCNc in table 1 is the CCN

Table 1. Instrumentation that was used for the different measurements.

Particle type	HH-TDMA	LACIS subsaturated	LACIS supersaturated	DMT-CCNc
Mixture of SA and AS		X		
NaCl and seawater		X	X	
Coated soot	X			X
HULIS (sample 1 and 2)	X	X	X	

counter described in Roberts and Nenes (2005) and Rose *et al* (2008), produced by Droplet Measurement Technologies. The sub- and supersaturated modes of operation of LACIS are described in Wex *et al* (2005) and Wex *et al* (2006), respectively.

3. Modeling

To extrapolate measurements done at subsaturation to the supersaturation regime, the Köhler equation was used, describing the water vapor saturation at the surface of the droplet (S_p) as a function of its water activity (a_w) and of its curvature as treated in the Kelvin term (K):

$$S_p = K a_w = \exp(4 M_w \sigma / R T \rho_w d_{wet}) \exp(-\phi \nu n_{sol}/n_w). \quad (1)$$

The Kelvin term depends on the surface tension σ of the solution, together with the molecular weight of water M_w, the universal gas constant R, the temperature T, the density of water ρ_w, and the droplet diameter d_{wet}. In the water activity term, ϕ is the osmotic coefficient, ν is the number of molecules or ions the substance dissociates to in solution, and n_{sol} and n_w are the number of moles of the solute and of water, respectively.

As proposed in Wex *et al* (2007a), a_w can be written such that it contains only a single unknown parameter, ρ_{ion}:

$$\rho_{ion} = \phi \nu \rho_{sol}/M_{sol}$$
$$\left[\text{and therewith } a_w = \exp(-\rho_{ion} V_{sol}/n_w)\right] \quad (2)$$

where ρ_{sol} is the density and M_{sol} is the molecular weight of the solute, and V_{sol} is the volume of the dry particle.

ρ_{ion} can be adjusted so that the modeled hygroscopic growth is in agreement with the measurements. This approach avoids the necessity to obtain knowledge of the values of the different separate parameters ϕ, ν, ρ_{sol}, and M_{sol}, but still permits us to extrapolate the measured hygroscopic growth of aerosol particles to their activation behavior. Using this approach, there are two unknowns in the Köhler equation: ρ_{ion} in the water activity term and the surface tension σ in the Kelvin term.

It was shown in Wex *et al* (2008) that the value used for σ only has a small influence on the hygroscopic growth (and therefore only has a small influence on ρ_{ion}), whereas it does have a big influence on the activation of aerosol particles with atmospheric relevant sizes. Often, when determining the activation behavior of atmospheric aerosol particles, the value of σ for pure water ($\sigma_w = 72.8$ mN m^{-1} at 20 °C) is used. When comparing the particle activation determined via ρ_{ion} to the measured activation, it can become obvious if using σ_w is appropriate. This will be examined in the following for the different particle types used.
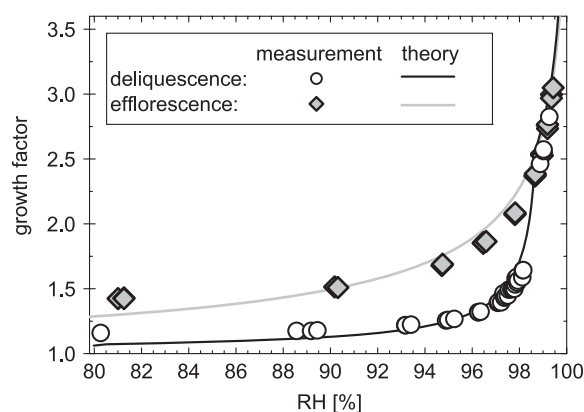

Figure 1. Measured deliquescence and efflorescence branches of the hygroscopic growth curve for the SA–AS particles with a dry size of 250 nm. The theoretical lines were derived following Laaksonen *et al* (1998) and Henning *et al* (2005).

4. Results for different particle types

In general, all particle types were examined following a similar procedure. The measured hygroscopic growth (i.e. measured equilibrium (=wet) diameters at different RHs) was used to determine ρ_{ion}. This was done separately for the different RHs at which measurements had been done. For this, in a first step, σ_w (72.8 mN m^{-1}) was used.

For all particle types but for the SA–AS-mixtures, the derived values of ρ_{ion} were used (together with σ_w and the dry diameters (or the supersaturations) at which the activation was measured) as input for the Köhler model. From this then, S_{crit} (or the critical diameter d_{crit}) was obtained from the maximum of the Köhler curve. These values then could be compared to the respective measured values.

4.1. Results for SA–AS mixtures

Figure 1 shows the measured hygroscopic growth factors for the SA–AS particles with a dry diameter of 250 nm. The efflorescence and deliquescence branch of the hygroscopic growth curve can be easily distinguished, showing that the particles only fully deliquesce at RHs between 98.1% (last measurement point where they are not yet completely dissolved) and 98.9% RH. Calculations following the theory proposed by Laaksonen *et al* (1998) and Henning *et al* (2005) for slightly soluble substances are also shown in figure 1. Measurements are in good agreement with this theory, which predicts a complete dilution of the SA–AS mixture at 98.7%.

The measured hygroscopic growth was used to derive values for ρ_{ion} for each measurement point separately (see
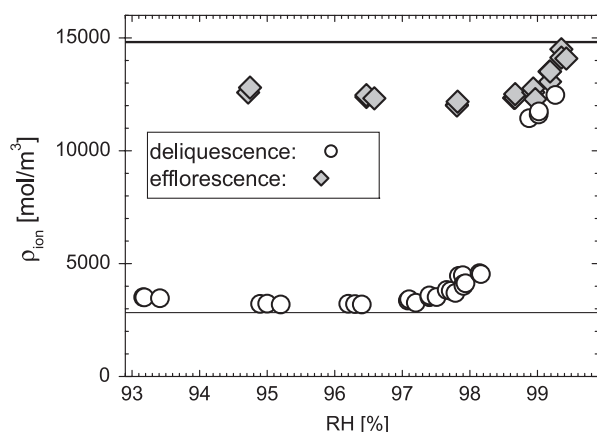
Figure 2. Values for ρ_{ion} derived from the measured hygroscopic growth shown in figure 1. The straight lines are a guide for the eye, indicating the value of ρ_{ion} if only the AS fraction made ions available to the particle solution (thin line) or if both SA and AS delivered ions, proportional to their volume fractions (thick line).
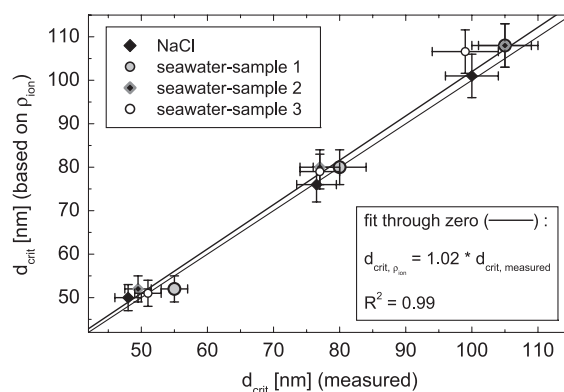

Figure 3. Comparison of measured and modeled critical diameters for the activation of NaCl particles and particles from seawater samples at supersaturations of 0.11%, 0.17%, and 0.32%. The thin line is the 1:1 line, and the thick line is the linear fit through zero. The *y*-error bars originate in the uncertainty of ρ_{ion}, i.e., of the RH in LACIS, while the *x*-error bars indicate the measurement uncertainty of LACIS in its supersaturation mode of operation.

figure 2). Also shown in figure 2, as a guide to the eye, is a thick line indicating ρ_{ion} as obtained when assuming that SA and AS were both completely dissolved (using molecular weights of 118 g mol^{-1} and 132 g mol^{-1}, densities of 1.566 g cm^{-3} and 1.77 g cm^{-3}, and a value for $(\phi\nu)$ of 1 and 2.2 for SA and AS, respectively). Similarly, the thin line indicates ρ_{ion} resulting from the ions of the AS fraction, only. For the deliquescence branch, it can be seen that a slightly larger amount of ions or molecules than those provided by the AS is in solution below the point of full deliquescence. This amount increases slowly as the deliquescence point is approached, at which ρ_{ion} then suddenly increases by a factor of about 2 and approaches values obtained for the efflorescence branch. For the efflorescence branch, values of ρ_{ion} are lower than expected for a fully dissolved particle by about 16%, possibly due to interaction between the ions and molecules, up to 99% RH. Above that, ρ_{ion} approaches the expected value quickly and is only low by 4% at 99.4%. This change in ρ_{ion} could be induced by the solution approaching ideal behavior as it gets more diluted at higher RHs.

4.2. Results for NaCl and seawater

When deriving ρ_{ion} from measured hygroscopic growth of NaCl and seawater particles, a decrease of the derived values of ρ_{ion} towards larger RHs was observed. This decrease follows the known non-ideality of pure NaCl, and can therefore be attributed to a change in the non-ideality of the solutions also for the seawater particles, as discussed in detail in Niedermeier *et al* (2008). Therefore, for modeling the activation, only the average of the values for ρ_{ion} derived at RHs above 95% was used.

As said above, a simple approach using σ_w was tried first. In the case of the seawater samples, d_{crit} had been measured at selected supersaturations, so d_{crit} was derived from the maximum in the Köhler equation for these supersaturations. Figure 3 shows the comparison of the measured and modeled

d_{crit} for NaCl particles and for the particles generated from the three seawater samples.

The agreement between measurement and calculation depicted in figure 3 ($R^2 = 0.99$, slope of a linear fit forced through zero: 1.02) shows that σ_w can be used to describe hygroscopic growth and activation consistently for NaCl particles and for particles consisting of seawater. However, it has to be said that possible surface active organic compounds present at the very top of the oceans, in the ocean microlayer, would not have been included in our seawater samples, due to the sampling depth. But it can be stated that σ_w can be used for droplets growing on a single inorganic salt as well as on mixtures of different inorganic salts, both of which are chemically relatively simple systems.

4.3. Results for coated soot particles

For the coated soot particles that were examined during LExNo, 18 experiments were run, with a different coating type or a different coating thickness in each experiment. Values of d_{wet} measured at 98% RH, were used, together with σ_w, to derive the values of ρ_{ion} shown in figure 4.

For this dataset, S_{crit} was measured for a known dry particle diameter of 84 nm, so here the maximum of the Köhler equation was used to derive S_{crit} for the differently coated particles. The resulting modeled values for S_{crit} are compared to measured values of S_{crit} in figure 5. As for the NaCl and seawater particles, a good agreement between measurements and calculations was found ($R^2 = 0.98$, slope of a linear fit through zero: 1.02), showing that also for the more complicated soot particles, the use of σ_w is appropriate.

The coated soot particles consist of a mixture of water insoluble and soluble substances. It should be noted that the parameter ρ_{ion} gives an effective value of the number of ions or molecules that are available in the solution per unit dry particle volume, i.e. it describes the overall behavior of the whole particle upon hydration and can be used for both pure substances and also internally mixed particles.
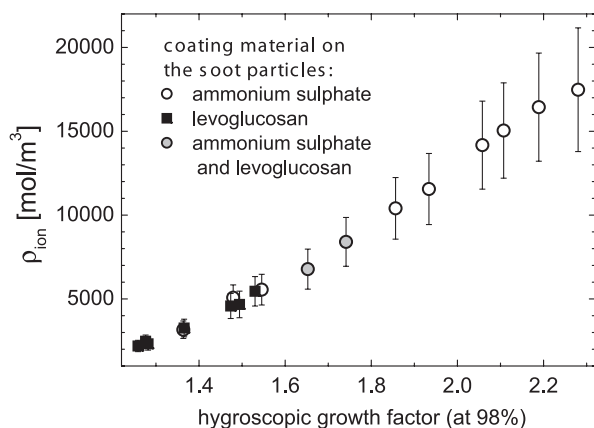
Figure 4. Values for ρ_{ion} derived from measured hygroscopic growth at 98% RH for the differently coated soot particles examined during LExNo. Error bars for ρ_{ion} originate in the measurement uncertainty of RH in the HH-TDMA.
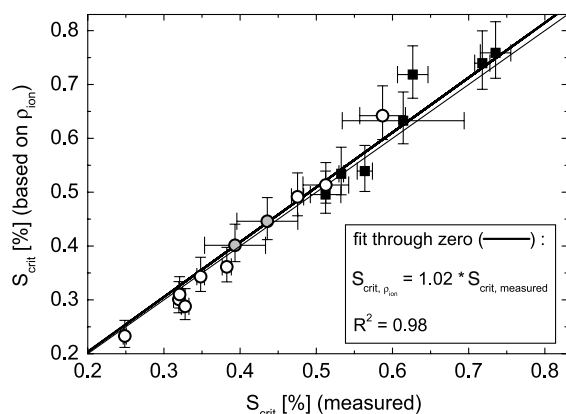

Figure 5. Comparison of measured and modeled critical supersaturations for the activation of coated soot particles examined during LExNo (for symbols see legend in figure 4). The thin line is the 1:1 line, and the thick line is the linear fit through zero. The *y*-error bars originate in the uncertainty of ρ_{ion}, i.e., in the RH in the HH-TDMA, while the *x*-error bars indicate the measurement uncertainty of the DMT-CCNc.

Figure 6. Values of ρ_{ion} derived from the measured hygroscopic growth when using σ_w. Measurements below 98% RH were done with the HH-TDMA for dry sizes of 100 nm, while measurements above 98% RH were done with LACIS for dry particle sizes of 200 nm for HULIS-sample-1 and 230 nm for HULIS-sample-2, respectively. The error bars originate in the measurement uncertainty of the RH.

Figure 7. Values of ρ_{ion} for HULIS-sample-1 (left panel) and HULIS-sample-2 (right panel), derived from the measured hygroscopic growth and from measured S_{crit}, using different σ. In both panels, data based on hygroscopic growth are located to the right, and data based on S_{crit} to the left of the gray inclined line, respectively. The black horizontal lines indicate the constant values of ρ_{ion} that were used to derive the concentration-dependent σ given in figure 9.

4.4. Results for HULIS particles

Two different HULIS samples were examined, both extracted from urban aerosol samples taken in Budapest. Measured d_{wet} and the accompanying saturations were again used to derive ρ_{ion}. The values of ρ_{ion} obtained when using σ_w are shown in figure 6. For HULIS-sample-1, ρ_{ion} is constant in the RH range above 95%. For HULIS-sample-2, ρ_{ion} decreases below 97% RH, possibly indicating a decrease of the number of dissolved molecules or ions towards lower RHs or a change of the non-ideality of the solution.

We also derived ρ_{ion} from the measured S_{crit}, using different assumptions on σ. The results are shown in figure 7, together with those values of ρ_{ion} derived from hygroscopic growth at the highest RHs. When σ_w was used, values for ρ_{ion} increased from sub to supersaturation (i.e. towards lower HULIS volume fractions), and decreased again for the more diluted solutions, i.e. for measurements done for particles with larger dry diameters (which are more diluted at the point of
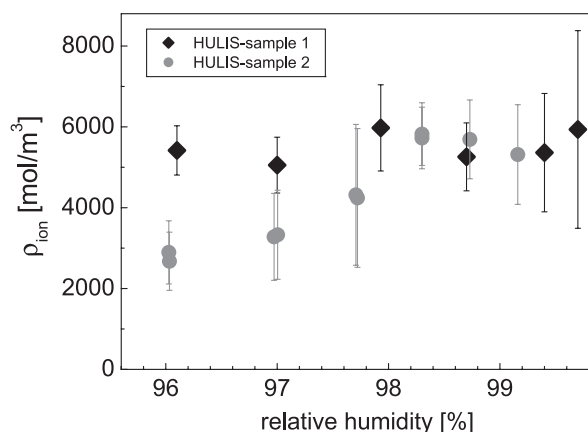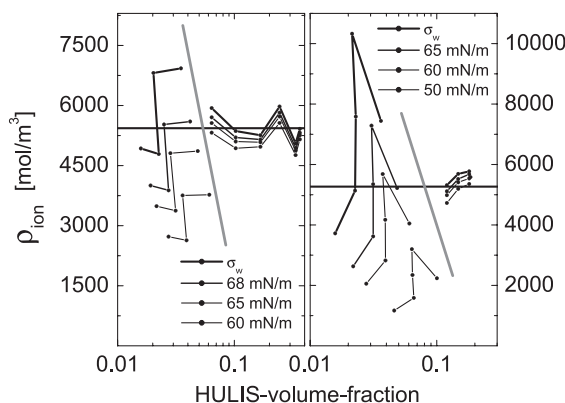
activation than particles of the same substance with smaller dry diameters, due to the Kelvin term). These results would imply that the number of ions or molecules in solution increased strongly from the sub- to the supersaturation regime, only to decrease again with increasing droplet dilution within the supersaturation range. This behavior can not be interpreted with physical reasoning. When using σ lower than σ_w, the first strong increase in ρ_{ion} from sub- to supersaturation was diminished, until it vanished at about 68 mN m^{-1} for HULIS-sample-1 and between 60 and 65 mN m^{-1} for HULIS-sample-2. However, ρ_{ion} still decreased towards more diluted droplet solutions. This decrease could be counteracted by assuming that σ was lower than σ_w for concentrations prevailing in the hygroscopic growth regime and increased towards more diluted solutions in the activation regime.
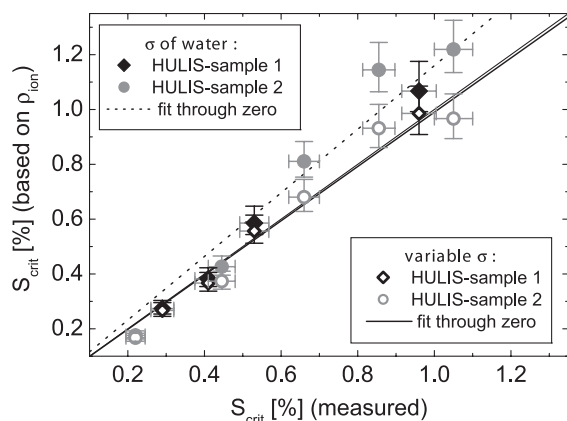
Figure 8. Comparison of measured and modeled S_{crit} for the activation of HULIS particles of the two samples. Dry diameters were 125, 100, 75 and 50 nm for HULIS-sample-1 and 167.5, 92.5, 60, 47 and 45.5 nm for HULIS-sample-2. Model results are given for both, using σ_w and using the variable σ (see figure 9 for the latter). The thin line is the 1:1 line, while the dotted and the thick line represent the linear fits through zero for the two different assumptions on σ. Slopes of the fits and R^2 values are given in table 2. The *y*-error bars originate in the uncertainty of ρ_{ion}, i.e., of the RH, while the *x*-error bars indicate the measurement uncertainty of LACIS in its supersaturation mode of operation.

A further interesting feature that can be seen from figure 7 is that ρ_{ion} derived for different values of σ does not vary much in the subsaturation regime, while it does vary strongly above saturation. This shows that hygroscopic growth is less sensitive to σ than the activation.

We estimated the deviation between measured and predicted S_{crit} that would arise from using σ_w, with the same model approach that was described for the other particle types above. For this, ρ_{ion} for HULIS-sample-1 was taken from all values obtained in the range above 95% RH (resulting in $\rho_{ion,HULIS1} = 5500$ mol m^{-3}), while only hygroscopic growth data measured with LACIS at RHs > 98% was used to derive an average ρ_{ion} for HULIS-sample-2 (resulting in $\rho_{ion,HULIS2} = 5448$ mol m^{-3}). The model results are included as filled symbols in figure 8. It can be seen that the deviation between modeled and measured S_{crit} for supersaturations above 0.6% increases strongly. This supersaturation range corresponds to dry particle diameters below 70 nm. For these particles, the difference between measured and modeled S_{crit} ranges from 0.11% to 0.29% (absolute). Smaller particles are affected more strongly, because, as already said above, particles of the same material but with smaller dry sizes have smaller growth factors at the point of activation, due to their larger Kelvin term. Thus, they are composed of more concentrated solutions. HULIS has been described as a surface active substance in the past (Kiss *et al* 2005, Salma *et al* 2006, Dinar *et al* 2006, Taraniuk *et al* 2007). And it already was reported by Szyszkowski (1908) that the surface tension of a droplet can depend on the concentration of the dissolved substance.

Based on the above described results, in a further step, a constant ρ_{ion} was used together with a variable, concentration-dependent σ (Ziese *et al* 2008). For this, an iterative process described in detail in Ziese *et al* (2008) was developed. The
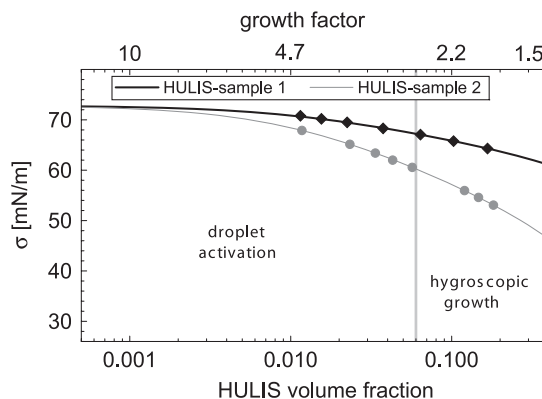

Figure 9. Values for σ varying with concentration for the two different HULIS samples, as derived in Ziese *et al* (2008). The straight gray line roughly divides the concentration range into a hygroscopic growth and an activation regime. The symbols indicate the values of σ at the respective concentration for the different measurements.

Table 2. Values for R^2 and the slope of a fit through zero (S) for the comparison of measured and modeled d_{crit} or S_{crit} for the different particle types.

Particle type	σ	R^2	S
NaCl and seawater	σ_w	0.99	1.02
Coated soot	σ_w	0.98	1.02
HULIS	σ_w	0.95	1.16
HULIS	Variable	0.97	0.99

resulting concentration-dependent values of σ are shown in figure 9. These values of σ can be interpreted as being the effective σ for the activation. Respective values for ρ_{ion} for HULIS-sample-1 and 2 were determined as 5434 and 5268 mol m^{-3}. These values are also indicated as horizontal lines in figure 7.

Using these values of ρ_{ion} together with the respective values for σ (indicated in figure 9), values of S_{crit} given as open symbols in figure 8 were derived. These values are in better agreement with the measurements than those S_{crit} derived using σ_w, with generally smaller differences between measured and modeled S_{crit} (below 0.08% (absolute)). The better agreement can also be seen from the values collected in table 2. Hence, omitting a surface tension lowering (including a possible variation of σ with concentration) can lead to an overestimation of S_{crit}, increasingly so for decreasing particle sizes.

It should be noted here that partitioning effects as described and discussed for example by Sorjamaa *et al* (2004), Kokkola *et al* (2006), Topping *et al* (2007) are implicitly included in the parameters ρ_{ion} and σ, due to the fact that these parameters were derived from measurements directly.

5. Discussion

In all of the different examples above, we found that ρ_{ion} changed with RH in the range above 90%. This change was in the range that can be expected for changing non-ideal behavior,

15–30%, for particles of NaCl, of seawater, and of the SA–AS mixture when the particles were already diluted. The change in ρ_{ion} was very pronounced for the deliquescence jump of the SA–AS particles and for HULIS-sample-2, with ρ_{ion} increasing by a factor $\geqslant 2$, respectively, in the observed RH range. This is more than would be expected for a change in non-ideal behavior with the changing particle concentration in the range examined here. The slightly soluble behavior of SA is responsible for this increase in ρ_{ion} for the SA–AS particles and we assume that HULIS-sample-2 also contained a fraction of slightly soluble substances.

When ρ_{ion} was derived at high RHs ($\geqslant 95\%$ for NaCl, seawater and HULIS-sample-1, $\geqslant 98\%$ for coated soot particles and HULIS-sample-2), it was possible to extrapolate the hygroscopic growth to the activation regime, obtaining S_{crit} or d_{crit} in good agreement with the measured values for all particle types. For all but the HULIS particles, this could be done assuming the surface tension to be that of water. Assuming a constant ρ_{ion} in the high RH range up to supersaturation was therefore shown to be eligible, at least for the particle types examined here.

The fact that modeling of S_{crit} or d_{crit} using σ_w worked out well with all examined particle types except HULIS is coherent with up-to-date knowledge, since neither inorganic salts (NaCl, AS, inorganic seawater components) nor levoglucosan would have been expected to influence σ much, whereas HULIS has been described to cause a lowering of σ before (Facchini *et al* 2000, Kiss *et al* 2005, Salma *et al* 2006, Dinar *et al* 2006, Taraniuk *et al* 2007).

The actual σ in particles during the activation process cannot be measured directly. Measurements for bulk solutions (or 'large' droplets used for the pendant droplet method, with sizes of several 100 μm to mm) are often done after σ has equilibrated. Such equilibrium values for σ measured for HULIS solutions with concentrations of 1 g l^{-1} were reported to be as low as 40–50 mN m^{-1} (Kiss *et al* 2005, Salma *et al* 2006, Taraniuk *et al* 2007). The equilibrium value for σ for a 1 g l^{-1} solution of our HULIS-sample-1 was determined as 50 mN m^{-1} (Salma *et al* 2006). No values for σ have been reported for more concentrated solutions, although a concentration of 1 g l^{-1} is still about two to three orders of magnitude below those of HULIS particles that have grown to their equilibrium sizes, and about a factor of 10–100 below those of HULIS particles that are just activating.

The measured values of σ are generally lower than the results from our investigations (see figure 9). Both Salma *et al* (2006) and Taraniuk *et al* (2007) found decreasing equilibrium values of σ with increasing concentration. However, during our measurements of S_{crit}, the particles were even more concentrated. Therefore, the difference between the values obtained from bulk solutions and those derived in our study cannot be explained by the different concentrations.

But different other reasons can be given: for example, different timescales, micelle formation, and partitioning. Concerning different timescales, Salma *et al* (2006) and Taraniuk *et al* (2007) showed measurements of a time-dependent σ, with equilibrium developing only after minutes for the examined large droplets used for the pendant drop

method. Diffusion coefficients estimated for HULIS based on these equilibrium surface tensions, as done in Taraniuk *et al* (2007), might not apply for the activation process, where equilibrium conditions cannot be assumed. Also, the concentration in solutions from which surface tensions usually are measured are at least an order of magnitude below those prevailing during activation. Taraniuk *et al* (2007) examined solution concentrations up to 3 g l^{-1}, which are below the reported critical micelle concentration (CMC) for humic acids (CMCs are given in (von Wandruszka 2000) as 'values as high as 10 g l^{-1}'), while the CMC is likely to be exceeded in activating droplets and for HULIS particles that have only grown hygroscopically. The micelle formation could increase the surface tension due to the take up of the molecules with surface active properties in the micelles. Also, partitioning between bulk and surface is likely to differ from bulk solutions (and large droplets) to activating droplets (Sorjamaa *et al* 2004, Kokkola *et al* 2006, Topping *et al* 2007). Due to these differences in the effect of surface active substances on a bulk solution and on droplets during activation, the difference between the values for the effective sigma derived in our work and those derived from bulk measurements or large droplets is not astounding.

Concluding, it has to be said that predicting S_{crit} *a priori* is difficult, even when based on hygroscopic growth measurements at high RHs. Due to the higher chemical complexity, this will be even more difficult for atmospheric aerosol particles. This applies also to studies in which the chemical composition, for example determined from mass spectrometry, is used to predict S_{crit}. Here, an additional problem occurs, due to the unknown interactions of the different chemical compounds. Therefore, using hygroscopic growth at high RHs to predict S_{crit} is advantageous, because in this case ρ_{ion} can be derived at conditions close to those at activation, having intrinsically included information on non-ideal behavior and diminishing the possibility of the presence of yet undissolved slightly soluble substances. However, no matter how the hygroscopic growth is parameterized, the efficient value of σ during the activation process still remains unknown, unless it can be assumed that using σ_w is appropriate.

6. Summary and conclusions

Hygroscopic growth up to 99.5% and S_{crit} or d_{crit} were measured for different particle types. The examined particle types consisted of either a mixture of SA and AS, NaCl, seawater, coated soot, or of one of two different HULIS samples extracted from atmospheric aerosol.

The measured hygroscopic growth data were extrapolated to the supersaturation regime and results were compared to the respective measured S_{crit} or d_{crit}. The model approach used for this extrapolation included a simple form of the Köhler equation. The Raoult term of the Köhler equation was reformulated, so that only a single parameter, ρ_{ion}, was unknown. This parameter was adjusted such that the measured hygroscopic growth was described well by the Köhler model. A separate adjustment of ρ_{ion} at the different RHs at which measurements were made showed a change in ρ_{ion} towards

large RHs. For most of the examined particle types this change was small, about 15–30%, and it can be explained by a change in non-ideal behavior. Changes by a factor of $\geqslant 2$, however, were observed for dry particles consisting of the SA–AS-mixture and for one of the two HULIS samples. For the former, the change was caused by the presence of the slightly soluble succinic acid. The presence of slightly soluble substances in the HULIS sample needs additional experimental proof.

Therefore, it becomes obvious that the assumption of a constant parameter (e.g. constant ρ_{ion}) describing the hygroscopicity in the water activity term may not always be justified, as the value of this parameter can change due to non-ideal behavior and to slightly soluble substances.

Nevertheless, on extrapolation of the measured hygroscopic growth to the activation regime, the assumption of a constant ρ_{ion} for high RHs $\geqslant 95\%$ or $\geqslant 98\%$ (depending on the substance) led to values for S_{crit} and d_{crit} that were in excellent agreement with the measured ones, indicating that for the examined substances a further large change in ρ_{ion} from high RHs to supersaturation does not have to be expected.

This extrapolation could be done assuming the surface tension of water for all but for the HULIS particles. Here, good agreement between measured and modeled S_{crit} was obtained, when a concentration-dependent σ was assumed. This is consistent with the known surface active behavior of HULIS. The values derived for σ at the points of activation, however, are larger than those that have been reported for bulk measurements or measurements on large droplets before. We propose that this discrepancy can be due to different timescales, micelle formation, or differences in the partitioning between bulk and surface in the very concentrated solutions and on the short timescales that prevail during the activation process for the HULIS particles. And we further propose that information about the effective σ that governs the activation process can be obtained by studies such as the one described for HULIS here.

However, we would also like to mention that the hygroscopic growth alone, even that at high RHs, does not give enough information to enable a prediction of the activation behavior for those cases where σ is not that of water, because hygroscopic growth, especially below 95% RH, is not sensitive to σ, whereas σ does have a large influence on the particle activation behavior (Wex *et al* 2008). The same also holds true for predictions of activation behavior based on measurements of the chemical composition, for which σ also has to be known, and which face the additional problem that interactions between the different chemical compounds are unknown, whereas they are intrinsically included in the hygroscopic growth at high RHs.

Acknowledgments

References

Asa-Awuku A, Nenes A, Sullivan A P, Hennigan C J and Weber R J 2008 Investigation of molar volume and surfactant characteristics of water-soluble compounds in biomass burning aerosol *Atmos. Chem. Phys.* **8** 799–812

Baltensperger U *et al* 2005 Secondary organic aerosols from anthropogenic and biogenic precursors *Faraday Discuss.* **130** 265–78

Bigg E 1986 Discrepancy between observation and prediction of concentrations of cloud condensation nuclei *Atmos. Res.* **20** 81–6

Brechtel F J and Kreidenweis S M 2000a Predicting particle critical supersaturation from hygroscopic growth measurements in the humidified TDMA. Part I: theory and sensitivity studies *J. Atmos. Sci.* **57** 1854–71

Brechtel F J and Kreidenweis S M 2000b Predicting particle critical supersaturation from hygroscopic growth measurements in the humidified TDMA. Part II: laboratory and ambient studies *J. Atmos. Sci.* **57** 1872–87

Broekhuizen K, Chang R Y-W, Leaitch W R, Li S-M and Abbatt J P D 2006 Closure between measured and modeled cloud condensation nuclei (CCN) using size-resolved aerosol composition in downtown Toronto *Atmos. Chem. Phys.* **6** 2513–24

Chang R Y-W, Liu P S K, Leaitch W R and Abbatt J P D 2007 Comparison between measured and predicted CCN concentrations at Egbert, Ontario: focus on the organic aerosol fraction at a semi-rural site *Atmos. Environ.* **41** 8172–82

Cruz C N and Pandis S N 1997 A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei *Atmos. Environ.* **31** 2205–14

Cruz C N and Pandis S N 1998 The effect of organic coating on the cloud condensation nuclei activation of inorganic atmospheric aerosol *J. Geophys. Res.* **103** 13111–23

Dinar E, Taraniuk I, Graber E R, Katsman S, Moise T, Anttila T, Mentel T F and Rudich Y 2006 Cloud condensation nuclei properties of model and atmospheric HULIS *Atmos. Chem. Phys.* **6** 2465–81

Facchini M C, Decesari S, Mircea M, Fuzzi S and Loglio G 2000 Surface tension of atmospheric wet aerosol and cloud/fog droplets in relation to their organic carbon content and chemical composition *Atmos. Environ.* **34** 4853–7

Forster P *et al* 2007 Changes in atmospheric constituents and in radiative forcing *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge: Cambridge University Press)

Graber E R and Rudich Y 2006 Atmospheric HULIS: how humic-like are they? A comprehensive and critical review *Atmos. Chem. Phys.* **6** 729–53

Hennig T, Massling A, Brechtel F J and Wiedensohler A 2005 A tandem DMA for highly temperature-stabilized hygroscopic particle growth measurements between 90% and 98% relative humidity *J. Aerosol Sci.* **36** 1210–23

Henning S, Rosenørn T, D'Anna B, Gola A A, Svenningsson B and Bilde M 2005 Cloud droplet activation and surface tension of mixtures of slightly soluble organics and inorganic salt *Atmos. Chem. Phys.* **5** 575–82

Huff Hartz K E, Tischuk J E, Chan M N, Chan C K, Donnahue N M and Pandis S N 2006 Cloud condensation nuclei activation of limited solubility organic aerosol *Atmos. Environ.* **40** 605–17

Kiss G, Tombacz E and Hansson H C 2005 Surface tension effects of humic-like substances in the aqueous extract of tropospheric fine aerosol *J. Atmos. Chem.* **50** 279–94

Kokkola H, Sorjamaa R, Peräniemi A, Raatikainen T and Laaksonen A 2006 Cloud formation of particles containing humic-like substances *Geophys. Res. Lett.* **33** L10816

Laaksonen A, Korhonen P, Kulmala M and Charlson R J 1998 Modification of the Köhler equation to include soluble trace gases and slightly soluble substances *J. Atmos. Sci.* **55** 853–62

Martin G M, Johnson D W and Spice A 1994 The measurement and parameterization of effective radius of droplets in warm stratocumulus clouds *J. Atmos. Sci.* **51** 1823–42

Medina J, Nenes A, Sotiropoulou R-E P, Cottrell L D, Ziemba L D, Beckman P J and Griffin R J 2007 Cloud condensation nuclei closure during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign: Effects of size-resolved composition *J. Geophys. Res.* **112** D10S31

Niedermeier D, Wex H, Voigtländer V, Stratmann F, Brüggemann E, Kiselev A, Henk H and Heintzenberg J 2008 LACIS-measurements and parameterization of sea-salt particle hygroscopic growth and activation *Atmos. Chem. Phys.* **8** 579–90

Petters M D and Kreidenweis S M 2007 A single parameter representation of hygroscopic growth and cloud condensation nucleus activity *Atmos. Chem. Phys.* **7** 1961–71

Prenni A J, DeMott P J, Kreidenweis S, Sherman D E, Russell L M and Ming Y 2001 The effects of low molecular weight dicarboxylic acids on cloud formation *J. Phys. Chem.* **105** 11240–8

Prenni A J, Petters M D, Kreidenweis S M, DeMott P and Ziemann P J 2007 Cloud droplet activation of secondary organic aerosol *J. Geophys. Res.* **112** D10223

Roberts G and Nenes A 2005 A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements *Aerosol Sci. Technol.* **39** 206–21

Rose D, Frank G P, Dusek U, Gunthe S S, Andreae M O and Pöschl U 2008 Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment *Atmos. Chem. Phys.* **8** 1153–79

Saathoff H, Neumann K-H, Schnaiter M, Schöck W, Möhler O, Schurath U, Weingartner E, Gysel M and Baltensperger U 2003 Coating of soot and $(NH_4)_2SO_4$ particles by ozonolysis products of α-pinene *J. Aerosol Sci.* **34** 1297–321

Salma I, Ocskay R, Varga I and Maenhaut W 2006 Surface tension of atmospheric humic-like substances in connection with relaxation, dilution, and solution pH *J. Geophys. Res.* **111** D23205

Sorjamaa R, Svenningsson B, Raatikainen T, Henning S, Bilde M and Laaksonen A 2004 The role of surfactants in Köhler theory reconsidered *Atmos. Chem. Phys.* **4** 2107–17

Stratmann F, Kiselev A, Wurzler S, Wendisch M, Heintzenberg J, Charlson R J, Diehl K, Wex H and Schmidt S 2004 Laboratory studies and numerical simulations of cloud droplet formation under realistic super-saturation conditions *J. Atmos. Oceanic Technol.* **21** 876–87

Stratmann F *et al* 2008 LExNo—hygroscopic growth and activation of laboratory-generated aerosol particles imitating combustion aerosols, in preparation

Stroud C A *et al* 2007 Cloud activating properties of aerosol observed during CELTIC *J. Atmos. Sci.* **64** 441–59

Svenningsson B *et al* 2006 Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance *Atmos. Chem. Phys.* **6** 1937–52

Szyszkowski B 1908 Experimentelle Studien über kapillare Eigenschaften der wässrigen Lösungen von Fettsäuren *Z. Phys. Chem.* **64** 385–414

Taraniuk I, Graber E R, Kostinski A and Rudich Y 2007 Surfactant properties of atmospheric and model humic-like substances (HULIS) *Geophys. Res. Lett.* **34** L16807

Topping D O, McFiggans G B, Kiss G, Varga Z, Facchini M C, Decesari S and Mircea M 2007 Surface tension of multi-component mixed inorganic/organic aqueous systems of atmospheric significance: measurements, model predictions and importance for cloud activation predictions *Atmos. Chem. Phys.* **7** 2371–98

VanReken T M, Ng N L, Flagan R C and Seinfeld J H 2005 Cloud condensation nucleus activation properties of biogenic secondary organic aerosol *J. Geophys. Res.* **110** D07206

Varutbangkul V, Brechtel F J, Bahreini R, Ng N L, Keywood M D, Kroll J H, Flagan R C, Seinfeld J H, Lee A and Goldstein A H 2006 Hygroscopicity of secondary organic aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related compounds *Atmos. Chem. Phys.* **6** 2367–88

Vestin A, Rissler J, Swietlicki E, Frank G P and Andreae M O 2007 Cloud-nucleating properties of the Amazonian biomass burning aerosol: cloud condensation nuclei measurements and modeling *J. Geophys. Res.* **112** D14201

Virkkula A, van Dingenen R, Raes F and Hjorth J 1999 Hygroscopic properties of aerosol formed by oxidation of limonene, α-pinene, and β-pinene *J. Geophys. Res.* **104** 3569–79

von Wandruszka R 2000 Humic acids: their detergent qualities and potential uses in pollution remediation *Geochem. Trans.* **1** 10

Wex H, Kiselev A, Stratmann F, Zoboki J and Brechtel F 2005 Measured and modeled equilibrium sizes of NaCl and $(NH_4)_2SO_4$ particles at relative humidities up to 99.1% *J. Geophys. Res.* **110** D21212

Wex H, Kiselev A, Ziese M and Stratmann F 2006 Calibration of LACIS as a CCN detector and its use in measuring activation and hygroscopic growth of atmospheric aerosol particles *Atmos. Chem. Phys.* **6** 4519–27

Wex H, Hennig T, Salma I, Ocskay R, Kiselev A, Henning S, Massling A, Wiedensohler A and Stratmann F 2007a Hygroscopic growth and measured and modeled critical super-saturations of an atmospheric HULIS sample *Geophys. Res. Lett.* **34** L02818

Wex H, Ziese M, Kiselev A, Henning S and Stratmann F 2007b Deliquescence and hygroscopic growth of succinic acid particles measured with LACIS *Geophys. Res. Lett.* **34** L17810

Wex H, Stratmann F, Topping D and McFiggans G 2008 The Kelvin versus the Raoult term in the Köhler equation *J. Atmos. Sci.* at press

Ziese M, Wex H, Nilsson E, Salma I, Ocskay R, Hennig T, Massling A and Stratmann F 2008 Hygroscopic growth and activation of HULIS particles: experimental data and a new iterative parameterization scheme for complex aerosol particles *Atmos. Chem. Phys.* **8** 1855–66