HYGROSCOPICITY OF SECONDARY ORGANIC AEROSOL – Laboratory studies

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1. Hygroscopic properties of aerosol particles

Atmospheric aerosol particles play an important role in the global climate change and in the chemistry of the troposphere. Aerosol particles influence the Earth’s radiative budget both directly and indirectly. The direct effect is connected with scattering and absorption of incoming radiation by the aerosol particles. On the other hand, aerosol particles act as cloud condensation nuclei (CCN). Cloud properties and precipitation are influenced by number concentration and size distribution of the cloud droplets. This indirect effect of aerosol particles leads to changes of the planetary albedo and hydrological cycle (Lohmann and Feichter, 2005). In addition, tropospheric aerosols are highly variable in space and time, and hence it is important to know how they are produced and transformed during transport.

Hygroscopic water uptake of atmospheric particles is of particular importance for all above mentioned effects, mainly because of increased particle sizes under high relative humidity (RH) conditions. Light scattering cross section and airway deposition efficiency strongly depend on particle size (Martin et al., 2004). CCN activity and hence potential aerosol cloud interactions are larger for hygroscopic particles, because hygroscopic growth enables them to overcome the Kelvin barrier at lower supersaturation. Lifetimes of atmospheric aerosol particles are also linked with CCN activity since wet deposition is the major pathway of aerosol removal apart from dry deposition (Bilde and Svenningsson, 2004). Changes in aerosol water uptake behavior can therefore lead to changes in both direct and indirect radiative forcing of climate (IPCC, 2001). Besides atmospheric relevance, hygroscopic growth is a crucial point in many aerosol measurement applications, simply because water condensation or evaporation alters many aerosol physical properties (e.g. size, mass, and optical properties) as soon as the instruments are not operated at ambient RH.

The hygroscopicity of aerosol particles is commonly express in terms of particle size or mass changes as a function of relative humidity (RH) under saturation conditions. The aerosol water content is obtained by comparing the wet and dry particle sizes or masses. When deliquescence (water uptake to form a solution) and efflorescence (water release to form a crystal) phase transition occur, a spontaneous sharp change in particle size arises.
Hygroscopicity data are important in parameterizing thermodynamic models and interpreting the mixing state of atmospheric particles (Chan et al., 1997; Clegg et al., 1997). They are also needed for modeling the physico-chemical properties of atmospheric particles, including their roles in global radiative forcing (Martin, 2000) and CCN activity (Rissler et al., 2004; Kreidenweis et al., 2005).

It is now widely recognized that understanding the impact of organic matter on the aerosol hygroscopicity and the RH of phase transitions is considerable important. However, the influence of chemical composition of these properties remains poorly characterized and is not yet fully understood. Unlike the inorganic fraction, which is now well-characterized, only a minor fraction of the organic components is identified. The organic components are ubiquitous in the atmospheric aerosol. The presence of organic compounds can alter the hygroscopic behavior of inorganic aerosol (Sanxena et al., 1995).

A large wide variety of experimental techniques are used to measure the hygroscopic growth of aerosol particles with its specific advantages and handicaps. These techniques are based on the detection of the effect of water absorption on particle mass, optical properties, or diameter. For examples, mass growth factor measurements are either conducted with the electrodynamic balance (EDB) technique where a single particle is levitated in an electromagnetic field under controlled RH conditions, or by mass determination of humidity controlled filter or impactor samples where the sample mass is determined by gravimetry, gas chromatography using thermal conductivity detection (GC-TCD) or a tapered element oscillating microbalance (TEOM). The tandem differential mobility analyzer (TDMA), also called Hygroscopic TDMA by some researchers (Liu et al., 1978; Rader and McMurry, 1986; Gysel et al., 2004) has been widely used in laboratory studies to determine the hygroscopic proprieties of SOA formed in environmental chambers. A key issue is investigating the hygroscopicity of the particles is if the particles have attained their equilibrium state in the measurement. Secondary organic aerosol (SOA) is formed by the gas particle partitioning of low-volatility oxidation products of gaseous organic species and can make up a significant fraction of the organic aerosol mass in urban areas. Biogenic terpenes have been identified as precursors of SOA, predominantly in rural or forested areas. Knowledge of
water uptake properties of the SOA is required for understanding aerosol evolution and its effect on the regional visibility, cloud formation and climate.

2. Hygroscopicity measurements

The most common device for hygroscopicity measurements is Hygroscopic Tandem Differential Mobility Analyzer (H-TDMA). Over the last 25 yr, H-TDMA instruments have been used in laboratory studies and field campaigns in various environments globally to determine the water uptake on submicrometre particles at subsaturated conditions (Swietlicki et al., 2008). The H-TDMA is designed based on the pioneering work (TDMA) of Liu et al. (1978). The principle of H-TDMA is to extract a narrow size cut from a polydisperse aerosol, expose this to a well defined enhanced relative humidity (RH) and determine the increase of the particle diameter due to the water uptake at this enhanced RH (Swietlicki et al., 2008).

2.1 Operation principle of H-TDMA

A schematic drawing of the H-TDMA system is shown in Fig. 1 (Massling et al., 2007). The H-TDMA setup consists of two DMAs in series. The first DMA is used to select monodisperse particles from particle population dried prior to sampling. The air flow leaving the first DMA is divided into two parts. One of them is directed to the first condensation particle counter (CPC), where the particle number is counted. Another part is humidified by passing through an aerosol humidifier with a given RH. Afterwards, the number size distribution of conditioned particles is measured by the second DMA combined with the second CPC. The RH in the sheath and excess flows for the second DMA are controlled. The detailed description of this system can be found in Massling (2002) or Väkevä (2002).
The output of the H-TDMA system is the hygroscopic growth factors, $GF$, defined by the ratio of the wet to the dry particle number mean diameter (Eq. 1) at a given RH (Massling et al., 2007).

$$GF = \frac{D_{P, wet}}{D_{P, dry}} \quad (1)$$

The $GF$ can be converted into a soluble fraction of particles ($\varepsilon$) (Svenningsson et al., 1994). When calculating $\varepsilon$ from H-TDMA data, a reference compound is needed. For $(\text{NH}_4)_2\text{SO}_4$, $\varepsilon_{AS}$ is calculated according to:

$$\varepsilon_{AS} = \frac{GF_{AS}^3 - 1}{GF_{AS}^3 - 1} \quad (2)$$

Here, $GF$ is the measured diameter growth factor, $GF_{AS}$ is the growth factor of a fully soluble particle composed entirely of the same solute material, in this case ammonium sulphate ($\varepsilon_{AS} = 1$), for the same humidified size and RH as for the observed particle (Swietlicki et al., 2008). The soluble volume fraction $\varepsilon$ can be considered as a proxy for the chemical composition. Thus, hygroscopicity can be utilized to infer the chemical information on the measured particles. The output of H-TDMA can also provide the information on mixing state of the atmospheric aerosols.

With regard to the measurement errors, Svenningsson et al. (2008) summarized the sources of measurement errors for H-TDMA measurement very recently. The error sources include: (1) RH and temperature variability; (2) the DMA electrical mobility classification; (3) particle non-equilibrium conditions in the second DMA. They also
pointed out that the reported $G_f$ obtained from H-TDMA measurements are estimated to within $\pm 0.05$.

### 2.2 Improvement of H-TDMA

During recent years, there are some instruments for hygroscopicity measurements were developed. In the following paragraphs, these improved instruments will be introduced individually in brief.

In order to measure aerodynamic hygroscopic growth factor of big aerosol particles, a new setup based on the combination of a differential mobility analyser (DMA) and aerodynamic particle sizer (APS) is developed by Leinert and Wiedensohler (2008). This setup named H-DMA-APS can measure the aerodynamic hygroscopic growth at up to 90% RH for micrometer-size aerosol particles. Fig. 2 shows the schematic drawing of this setup.

![Figure 2: Schematic setup of H-DMA-APS (Leinert & Wiedensohler, 2008).](image_url)

About hygroscopicity measurements for nanoparticles, Sakurai et al. (2003a, b) developed the setup, Nano-TDMA, which can detect the particles down to 4 nm. Previously, they used this system to study the diesel nanoparticles. Recently, the system was utilized to infer the chemical composition of the newly formed particles in ambient atmosphere (Sakurai et al., 2005).
In 2005, Henniga et al. (2005) described a design of a high humidity tandem differential mobility analyzer (HHTDMA) to determine aerosol hygroscopic growth factors at RH between 90% and 98% under highly temperature-stabilized conditions. This setup is displayed in Fig. 3. This setup was mainly used in laboratory studies (Wex, et al., 2007). Weingartner et al. (2002) developed a low-temperature H-TDMA system to avoid volatilization of semi-volatile material during measurements at subfreezing temperatures at a high alpine site.

Cubison et al. (2005) present a new design of hygroscopic tandem differential mobility analyser (HTDMA) capable of rapidly switching between measurement at constant humidity and the determination of humidograms.

For studying aerosol particles interactions with organic vapor, Joutsensaari et al. (2001) developed and constructed a novel instrument, Organic Tandem Differential Mobility Analyzer (OTDMA). The main idea is to use the organic vapor in the system instead of water vapor. The structure of OTDMA is shown in Fig. 4.
3. Hygroscopic properties of SOA - state of knowledge

Currently, few laboratory studies on the hygroscopicity of secondary organic aerosol (SOA) formed in environmental chambers exist. Most of these studies provide information about the growth factors (GF, defined as the ratio between wet and dry particle diameter) of SOA obtained from various precursors in the presence or absence of seed aerosol (ammonium sulfate, diesel soot, ‘Palas’ soot) (Varakutbangkul et al., 2006; Saathoff et al., 2003; Baltensberger et al., 2005; Cocker et al. (2001a)), whereas only few experiments have been made to establish the ability of SOA to act as CCN (VanReken et al., 2005; Huff Hartz et al., 2005, Prenni et al., 2007).

3.1 Hygroscopicity of pure SOA

All studies reported that the pure SOA products are slightly hygroscopic and do not exhibit deliquescence or efflorescence behavior. For example, Varakutbangkul et al., 2006, measured the GFs (at 85%RH) between 1.09-1.16 for ozonolysis products of cycloalkenes, 1.06-1.1 for photooxidized monoterpenes and oxygenated terpenes and 1.01-1.04 for photooxidized sesquiterpenes. They explain the lowest values as being due to the formation of less hygroscopic oligomers, whereas the larger values are attributed to the
formation of highly oxidized species which tend to be more hygroscopic. Similar values have been reported by Virkkula et al., 1999, GF=1.1 at 84 %RH for products of α-pinene and limonene. The authors found that the mechanisms of SOA formation may influence to some extent the GFs. The reaction products of photooxidation of α-pinene were found to be slightly more hygroscopic (GF=1.09 ± 0.01) than the reaction products of ozonolysis of α-pinene (GF=1.07 ± 0.01). Saathoff et al., 2003 observed an increase of hygroscopicity of oxidation products of α-pinene with the residence time in the chamber. The GF measured for particles of 100 and 200 nm was 1.106 ± 0.002 at 85 %RH, which is in agreement with the aforementioned studies. Baltensberger et al., 2005, have measured as well an increase in the hygroscopicity of 1,3,5 trimethylbenzene SOA during the first 7 hours of the experiment, and no changes after this time. The humidograms of 1,3,5 trimethylbenzene SOA were found to resemble those of humic-like substances, with the exception that the latest shows efflorescence. Cocker et al., (2001a) also found that the GF of SOA from photooxidation of m-xylene, photooxidation of 1,3,5 trimethylbenzene and ozonolysis increases in the first 7 hours of the experiment.

3.2 Hygroscopicity of seeded SOA

Varatbangkul et al., (2006), Virkkula et al., (1999), have investigated the hygroscopic proprieties of SOA formed in presence of (NH₄)₂SO₄ aerosol. Their results indicate that the organic fraction has no influence on the deliquescence of (NH₄)₂SO₄ which occurred at 80% RH, same as for the pure (NH₄)₂SO₄. Both authors found also a decrease of the GF of (NH₄)₂SO₄ particles when SOA condenses on their surface. Varatbangkul et al., (2006), measured at the beginning of the seeded experiment a GF which was equal to that of pure (NH₄)₂SO₄ but decreased after the less hygroscopic oxidation products partitioned into the particle phase. Virkkula et al., (2003) reported that the GF of (NH₄)₂SO₄ decreased from 1.5 before the start of terpene oxidation to 1.1 at 84 %RH (which is closed to that observed for the pure organic aerosol) as the oxidation products condensed on the particle. The GF was found to be inverse proportional to the organic volume fraction and not the thickness of the organic layer. This indicates that the total water uptake can be represented as the sum of the water taken up by the organic and inorganic
fraction. Cocker et al., (2001a) have investigated the hygroscopicity SOA formed by ozonolysis of $\alpha$-pinene in presence of (NH$_4$)$_2$SO$_4$ aerosol. They also found a reduction of GF of (NH$_4$)$_2$SO$_4$ seed. A reduction in the GF of SOA containing a (NH$_4$)$_2$SO$_4$ has also been reported by Meyer et al., (2008), which measured a GF of 1.07 after a 1.7 hour of the experiment.

Saathoff et al., (2003) have performed $\alpha$-pinene ozonolysis experiments in presence of diesel soot, ‘Palas’ soot and (NH$_4$)$_2$SO$_4$ seed. They measured for SOA coated (NH$_4$)$_2$SO$_4$ a GF of 1.121 at RH=90.3 % (after 6 hours of the experiment), 1.1 and 1.08 at RH= 90% for SOA coated diesel particles (for 100 and 200 nm sized particles) and 0.932 and 0.92 for SOA coated ‘Palas’soot. The fact that the latest values are smaller than 1 is explained by the authors as being due to the compaction of the soot agglomerates induced by the SOA coating.

It has been shown that the presence of a SOA in a particle can reduce significantly the hygroscopicity of aerosol particles at high RHs, compared with that of pure inorganics, but does not suppress it. On the other hand the SOA present in an aerosol particle can extend the range of RHs over which the particles take up water, contributing in this way to the aerosol physicochemical and optical proprieties. The values observed for the GFs of seeded SOA as well of purely nucleated SOA can explain the values of 1.1 often measured for the ‘less hygroscopic mode’ of continental atmospheric aerosol (Virkkula et al., (1999)).

3.3 Cloud droplet activation of SOA

At the moment there are only few studies on the ability of SOA to act as CCN nuclei. VanReken et al., studied the CCN activation of SOA formed by monoterpenes ozonolysis. They reported that $\alpha$-pinene SOA was the least CCN active and limonene SOA was the most CCN active, but all SOA became less CCN active with time. Nevertheless, their results are not in agreement with those of Prenni et al., (2007), which did not observe a significant change with time in the CCN activity of $\alpha$-pinene SOA and neither that the CCN activity depends on the SOA precursors.
Huff Hartz et al., (2005) investigated the ability of SOA from ozonolysis of monoterpenes and sesquiterpenes to act as CCN. Monoterpenes SOA was found to activate as highly water soluble organics whereas sesquiterpenes SOA is less active.

4. Problems and research needed

Up to now, there have been few laboratory investigations on the hygroscopicity of SOA. Those that exist are based on a limited number of hydrocarbon precursors, and some provide data on growth factors only at a single RH. More laboratory and environmental chamber experiments under atmospherically relevant conditions are required to elucidate the SOA formation pathways (heterogeneous and multiphase reaction pathways) and their ageing processes.

In order to obtain more accurate information on SOA hygroscopicity, the improvement of the measurements techniques needs to be done. The current hygroscopicity measurements with H-TMDA are very sensitive to the RH and temperature of DMA2. Usually, the RH and temperature under laboratory conditions can be controlled very well. But, it is difficult for the field measurements. This may lead to larger measurement uncertainties. So, minimizing the influence of RH and temperature variability is a real challenge. Up to now, most of the H-TMDA data is taken at only one RH (often 90%), making it difficult to draw firm conclusions regarding the behavior at lower RH, which may involve deliquescence and the existence of metastable states (Swietlicki et al., 2008). Therefore, the investigation of hygroscopic properties of particles under different RH should be performed for the future studies.

Another issue related to the operating principle of H-TDMAs is whether the particles have attained equilibrium state in the measurements. In most TDMA studies, a residence time in the order of seconds is used to humidification or dehumidification. There have been observations that not all types of submicrometer particles, including atmospheric particles, attain their equilibrium sized within this time scale. Therefore experiment with different residence times should be conducted and explicitly stated in future TDMA measurements.
References


