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Hygroscopicity of nanoparticles produced from homogeneous nucleation in the CLOUD experiments

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Abstract

Sulfuric acid, amines and oxidized organics have been found to be important compounds in the nucleation and initial growth of atmospheric particles. Because of the challenges involved in determining the chemical composition of objects with very small mass, however, the properties of the freshly nucleated particles and the detailed pathways of their formation processes are still not clear. In this study, we focus on a challenging size range, i.e. particles that have grown to diameters of 10 and 15 nm following nucleation, and measure their water uptake. Water uptake constrains their chemical composition. We use a nanometer-hygroscopicity tandem differential mobility analyzer (nano-HTDMA) at subsaturated conditions (ca. 90 % relative humidity at 293 K) to measure the hygroscopicity of particles during the seventh Cosmics Leaving OUtdoor Droplets (CLOUD7) experiments performed at CERN in 2012. In CLOUD7, the hygroscopicity of nucleated nanoparticles was measured in the presence of sulfuric acid, sulfuric acid-dimethylamine, and sulfuric acid-organics derived from α-pinene oxidation. The hygroscopicity parameter κ decreased with increasing particle size indicating decreasing acidity of particles. No clear effect of the sulfuric acid monomer concentrations on the hygroscopicities of 10 nm particles produced from sulfuric acid and dimethylamine was observed, whereas the hygroscopicity of 15 nm particles sharply decreased with decreasing sulfuric acid monomer concentrations. In particular, when the concentrations of sulfuric acid was 5.1×10^6 molecules cm^{-3} in the gas phase, and the dimethylamine mixing ratio was 11.8 ppt, the measured κ of 15 nm particles was 0.31 ± 0.01 close to the value reported for dimethylamine sulfate (DMAS) ($\kappa_{\mathrm{DMAS}} \sim 0.28$). Furthermore, the difference in κ between sulfuric acid and sulfuric acid-dimethylamine experiments increased with increasing particle size. The κ values of particles in the presence of sulfuric acid and organics were much smaller than those of particles in the presence of sulfuric acid and dimethylamine. This suggests that the organics produced from α-pinene ozonolysis play a significant role in particle growth already at 10 nm sizes.

1 Introduction

Aerosol particles can be directly emitted into the atmosphere from natural and anthropogenic sources (primary aerosols) or can be produced by gas-to-particle conversion process (secondary aerosols). They affect regional and global climate by absorbing and scattering light and by acting as cloud condensation nuclei (CCN) and ice nuclei (IN). Although physical and chemical properties of atmospheric aerosol particles have been widely studied, large uncertainties remain, both in their direct and indirect climate effects (IPCC, 2013). Hygroscopicity, the ability of particles to take up water, is important when considering climate effects, and can usefully constrain the chemical composition of size-resolved nanoparticles (Riipinen et al., 2009; Ristovski et al., 2010; Sakurai et al., 2005).

Experimental and theoretical studies have shown that sulfuric acid is an important ingredient in particle formation (Kulmala et al., 2004; Weber et al., 1997). It has also been shown that new particle formation in the boundary layer cannot be explained by pure sulfuric acid-water nucleation (Kirkby et al., 2011). Other compounds such as ammonia and/or organics are needed to explain observed atmospheric particle formation and growth, and have thus been widely studied. Much of the recent focus has been on the effect of amines on particle formation. Both experimental and computational studies have indicated that amines enhance particle formation significantly more than ammonia (Almeida et al., 2013; Barsanti et al., 2009; Berndt et al., 2010; Bzdek et al., 2010; Erupe et al., 2011; Kurtén et al., 2008; Kürten et al., 2014; Loukonen et al., 2010; Paasonen et al., 2012; Pratt et al., 2009; Zhao et al., 2011). Moreover, alkylaminium salts in atmospheric particles with sizes of 8–10 nm have been observed during new nanoparticle formation events (Smith et al., 2010). Still, physicochemical properties of nanoparticles produced by homogeneous nucleation of amines with sulfuric acid-water and their subsequent growth are not yet well understood.

Both laboratory experiments and field observations have shown that organic compounds play important roles in atmospheric particle formation and growth and make up a large fraction of the submicron aerosol mass (Hallquist et al., 2009; Jimenez et al., 2009; Metzger et al., 2010). Most chamber studies have focused either on secondary organic aerosol (SOA) mass yields or on identifying and quantifying the compounds produced from oxidation (Griffin et al., 1999; Hao et al., 2011; Hennigan et al., 2011; Kroll et al., 2005). Chemical aging processes with various oxidants have also been studied (Donahue et al., 2012; Henry and Donahue, 2012; Henry et al., 2012; Pierce et al., 2011; Yasmeen et al., 2012). Several useful studies also have been performed on the hygroscopic properties of SOA produced either in laboratory or in the atmosphere, including the effect of oxygen-carbon (O : C) ratio on hygroscopicity (Chang et al., 2010; Duplissy et al., 2011; Engelhart et al., 2008; Frosch et al., 2011; Jimenez et al., 2009; Lambe et al., 2011; Massoli et al., 2010; Roberts et al., 2010; Sjogren et al., 2008; Varutbangkul et al., 2006; Virkkula et al., 1999). Jimenez et al. (2009) and Duplissy et al. (2011) found that hygroscopicity of SOA increased with increasing oxidation level at subsaturated conditions (ca. 90–95 % RH), while Frosch et al. (2011) showed that the relationship between the hygroscopicity of particles with diameters in the 59–200 nm range and O : C ratio in the 0.3–0.6 range was weak at supersaturated conditions. Massoli et al. (2010) reported that the hygroscopicity parameter increased with oxidation level both in subsaturated and supersaturated conditions. Although many studies on physical and chemical properties of SOA have been performed, there are still significant gaps in our understanding of the detailed initial growth pathways, and of the properties of freshly nucleated nanoparticles.

In this study, we focus on determining the hygroscopicity of nanoparticles generated by homogeneous nucleation of sulfuric acid with organic compounds such as dimethylamine and α-pinene oxidation products in the CLOUD chamber at CERN. The measurements were performed with a nanometer-hygroscopicity tandem differential mobility analyzer (nano-HTDMA) (Keskinen et al., 2011) during the CLOUD7 experiments. Volume fractions of inorganic sulfates and dimethylamine sulfate (DMAS) in the nanoparticles were estimated from nano-HTDMA results and Zdanovskii–Stokes–Robinson (ZSR) relation (Choi and Chan, 2002; Kim et al., 2011; Meyer et al., 2009;

Petters and Kreidenweis, 2007). Moreover, simulation results from thermodynamic phase equilibrium model E-AIM (Extended Aerosol Inorganics Model; Clegg et al., 1992; Ge et al., 2011; Wexler and Clegg, 2002; http://www.aim.env.uea.ac.uk/aim/aim.php) were combined to provide further information on chemical properties of nucleated nanoparticles.

2 Experimental methods

2.1 CLOUD chamber

The experiments were carried out with the CLOUD chamber at CERN which has been described by Kirkby et al. (2010) and Almeida et al. (2013). In brief, the CLOUD chamber is a cylindrical electropolished stainless steel tank with a volume of 26.1 m^3. An ultraviolet (UV) light system which can control the aperture of the UV light (Kupc et al., 2011) and two stainless steel fans for mixing vapors (Voigtländer et al., 2012) are installed in the chamber. During CLOUD7 experiments, temperature and relative humidity in the chamber were constant at 278 K (±0.5 K) and 38 % (±1 %), respectively. The experiments could be classified into three groups depending on the nucleation conditions; neutral (N), ground-level galactic cosmic rays (GCR), and charged pion beam (π). In the neutral nucleation experiments, small ions in the chamber were removed with electric fields (±20 $kV\,m^{-1}$). The chamber was exposed to a positively-charged pion beam (Duplissy et al., 2010) during the charged pion beam nucleation experiments, whereas no electric clearing fields and no pion beam were used at GCR condition. Precursor vapors such as sulfur dioxide (SO_2), dimethylamine ($(CH_3)_2NH$), and α-pinene ($C_{10}H_{16}$) were continuously provided into the CLOUD chamber to produce particles.

Size distributions of particles produced in the chamber were continuously monitored with a scanning mobility particle sizer (SMPS). Sulfuric acid concentration was measured using a chemical ionization mass spectrometer (CIMS) (Kürten et al., 2011), concentrations of dimethylamine, ammonia, and α-pinene were observed with a proton transfer reaction-time-of-flight mass spectrometer (PTR-TOF-MS) (Schnitzhofer et al., 2014). The concentrations of SO_2 and O_3 were also continuously measured by a SO_2 detector (42i-TLE, Thermo Fisher Scientific, Inc.) and an O_3 monitor (TEI 49C, Thermo Environmental Instruments), respectively. The detailed experimental conditions performed in this study can be seen in Table 1.

2.2 Nano-HTDMA

The nano-HTDMA system (Keskinen et al., 2011) was applied to determine hygroscopic growth of nucleated nanoparticles at a constant subsaturated relative humidity. It consisted of two different mobility analyzers (DMA1 and DMA2; TSI 3085, USA) (Chen et al., 1998), an aerosol humidifier, and a condensation particle counter (CPC; TSI 3785, USA), as shown in Fig. 1. The TDMA measurement technique has been described in previous studies (McMurry and Stolzenburg, 1989; Hämeri et al., 2000; Sakurai et al., 2005). Briefly, nanoparticles generated in the CLOUD chamber were dried to about 10–15 % RH, and then passed through a bipolar diffusion charger (^{85}Kr, TSI) before entering the nano-HTDMA system. The nanoparticles with a certain electrical mobility were classified from charged polydisperse aerosols by DMA1. The RH of aerosol sample after passing through DMA1 was ~ 4.5 %. The selected nanoparticles passed through the aerosol humidifier made from GoreTex tubing with a 5 s residence time at the targeted RH. This residence time should be enough for the particle to reach their equilibrium GF (Duplissy et al., 2009). The relative humidity (RH) of the aerosol flow, the sheath air, and the excess air in DMA2 were continuously monitored using capacitive RH sensors (Vaisala model HMP 110). The RH was kept constant to within 1.5 % of the set values. After humidifying, the size and number concentration of the particles were measured with DMA2 and CPC to determine the change in particle size due to interaction with water vapor. Based on these results, log-normal number size distributions were fitted to the distributions to estimate the geometric mean diameter (GMD) with a standard DMA data inversion algorithm (Reischl, 1991). The use of GMD is relevant for this study as the sampled aerosol were internally mixed. In this study, the measurements were performed at $90 \pm 1.5\,\%$ RH for 10 and 15 nm particles. The flow rate of the aerosol sample was $1\,\mathrm{L\,min^{-1}}$. The ratio of sample aerosol flow to sheath air flow of the DMA was 1 : 10. The calibration of the nano-HTDMA was carried out by using sodium chloride and ammonium sulfate nanoparticles before and after the CLOUD7 experiments.

3 Data analysis and theory

3.1 Hygroscopic growth factor and hygroscopicity parameter κ

The hygroscopic growth factor (HGF) is a measure of the diameter growth of the size-selected particles at a certain RH compared with dry conditions, and is defined as:

$$\mathrm{HGF} = \frac{d_{\mathrm{p,GMD}}(\mathrm{RH})}{d_{\mathrm{P,GMD}}(\mathrm{dry})} \qquad (1)$$

where $d_{\mathrm{p,GMD}}(\mathrm{RH})$ is the geometric mean diameter (GMD) of the particles at the elevated RH (ca. 90 %) and $d_{\mathrm{p,GMD}}(\mathrm{dry})$ is the GMD for particles at dry conditions ($\sim 4.5\,\%$ RH).

In many cases it is useful to represent hygroscopic properties with a single hygroscopicity parameter κ, defined by Petters and Kreidenweis (2007):

$$\kappa = (\mathrm{HGF}^3 - 1)\left(\frac{K_e}{S} - 1\right) \qquad (2)$$

where S is the saturation ratio ($S = \frac{\mathrm{RH}}{100}$) and K_e the Kelvin factor, defined as below:

$$K_e = \exp\left(\frac{4M_{\mathrm{w}}\sigma_{\mathrm{w}}}{RT\rho_{\mathrm{w}}d_{\mathrm{p}}}\right). \qquad (3)$$

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Here M_w is the molecular weight of water, σ_w the surface tension of the water, R the ideal gas constant, T the temperature, ρ_w the density of water, and d_p the diameter after humidification ($d_\mathrm{p,GMD}(\mathrm{RH}) = d_\mathrm{p,GMD}(\mathrm{dry}) \times \mathrm{HGF}$). The κ values are in the range from zero for insoluble particles such as black carbon to larger than one for water soluble salt particles (Jurányi et al., 2009; Petters and Kreidenweis, 2007).

In order to obtain indirect chemical composition information from the nano-HTDMA results in experiments B–D (Table 1), we use the Zdanovskii–Stokes–Robinson (ZSR) relation that assumes that the water uptake volume of a mixture is the independent sum of the water uptake volume of each individual component. The organic volume fraction can then be estimated by assuming a two-component system consisting of organic and inorganic sulfate as (Keskinen et al., 2013):

$$\varepsilon_\mathrm{DMAS} = \frac{(\kappa - \kappa_\mathrm{inorg})}{(\kappa_\mathrm{DMAS} - \kappa_\mathrm{inorg})} \tag{4}$$

where κ is the hygroscopicity obtained from the nano-HTDMA measurements, κ_DMAS and κ_inorg are hygroscopicity parameters for dimethylamine sulfate (DMAS) and inorganic sulfates, respectively. In this study, we assumed that the inorganic sulfates in the particles are sulfuric acid and ammonium sulfate. Although ammonia was not injected in the chamber during these experiments, measurements by the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS; Smith et al., 2004) showed that ammonium is a significant constituent of 5–20 nm particles during these new particle formation events (Lawler et al., 2015). To obtain better approximation of DMAS volume fraction, we assumed that inorganic sulfates also consist of ammonium sulfate in addition to sulfuric acid. Keskinen et al. (2013) showed that hygroscopic properties of particles at a diameter of 150 nm in the presence of sulfuric acid and ammonia are in good agreement with theoretical predictions of ammonium sulfate. The κ_inorg values of sulfuric acid and ammonium sulfate were assumed as 0.70 (Sullivan et al., 2010) and 0.47 (Topping et al., 2005), respectively. The κ_DMAS was assumed as 0.28 derived from hygroscopic growth factors for dry diameters 80–240 nm measured by Qiu and Zhang (2012).

3.2 Thermodynamic equilibrium modeling

The E-AIM was used to estimate molecular ratio of base and acid for particles consisting of sulfuric acid, dimethylamine, and ammonia. In the model, acid deprotonation and base protonation are taken into account in the aqueous phase. Sulfuric acid is a strong acid and is assumed to deprotonate at least singly when present in aqueous solutions. It may also deprotonate a second time to form sulfate ions. Dimethylamine and ammonia are bases that have a single protonation product. Mole fractions of the deprotonated acids and protonated bases are estimated using the acid dissociation constants of the compounds defined in E-AIM (Ge et al., 2011). The density of the aqueous solution in the model is parameterized according to Clegg et al. (2013) and surface tension is obtained from measurements by Hyvärinen et al. (2004). The E-AIM does not take into account the surface curvature of particles. Thus, when estimating the water uptake of a nanoparticle with a certain dry size and composition, the equilibrium vapor pressure for water vapor obtained from E-AIM needs to be corrected for the Kelvin effect by multiplying with the Kelvin term, which requires iterating to find the equilibrium.

Based on the TDCIMS observation (Lawler et al., 2015), we assumed that particles consisted of sulfuric acid, dimethylamine, and ammonia and that the base in the particle consisted of 50 % dimethylamine and 50 % ammonia. Also, we assumed that no particle evaporation took place in the sampling lines or in the instrument. The assumption was tested by modelling the particle evaporation in the sampling lines and inside the HTDMA and based on the model results the evaporation was negligible (Ahlm et al., 2015). By calculating the water uptake (and the resulting HGF) in E-AIM for particles of different base/acid molecular ratios, the composition of the particles could be estimated.

4 Results and discussion

4.1 The role of dimethylamine or α-pinene secondary organic compounds in hygroscopicities of nucleated nanoparticles

In this section, the role of dimethylamine or α-pinene secondary organic compounds in defining the hygroscopicities of nanoparticles is investigated (Exp. A and D–F). The concentrations of sulfuric acid, dimethylamine, and α-pinene in the chamber for the different experiments are shown in Table 1. The κ values of 10 and 15 nm particles produced by sulfuric acid, sulfuric acid-dimethylamine, and sulfuric acid-organics are shown in Fig. 2. In Exp. A, the hygroscopicities of particles in the presence of sulfuric acid only were examined. The κ values (± standard deviation) of nucleated nanoparticles were 0.64 ± 0.02 and 0.52 ± 0.02 for 10 and 15 nm, respectively (the HGF of 10 and 15 nm particles were 1.55 ± 0.02 and 1.56 ± 0.02, as shown in Table 1). Here the error bars represent the standard deviation of the measurements from the mean value. The κ values are slightly lower than previous results for sulfuric acid ($\kappa_{H_2SO_4} \sim 0.7$) reported elsewhere (Shantz et al., 2008; Sullivan et al., 2010). Also, the theoretical values for $\kappa_{H_2SO_4}$ corresponding to our experimental conditions and calculated by E-AIM is 1.1 (at RH 90 %). The reason for the lower measured κ values of the nucleated nanoparticles can be twofold: (1) existence of trace levels of contaminants such as ammonia and dimethylamine in the chamber, and/or (2) residual water in the nanoparticle after passing through DMA1. Although we supplied only sulfuric acid to the chamber and an overnight cleaning cycle (100 °C for 12 h) was performed to remove contaminants before experiments, the Atmospheric Pressure interface Time-Of-Flight mass spectrometer (APi-TOF) measurements showed that trace levels of ammonia and dimethylamine still remained in the clusters (< 2 nm) (Bianchi et al., 2014) most probably due to wall adsorption from previous experiments. Ammonia and dimethylamine were also found in the nanoparticles (< 40 nm) from TDCIMS measurement (Lawler et al., 2015). This observation suggests that trace levels of these ammonia and dimethylamine in the chamber may be present in the nucleated nanoparticles, hence decreasing the κ values.

The hygroscopic properties of nucleated nanoparticles in the presence of sulfuric acid and dimethylamine were determined in Exp. D. Although dimethylamine was continuously supplied into the chamber to maintain a concentration of 23.8 ppt, the observed κ values for 10 nm particles agree to within 4 % with the results for particles in the presence of sulfuric acid, as can be seen in Fig. 2. In the case of the 15 nm particles, however, the hygroscopicities of sulfuric acid-dimethylamine particles were 12 % lower than those for sulfuric acid particles. This decline of hygroscopicity for 15 nm particles is probably caused by an increasing amount of aminium salts during the growth process. E-AIM model results show that the observed increases in κ values could be explained by decreasing particle acidity with increasing particle size as shown in Table 2. Our results indicate that the ratio of dimethylamine to sulfuric acid increases when particles grow from 10 to 15 nm. It should be noted that the monodisperse particle growth model, MABNAG, predicts lower acidity in the 10 and 15 nm particles than do the HTDMA-based estimates under the same experimental conditions (Ahlm et al., 2015). The reason for this discrepancy is still unknown; it may be related to measurement uncertainties at the 10 and 15 nm size range, or to the incomplete understanding of the growth process of particles formed from sulfuric acid and dimethylamine. Chan and Chan (2013) observed evaporation of dimethylamine from aminium sulfate particles upon drying at 3 % RH using an electrodynamic balance. Ouyang et al. (2015) also concluded that dry particles consisting of dimethylamine and sulfuric acid in the size range 5–8.5 nm would be unstable under ambient conditions. In our HTDMA measurements the particles were dried before measuring the growth factor, so therefore some of the dimethylamine may have evaporated from the particles prior to growth factor measurements, increasing the acidity of the particles. Based on the thermodynamic condensation model simulation, the base/acid molar ratio may have decreased in the sampling line as much as 15 % (in the experiment with 40 ppt of dimethylamine) (Ahlm et al., 2015) compared to the value in the chamber. However, the difference between the base/acid ratio of growing particles predicted with the model and that derived from measured growth factors is much larger than this. It is, therefore, unlikely that evaporation of dimethylamine alone would explain this discrepancy.

We also investigated the hygroscopicities of nanoparticles produced in the chamber in the presence of α-pinene, sulfuric acid, and O_3 (Exp. E and F). In these experiments, hydrogen (H_2) was added to suppress OH radical from α-pinene oxidation in order to probe the role of ozonolysis on new particle formation (Praplan et al., 2015). Although the concentrations of sulfuric acid were higher during the sulfuric acid-organics experiments than during the sulfuric acid-dimethylamine experiments, the HGFs of particles in the presence of sulfuric acid and organics were much smaller than those of particles in the presence of sulfuric acid and dimethylamine, as can be seen in Table 1. As shown in Fig. 2, the hygroscopicity of 10 nm particles when α-pinene ozonolysis products are present is significantly lower that observed in the sulfuric acid or sulfuric acid-dimethylamine experiments; moreover it decreases with increasing size. It has previously been reported that the hygroscopicity of organics from α-pinene oxidation is clearly lower than the hygroscopicity of sulfuric acid (or ammonia-containing sulfate compounds) (Qiu and Zhang, 2012; Massoli et al., 2010). Hence, the present results indicate that the organic-oxidation products contribute significantly to the composition of both 10 and 15 nm particles, and, thereby, to their growth.

4.2 The effect of sulfuric acid concentration on hygroscopicity of particles in the presence of sulfuric acid and dimethylamine

We also investigated the effect of sulfuric acid concentration on the hygroscopicity of 10 and 15 nm particles (Exp. B–D) when while SO_2 and dimethylamine were continuously added to the chamber during the analysis period, at a constant paste, the UV light intensity was varied during the course of the experiment by changing the light aperture. The sulfuric acid monomer concentrations at an aperture of 20, 40 and 100 % UV were 5.1×10^6, 7.6×10^6, and 12.3×10^6 molecules cm^{-3}, respectively; in the discussion that follows we will refer to these concentrations as low, medium, and high,

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respectively. The growth rate (GR) of particles from 4 to 15 nm diameter increases from 2.35 to 8.41 nm h^{-1} with increasing sulfuric acid concentration from 5.1×10^6 to 12.3×10^6 molecules cm^{-3}. The large increase in the GR is probably due to a combination of the enhanced kinetic condensation of sulfuric acid (and dimethylamine) molecules and the increase in the number concentration of the formed particles, enhancing growth by coagulation (Ahlm et al., 2015). However, there were no remarkable differences among the hygroscopicities of 10 nm particles, as shown in Fig. 3a. The κ values (± standard deviation) of the 10 nm particles were 0.58 ± 0.01, 0.60 ± 0.01, and 0.61 ± 0.02 for low, medium, and high, respectively. It suggests that the composition of 10 nm particles does not change significantly over this range of sulfuric acid gas-phase concentrations. This is reasonable due to the excess of dimethylamine in the chamber relative to the sulfuric acid.

In contrast to the insensitivity of hygroscopicity for 10 nm particles to sulfuric acid levels, the hygroscopicity of 15 nm particles increases with increasing sulfuric acid. The κ values (± standard deviation) were 0.31 ± 0.01, 0.42 ± 0.02, and 0.45 ± 0.02 for low, medium, and high sulfuric acid, respectively. Especially, the κ value for low sulfuric acid was close to that of DMAS at 90 % RH ($\kappa_{\mathrm{DMAS}} \sim 0.28$) (Qiu and Zhang, 2012). This suggests that more aminium salts can be involved in 15 nm particles with decreasing sulfuric acid concentrations. The DMAS volume fractions (± standard deviation) derived from Eq. (4) varied from 0.28 ± 0.02 to 0.20 ± 0.05 for 10 nm particles and from 0.82 ± 0.03 to 0.37 ± 0.06 for 15 nm particles depending on the sulfuric acid concentrations (Fig. 3b). In summary, our measurements support the view that the contribution of dimethylamine to particle growth increases with increasing particle size.

5 Summary and conclusions

The hygroscopic properties of nucleated nanoparticles in the presence of sulfuric acid, sulfuric acid-dimethylamine, and sulfuric acid combined with organics derived from α-pinene ozonolysis were investigated with the nanometer-hygroscopicity tandem differential mobility analyzer (nano-HTDMA). The hygroscopicities decreased with increasing particle size, consistent with a decrease of particle acidity with increased particle size. The obtained hygroscopicity parameter κ values of 10 nm particles in the presence of sulfuric acid-dimethylamine were similar to those of particles in the presence of sulfuric acid with trace levels of contaminants within 4 % (κ of sulfuric acid-dimethylamine and sulfuric acid were 0.61 ± 0.02 and 0.64 ± 0.02, respectively). For 15 nm particles, however, the hygroscopicities of sulfuric acid-dimethylamine particles were lower by 12 % compared with results of sulfuric acid particles. This finding suggests that the contribution of dimethylamine to growth increases as the particles grow from 10 to 15 nm. In the presence of sulfuric acid and organics, the HGFs were much smaller than those in the presence of sulfuric acid and dimethylamine regardless of sulfuric acid concentration. This is because the hygroscopicities of organics derived from α-pinene oxidation were smaller than of dimethlyaminium sulfate and/or α-pinene oxidation products contributed more to the particles mass. In contrast to the sulfuric acid-dimethylamine experiments, hygroscopicities of 10 nm particles in sulfuric acid-organic experiments were clearly lower than in the sulfuric acid experiments; moreover, the hygroscopicity decreased with increasing size, indicating that the organic compounds are able to contribute significantly to growth and composition of both 10 and 15 nm particles. This is probably due to the very low saturation vapor pressures of organic compounds produced from α-pinene oxidation (Ehn et al., 2014).

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Table 1. Summary of the experimental conditions. The experiments were performed in the presence of sulfuric acid (Exp. A), sulfuric acid and dimethylamine (Exp. B–D), and sulfuric acid and organics produced from α-pinene ozonolysis (Exp. E–F). H_2SO_4, $(CH_3)_2NH$, $C_{10}H_{16}$, and O_3 refer to gas concentrations of sulfuric acid, dimethylamine, α-pinene, and ozone, respectively. Here the error in the HGF values indicates the standard deviation for the measured results. UV aperture indicates UV lamp aperture opening in %, which in turn provides different UV intensities inside the chamber (Kupc et al., 2011).

No.	Experiments	H_2SO_4 (10^6 molecules cm^{-3})	$(CH_3)_2NH$ (ppt)	$C_{10}H_{16}$ (ppt)	O_3 (ppb)	UV aperture (%)	HGF 10 nm	HGF 15 nm
A	Sulfuric acid	35.2	0	0	23.5	100	1.55 ± 0.02	1.56 ± 0.02
B	Sulfuric acid-dimethylamine	5.1	11.8	0	23.5	20	1.49 ± 0.01	1.36 ± 0.01
C	Sulfuric acid-dimethylamine	7.6	23.8	0	23.5	40	1.50 ± 0.01	1.45 ± 0.01
D	Sulfuric acid-dimethylamine	12.3	23.8	0	23.5	100	1.50 ± 0.02	1.47 ± 0.02
E	Sulfuric acid-organics I	15.1	0	420	22.5	0	1.35 ± 0.01	1.33 ± 0.02
F	Sulfuric acid-organics II	19.4	0	910	23.0	0	1.31 ± 0.01	1.29 ± 0.01

Table 2. Molecular ratio of base and acid compounds from E-AIM model, assuming no evaporation of dimethylamine from the particles. The E-AIM results were derived from the HGF results of particles. Based on TDCIMS measurements, we assumed that the acid compound is only sulfuric acid and base compounds consist of 50 % ammonia and 50 % dimethylamine in the particles.

No.	Experiments	Molecular ratio (base/acid)	
		10 nm	15 nm
A	Sulfuric acid	0.2	1.0
D	Sulfuric acid-dimethylamine	0.3	1.0

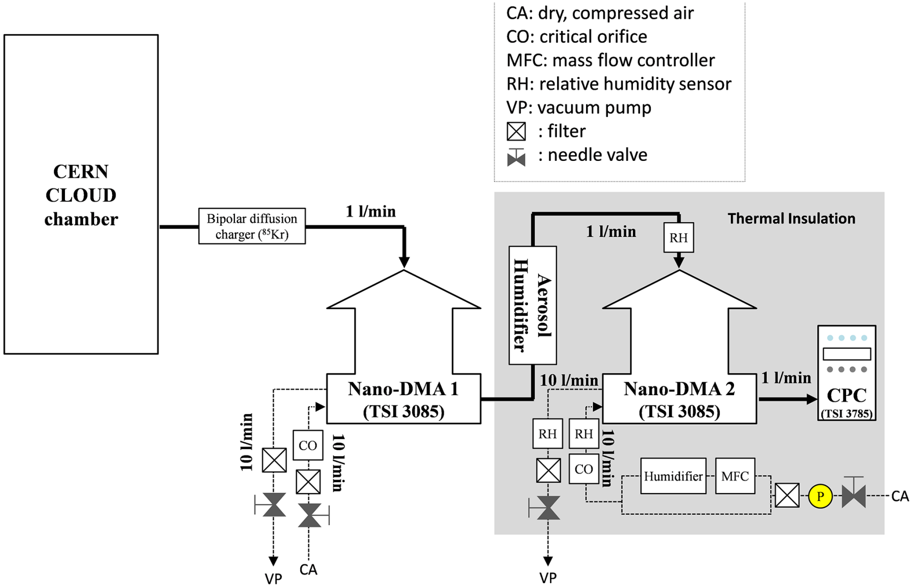

Figure 1. A schematic drawing of the nano-TDMA system used in this study.

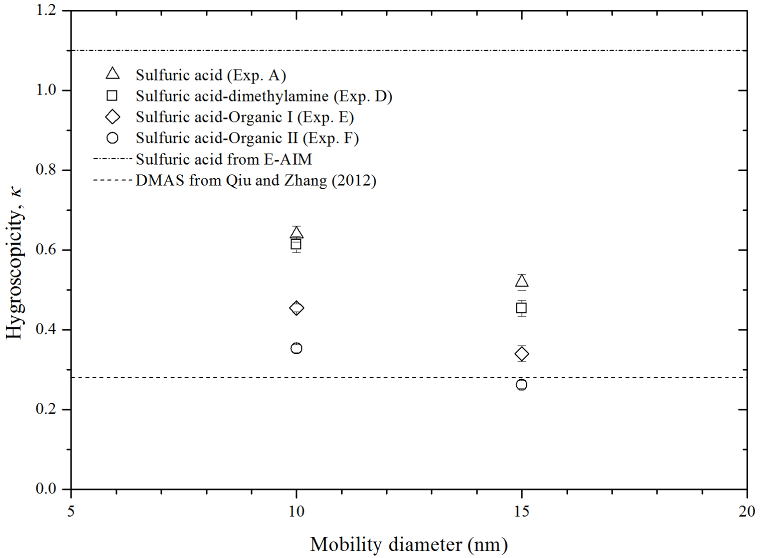

Figure 2. Comparison of hygroscopicity (κ) for 10 and 15 nm particles in the presence of sulfuric acid (Exp. A), sulfuric acid-dimethylamine (Exp. D), and sulfuric acid-organics produced by α-pinene oxidation with OH scavenger (Exp. E-F). The theoretical κ of sulfuric acid (dash dot line) from E-AIM and κ of DMAS (dash line) from Qiu and Zhang (2012) are also presented. The α-pinene concentrations during sulfuric acid-organic I and sulfuric acid-organic II were 420 and 910 ppt, respectively, as can be seen in Table 1. Error bars show a standard deviation from measurements data.

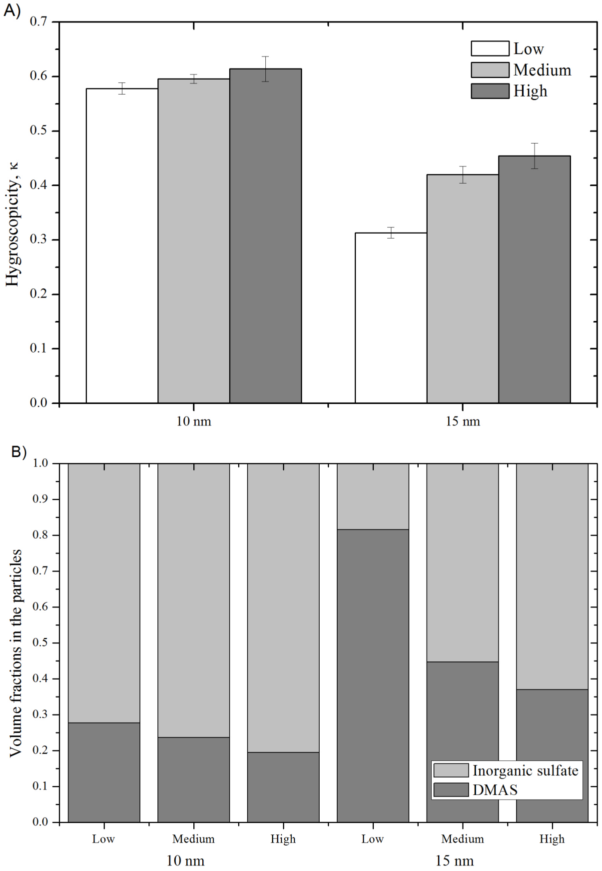

Figure 3. (a) Comparison of hygroscopicity of 10 and 15 nm particles produced from sulfuric acid and dimethylamine; **(b)** estimated volume fractions in the particles depending on UV aperture (Exp. B–D). The concentrations of sulfuric acid were 5.1×10^6, 7.6×10^6, and 12.3×10^6 molecules cm^{-3} for low, medium, and high, respectively.