CCN activity of aliphatic amine secondary aerosol

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Received: 26 September 2013 – Accepted: 29 November 2013 – Published: 2 January 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

Aliphatic amines can form secondary aerosol via oxidation with atmospheric radicals (e.g. hydroxyl radical and nitrate radical). The particle composition can contain both secondary organic aerosol (SOA) and inorganic salts. The fraction of organic to inorganic materials in the particulate phase influences aerosol hygroscopicity and cloud condensation nuclei (CCN) activity. SOA formed from trimethylamine (TMA) and butylamine (BA) reactions with hydroxyl radical (OH) is composed of organic material of low hygroscopicity (single hygroscopicity parameter, $\kappa \leq 0.25$). Secondary aerosol formed from the tertiary aliphatic amine (TMA) with $\text{N}_2\text{O}_5$ (source of nitrate radical, NO$_3$), contains less volatile compounds than the primary aliphatic amine (BA) aerosol. TMA+$\text{N}_2\text{O}_5$ form semi-volatile organics in low RH conditions that have $\kappa \sim 0.20$, indicative of slightly soluble organic material. As RH increases, several inorganic amine salts are formed as a result of acid-base reactions. The CCN activity of the humid TMA-$\text{N}_2\text{O}_5$ aerosol obeys Zdanovskii, Stokes, and Robinson (ZSR) ideal mixing rules. Higher CCN activity ($\kappa > 0.3$) was also observed for humid BA+$\text{N}_2\text{O}_5$ aerosols compared with dry aerosol ($\kappa \sim 0.2$), as a result of the formation of inorganic salts such as NH$_4$NO$_3$ and butylamine nitrate ($\text{C}_4\text{H}_{11}\text{N} \cdot \text{HNO}_3$). Compared with TMA, BA+$\text{N}_2\text{O}_5$ reactions produce more volatile aerosols. The BA+$\text{N}_2\text{O}_5$ aerosol products under humid experiments were found to be very sensitive to the temperature within the stream-wise continuous flow thermal gradient CCN counter. The CCN counter, when set above a $21 ^\circ\text{C}$ temperature difference, evaporates BA+$\text{N}_2\text{O}_5$ aerosol formed at RH $\geq 30\%$; $\kappa$ ranges from 0.4 to 0.7 and is dependent on the instrument supersaturation (ss) settings. The aerosol behaves non-ideally, hence simple ZSR rules cannot be applied to the CCN results from the primary aliphatic amine system. Overall, aliphatic amine aerosol systems $\kappa$ ranges from $0.2 < \kappa < 0.7$. This work indicates that aerosols formed via nighttime reactions with amines are likely to produce hygroscopic and volatile aerosol whereas photochemical reactions with OH produce secondary organic aerosol of lower CCN activity. Thermal gradient CCN counters measurement will impact the observed CCN activity.
of volatile aerosol formed via a nitric acid pathway. The contributions of semi-volatile secondary organic and inorganic material from aliphatic amines must be considered for accurate hygroscopicity and CCN predictions from aliphatic amine systems.

1 Introduction

Atmospheric aerosol can influence climate by directly absorbing and scattering light and indirectly via their ability to act as cloud condensation nuclei (CCN) and influence cloud formation. Secondary aerosol, formed from oxidation reactions with gaseous precursors, is an important contributor to aerosol mass and CCN number. The relative contribution of inorganic/organic components plays a vital role in the determination of bulk CCN activity of ambient aerosol.

The ambient aerosol composition is complex. Approximately 25–50 % of fine particle mass is comprised of inorganic compounds (Gray et al., 1986), such as ammonium sulfate, nitrate, sea salt, wind-blown dust, etc. Organics make up ~20–90 % of the global aerosol composition in the troposphere (Kanakidou et al., 2005). Only a small fraction of the organic composition has been speciated and quantified using gas chromatography with mass spectrometry (Finlayson-Pitts and Pitts, 1986; Rogge et al., 1993; Saxena and Hildemann, 1996). Thus aerosol physical and thermodynamic properties are difficult to predict with little to no information about particle chemical speciation. Therefore, parameterizations are used to effectively represent the water uptake potential of atmospheric aerosols.

The hygroscopicity parameter (Petters and Kreidenweis, 2007), κ has been frequently used in recent studies to describe the nature of complex aerosol (e.g. Moore et al., 2012; Mikhailov et al., 2013; Tang et al., 2012; Asa-Awuku et al., 2011; Jimenez et al., 2009). Application of κ allows direct evaluation of aerosol CCN activity by combining aerosol properties, such as density, molecular weight and surface tension. Hygroscopicity values representative of atmospheric particulate matter range from 0.1 < κ < 0.9 (Petters and Kreidenweis, 2007) using previous ambient studies (Fitzger-
Ammonium sulfate and nitrate is abundant highly soluble and hygroscopic inorganic aerosol with $\kappa$ equal to 0.6 and 0.67, respectively. Whereas moderately hygroscopic organic species have CCN activities corresponding to $0.01 < \kappa < 0.5$ (Petters and Kreidenweis, 2007). This wide range indicates that there is large variance in ambient aerosol composition as well as the relative contribution of soluble and non-soluble components.

To date few studies have examined the CCN activity of amine aerosol formed from reactions with atmospheric oxidants or nitric acid. Particle phase amines have been repeatedly detected in field campaigns at different locations (summarized by Ge et al., 2011a). Recent chamber studies have confirmed both acid-base reactions and oxidation processes can lead to the formation of amine secondary aerosol (Silva et al., 2008; Murphy et al., 2007; Malloy et al., 2009b). Amines may also enhance or affect particle nucleation and the growth of nucleated particles to CCN relevant sizes (Loukonen et al., 2010; Berndt et al., 2010; Wang et al., 2010a, b). The solubility of multiple aliphatic aminium nitrates has been summarized in Table 5 in Ge et al. (2011b), which is comparable with or higher than that of ammonium nitrate. The presence of particulate amines has been reported to be coincident with enhanced water uptake of aerosol from a bovine source (Sorooshian et al., 2008); it can be hypothesized that aminium nitrates are highly hygroscopic, similar to ammonium nitrate. Thus, the presence of aminium nitrate salts in the ambient has the potential to impact regional air quality and CCN number concentrations.

This work focuses on the CCN behavior of trimethylamine (TMA, $C_3H_9N$) and butylamine (BA, $C_4H_{11}N$) secondary aerosols formed during daytime and nighttime atmospheric reactions. TMA is a tertiary amine precursor known to form secondary organic aerosol with hydroxyl radical (OH), ozone ($O_3$) (Murphy et al., 2007) and nitrate radical ($NO_3$) (Silva et al., 2008). Ambient and lab studies show that mass of TMA-containing particle-phase amines is dependent on RH (Glagolenko and Phares, 2004; Zhang et al., 2012; Rehbein et al., 2011; Tang et al., 2013). BA is a primary aliphatic amine which is less atmospherically abundant than TMA, but has been detected at high
concentrations near dairies, with concentration up to 187 ppb (Rabaud et al., 2003). Tang et al. (2013) reported the aerosol formation potential and the chemical nature (inorganic/organic) of the two aliphatic amines (TMA and BA). Tang et al. (2013) also discussed the effect of environmentally relative humidity on the reaction pathway and aerosol composition. Here we investigate the CCN activity of aerosol formed from dry and humid reactions with N$_2$O$_5$ and OH.

2 Experimental setup and instrumentation

Three series of experiments were conducted for both TMA and BA: OH photooxidation, NO$_3$-initiated, and acid-base reactions. The initial concentration of each reactant in the experiment was as follows: precursor amine (TMA or BA) 100 ppb, HNO$_3$ ∼ 300 ppb, or N$_2$O$_5$ (nitrate radical precursor) 300 ppb, or H$_2$O$_2$ (OH precursor) 1 ppm was used. Both dry and humid (relative humidity < 40 %) experiments were conducted for reactions between amine and OH/N$_2$O$_5$. All experiments were conducted in the 12 m$^3$ environmental reactor chamber at the Center for Environmental Research and Technology, College of Engineering, University of California, Riverside (CE-CERT/UCR). Relative humidity (RH) inside the chamber was maintained at or below 0.1 % RH during dry experiments. In humid experiments, water vapor was generated by bubbling purified air through distilled water and then passing the air through a 1 µm particle filter; RH was monitored using a LI-COR® LI-840A CO$_2$/H$_2$O analyzer. Additional details of the chamber facility, aerosol formation yield and experimental protocols are described in Tang et al. (2013).

A series of chemical and physical characterization instruments were used for the study of aerosol properties. A custom built scanning mobility particle sizer (SMPS) was used to monitor real time particle number and volume size (27–685 nm) distributions (Cocker et al., 2001). Total aerosol mass concentration was also calculated by combining time series of volume and aerosol density.
Particle mobility density ($\rho$) was measured using the coupled Aerosol Particle Mass Analyzer (APM) (Kanomax model 3600) and SMPS. In general, aerosol density was determined from the mass selected by the APM and the peak diameter from the SMPS located directly downstream of the APM. Density data was acquired every 75 s. Details of the instruments and theory are described elsewhere (Malloy et al., 2009a; Ehara et al., 1996).

A Volatility Tandem Differential Mobility Analyzer (VTDMA) was also custom built and used for online volatility measurement. The VTDMA consists of two differential mobility analyzers (DMA), one condensational particle counter (CPC) and one Dekati® thermodenuder (TD, residence time $\sim$ 17 s). The first DMA size-selects particles that transmit through the TD with diameter $D_i$, while the second DMA and CPC measures the diameter of particles coming out of the TD ($D_f$) by fitting a log-normal size distribution curve. Volume fraction remaining (VFR) is calculated as the volume ratio of particles before and after passing through the TD with temperature $T$, i.e. $VFR = (D_f/D_i)^3$.

Chemical composition of chamber SOA was measured with an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006; Jimenez et al., 2003). Non-refractory chemical species in the aerosol phase can be quantified, providing chemistry information of bulk aerosol as well as elemental composition. Particle-into-Liquid Sampler coupled to dual ion chromatographs (PILS-IC) quantified the particle phase inorganic salts. The configuration of the PILS-IC is described elsewhere (Orsini et al., 2003; Weber et al., 2001).

The CCN activity and supersaturated hygroscopicity is measured with a Droplet Measurement Technologies (DMT) Continuous-Flow Streamwise Thermal Gradient CCN Counter (CFSTGC) (Lance et al., 2006; Roberts and Nenes, 2005). Aerosol from the chamber was classified by a commercial SMPS (TSI 3080), followed in parallel by a condensation particle counter (CPC, TSI 3772) and the DMT CCN counter. The total aerosol concentration (CN) of the mono-disperse particles was counted by the CPC and the CCN concentration was measured by the CCN counter. The DMA used with the CCN counter was operated at a sheath-to-aerosol flow ratio of 10 : 1. Instrument ss
settings used in this study ranged from 0.2 % to 1 % and were calibrated using atomized \((\text{NH}_4)_2\text{SO}_4\) aerosol. Scanning Mobility CCN Analysis (SMCA) (Moore et al., 2010) provides size resolved CCN activity using data from the CCN counter and SMPS. By keeping constant instrument ss during the scanning cycle of the SMPS, we obtain the time series of CN and CCN counts, and then use an inversion procedure to determine the CCN/CN ratio as a function of dry mobility diameter. The critical activation diameter, \(d_{p50}\), corresponding to the CCN/CN ratio of 0.5, is determined for each ss. This procedure is repeated over multiple ss, giving a characterization of the size-resolved CCN properties every 135 s.

3 Theory

3.1 Temperature considerations for CCN measurement

Temperature settings of the DMT CCN counter can affect the CCN activity of volatile aerosol species (Asa-Awuku et al., 2009; Moore and Nenes, 2009; Romakkaniemi et al., 2013). The centerline ss of CCN counter is controlled by the flow rate \((Q)\) and temperature difference \((\Delta T)\) between the top \((T_1)\) and bottom \((T_3)\) at constant column absolute pressure (Fig. S1, Eq. 1, Roberts and Nenes, 2005). Selecting a linear combination of \(Q\) and \(\Delta T\) will maintain the same or very similar instrument ss. In standard operation, the change of ss is achieved by keeping constant inlet flow rate \((0.5 \text{ L min}^{-1})\) and varying \(\Delta T\). \(T_1\) (temperature at the top of the column) is identical to the aerosol sample temperature and is constant for all experiments. Therefore the change of \(\Delta T\) is determined by that of \(T_3\), temperature at the bottom of the column. Larger temperature gradients along the CCN column are required for higher ss at a constant flow rate, \(Q\). For high ss (e.g. > 1.0 %), temperatures at the exit of the DMT CCN column can exceed 35 °C. To examine measurement artifacts induced by high temperatures, the temperature gradient inside the CCN column will be varied while keeping the centerline ss
constant.

\[ \text{ss} \propto \frac{\Delta T}{Q} \]  

\[ (1) \]

4 \( \kappa \) of multi-component aerosol system

We use the \( \kappa \)-Köhler theory (Petters and Kreidenweis, 2007) to convert the measured activation diameters to the single hygroscopicity parameter, \( \kappa \), using the equations as follows,

\[ \kappa = \frac{4A^3}{27\ln^2 S_c d_{p50}^3} \]  

\[ (2) \]

\[ A = \frac{4M_w \sigma_w}{RT \rho_w} \]  

\[ (3) \]

where \( M_w \) and \( \rho_w \) are the molecular weight and density of water, respectively, \( R \) the universal gas constant, and \( T \), the ambient temperature. \( \kappa \)-Köhler theory assumes the surface tension of the droplet is that of pure water, \( \sigma_w = 0.072 \text{ N m}^{-1} \). \( S_c \) is the critical saturation for a dry particle of diameter \( d_{p50} \) determined with the Scanning Mobility CCN Analysis (SMCA).

For multi-component aerosol systems, the Zdanovskii, Stokes, and Robinson (ZSR) (Zdanovskii, 1948; Stokes and Robinson, 1966) mixing rule can be applied to predict the CCN activity. ZSR assumes that water uptake by each individual component of a particle is independent and additive. Therefore, the overall \( \kappa \) value is the sum of \( \kappa \) of each individual component weighted by its volume contribution to the total aerosol. We assume two components, including inorganic and organic in the aerosol phase of the amine oxidation products. Applying the ZSR, \( \kappa \) value of the bulk aerosol can be
estimated as follows (Petters and Kreidenweis, 2007):

$$\kappa = \sum_i \varepsilon_i \kappa_i = \varepsilon_s \kappa_s + \varepsilon_o \kappa_o$$  \hspace{1cm} (4)

where $\varepsilon_i$ is volume fraction of the inorganic/organic components in the aerosol; “s” and “o” subscripts refer to salt (inorganic) and organic components, respectively. $\varepsilon_s$ is calculated from the mass fraction, $m$, and density, $\rho$ as

$$\varepsilon_s = \frac{V_s}{V_s + V_o} = \frac{m_s}{\rho_s} + \frac{m_o}{\rho_o}$$ \hspace{1cm} (5)

$$\varepsilon_o = 1 - \varepsilon_s$$ \hspace{1cm} (6)

5 Results and discussion

5.1 Trimethylamine (TMA)

The reaction of TMA with OH and N₂O₅ can form aerosol of varied hygroscopicity and CCN activity. TMA photooxidation with OH in the absence of NOₓ formed organic aerosol with low hygroscopicity, $\kappa \sim 0.18$ (Table 1). Similarly, dry reactions between TMA and N₂O₅ produced organic-dominant (total aerosol salt mass fraction, $\varepsilon_s$, < 10 %) secondary aerosol with comparable hygroscopicity ($\kappa \sim 0.20$, Table 1). In humid experiments, nitric acid produced by N₂O₅ and NO₃ can be directly neutralized by TMA and first generation aerosol products to form inorganic salts (Tang et al., 2013). PILS-IC data confirmed the presence of TMA⁺, DMA⁺, MA⁺ and NO₃⁻ ions in the aerosol phase. The $\varepsilon_s$ was observed to stabilize at $\sim 0.15$ after 2 h of reaction at RH $\sim 22$ % (Tang et al., 2013). The CCN activity of the aerosol formed at RH $\sim 22$ % has $\kappa \sim 0.28$ due to the increased $\varepsilon_s$ over the dry experiment, higher than that of the aerosol only composed of organic species.
The difference in single parameter hygroscopicity is consistent with a two-component (organic and inorganic component) model of $\kappa$ additivity. The CCN activity of organic components in the multi-component TMA aerosol is estimated by applying the ZSR mixing rule with $\kappa$-Köhler theory. As the concentration of TMA$^+$ exceeds the sum of methyl and dimethyl amine ions (MA$^+$ and DMA$^+$), the inorganic components properties are assumed similar to those of C$_3$H$_9$N·HNO$_3$. Table 2 shows the measured $\kappa$ value, density, mass fraction and calculated volume fraction of C$_3$H$_9$N·HNO$_3$. The calculated $\kappa$ value for organic components in the humid TMA-NO$_3$ aerosol is 0.19, similar to that of the dry TMA-NO$_3$ aerosol. Despite the presence of a potential salt-forming reaction pathway under humid conditions, the mechanism for TMA SOA resulted in materials with similar hygroscopicity as those formed under dry conditions.

Comparison of the volume fraction remaining (VFR) of TMA-NO$_3$ secondary aerosols indicates subtle differences in the organic species formed in dry and humid reactions (Fig. 1b). Of the aerosol formed, the VFR is 70% for the TMA-N$_2$O$_5$ aerosol in the dry experiment after $\sim$ 17 s exposure at 100°C in the VTDMA. As RH and salt fraction increase, the aerosol becomes more volatile; $\sim$ 40% of the TMA-N$_2$O$_5$ aerosol formed at RH $\sim$ 22% remains, suggesting that $\sim$ 30% more aerosol partitioned from aerosol phase to gas phase. From our current knowledge of nitrate salts, the aminium salts formed are likely volatile. The equilibrium constant between NH$_3$, HNO$_3$ and NH$_4$NO$_3$ determines a high vapor pressure of NH$_4$NO$_3$ at ambient temperature (Stelson and Seinfeld, 1982a, b; Stelson et al., 1979). Assuming the inorganic salts (volume fraction 16.5% in total aerosol) evaporate completely at 100°C, the aerosol will lead to difference of 0.165 in the VFR instead of $\sim$ 0.3. In conclusion, “humid” organic aerosol is more volatile than dry TMA-N$_2$O$_5$ organic aerosol, despite similar hygroscopicity.

5.2 Butylamine (BA)

Hygroscopicity of BA secondary aerosols formed in dry and humid (RH $\sim$ 36%) OH photooxidation experiments are comparable to TMA aerosols (0.23 ± 0.01 vs. 0.25 ± 0.03, Table 1). However, the volatility of “humid” aerosol is notably higher than that of
dry aerosol at $T = 50^\circ$C (Fig. 1a). BA secondary aerosol formed in higher RH is another example of aerosol with similar CCN activity possessing dissimilar volatility.

BA secondary aerosols formed from reactions with $\text{N}_2\text{O}_5$ were more volatile than OH photooxidation SOA while susceptible to changes in temperature as well. We compared the VFR and hygroscopicity of BA-$\text{N}_2\text{O}_5$ aerosol formed under four different relative humidities (RH $< 0.1\%$, $\sim 12\%$, $\sim 23\%$ and $\sim 35\%$). BA-$\text{N}_2\text{O}_5$ aerosol formed at RH $< 0.1\%$ (i.e. dry) has VFR $< 0.5$ at $50^\circ$C, which is much more volatile than the TMA-$\text{N}_2\text{O}_5$ aerosol. Nevertheless, hygroscopicity of dry BA-$\text{N}_2\text{O}_5$ aerosol is similar with that of dry TMA-$\text{N}_2\text{O}_5$ aerosol, corresponding to the chemical nature of organic-dominant secondary aerosols.

As with TMA, increasing RH forms more aminium salts in the aerosol phase and increased volatility and CCN activity of BA secondary aerosol systems. Higher concentrations of water vapor enhanced the salt-forming pathways (e.g., the formation of nitric acid) such that significant amounts of inorganic salts formed in the humid experiments. Other than butylaminium nitrate ($\text{C}_4\text{H}_{11}\text{N} \cdot \text{HNO}_3$) via direct reaction of BA + HNO$_3$, additional pathways lead to the formation of another salt, ammonium nitrate (NH$_4$NO$_3$). Figure 2 shows the ratio of mass concentration ($\mu$gm$^{-3}$) of two cations, NH$_4^+$ and BA$^+$ in the total BA aerosol mass concentration ($\mu$gm$^{-3}$) using data collected by PILS-IC and SMPS. With higher RH, the relative contribution of ammonium ion (NH$_4^+$) in the total aerosol increased, while that of butylamine ion (BA$^+$) follows the opposite trend. As the $\kappa$ value of NH$_4$NO$_3$ is larger than that of $\text{C}_4\text{H}_{11}\text{N} \cdot \text{HNO}_3$ (0.74 vs. 0.53, Table 1), aerosol containing more NH$_4$NO$_3$ exhibited reasonably higher CCN activity. Similarly, higher volatility is observed with the elevation of RH and mass fraction of NH$_4$NO$_3$ in the BA-$\text{N}_2\text{O}_5$ reactions (Fig. 1b). As mentioned in Sect. 4.1, NH$_4$NO$_3$ has high vapor pressure even at ambient temperature, and the partitioning between particle and gas phase is a strong function of temperature and relative humidity. $\text{C}_4\text{H}_{11}\text{N} \cdot \text{HNO}_3$ particles formed from BA and HNO$_3$ in the same chamber reactor are also volatile, with VFR $< 0.1$ at VTDMA $T = 35^\circ$C, which is similar to that of humid BA-$\text{N}_2\text{O}_5$ aerosol
formed at 35% RH (Fig. 1b). Thus, higher relative humidity promotes the partitioning of BA secondary aerosol from particle phase to gas phase.

As CCN activity of humid BA-N$_2$O$_5$ aerosols is elevated by the presence of inorganic salts, the standard deviation of $\kappa$ values increases notably compared with that of dry aerosol and is greater than TMA secondary aerosol as well. In addition to time-dependent aerosol CCN activity, measured $\kappa$ values varied with changes of ss setting. Figure 3 shows the $\kappa$ values measured at different ss ranging from 0.23% to 0.87% for the BA-N$_2$O$_5$ reaction at RH $\sim$ 30%. Briefly, $\kappa$ measured at higher ss (i.e. the ss settings > 0.4%) was smaller than those measured at lower ss (i.e. the ss settings $\leq$ 0.4%), and the discrepancy was observed from the beginning to the end of the experiment. As defined in Petters and Kreidenweis (Petters and Kreidenweis, 2007), the hygroscopicity parameter $\kappa$ is only dependent on aerosol composition, not on the value of ss. Therefore, there are likely differences in the aerosol solute composition measured at high and low ss. To avoid the influence of relative humidity while examining the effect of temperature on the CCN activity measurement, similar ss ($\sim$ 0.38%) was achieved by adjusting the temperature difference ($\Delta T$) and flow rate ($Q$) as discussed in the theory section. It is to be noted that residence time of sampled aerosol was extended under the higher $\Delta T$ and lower $Q$ conditions.

Aerosol formed from humid (RH $\sim$ 30%) experiments between BA and NO$_3$ were re-examined using the same CCN counter with varying temperature difference ($\Delta T$) of the CCN column listed in Table 3. Calculated $\kappa$ values were shown in Fig. 4. $\kappa$ measured at $\Delta T$ = 7, 14 and 17°C are consistent, with standard deviation ±0.04, and show a slight decrease at the beginning of the experiments. However, when $\Delta T$ = 21°C and $Q$ = 167 cm$^3$ min$^{-1}$, it is not possible to determine the critical diameter needed for calculating $\kappa$; the CCN/CN ratio for all sizes from 10 to 250 nm was below 0.2 and the activation curve did not reach a plateau typical of CCN active aerosol. BA aerosol was unable to fully activate inside the CCN column as a result of the high temperature and longer residence time. High temperature favors particle to gas phase partitioning, and both C$_4$H$_{11}$N·HNO$_3$ and NH$_4$NO$_3$ are water-soluble, which may incur
more material losses to the CCN column wall during the longer retention time inside the CCN column. Thus, a shrinking particle size caused by evaporation and dissolution of volatile compounds is assumed to be responsible for the failure of activation. However, the measured CCN activity of dry $\text{C}_4\text{H}_{11}\text{N} \cdot \text{HNO}_3$ and $\text{NH}_4\text{NO}_3$ particles may be less sensitive to temperature change of the CCN counter column during the measurement. No distinct difference between critical diameters measured with $\Delta T = 7$ and $21 \, ^{\circ}\text{C}$ was observed for dry atomized $\text{NH}_4\text{NO}_3$ aerosol, as well as $\text{C}_4\text{H}_{11}\text{N} \cdot \text{HNO}_3$ particles, for which only $10\%$ difference of $\kappa$ was discovered. It implies that even moderate RH ($\sim 30\%$) can modify the BA secondary aerosol gas-to-particle partitioning, which is amplified when exposed to supersaturated conditions.

### 6 Summary and conclusions

The formation of aliphatic amine secondary aerosol is complex and the reaction pathways can lead to the formation of organic and inorganic components. Changes in the single hygroscopicity parameter $\kappa$ reflect changes in aerosol chemical composition. The CCN activity for amine secondary aerosol is dependent on the reaction pathways. $\text{N}_2\text{O}_5$-initiated reaction pathways produce more CCN active aerosol than in OH radical systems, especially in humid conditions. The tertiary amine precursors form less volatile materials that can be described by a two component additive (inorganic/organic) hygroscopicity model. Variability in amine hygroscopicity, especially for primary aliphatic amines is due to the presence of volatile components. Tertiary aerosol does not exhibit variance in hygroscopicity while primary aliphatic amine aerosol is more susceptible to changes in temperature and RH.

The formation of salts will increase CCN activity. The behavior of BA aerosol within the CCN counter suggests that aerosol formed at lower RH may modify gas/particle partitioning if exposed to increasing RH. Hence as RH increases in a parcel of air the composition of secondary amine aerosol may become more CCN active. Because of their notable aerosol yields and the potential impacts on cloud formation and global...
climate, further study is required to understand the ambient nature of aliphatic amines. Specifically the vertical distribution of inorganic/organic partitioning of the aerosol from the surface to cloud-top altitudes should be investigated.

Furthermore, the time of day of aerosol formation must also be considered. OH and NO$_3$ reactions representative of daytime versus nighttime reactions produce aerosol of varied salt content and hence CCN activity. Nighttime secondary aliphatic amine atmospheric reactions are likely to promote the formation of hygroscopic material that can induce low level clouds and fogs. Thus, the contribution of amines to regional CCN is complex and requires additional controlled exploratory efforts.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/31/2014/acpd-14-31-2014-supplement.pdf.

Acknowledgements. This work was supported in part by the National Science Foundation (ENG 1032388 & ATM 0849765) and W. M. Keck Foundation. D. Vu acknowledges US Environmental Protection Agency (EPA) STAR Fellowship Assistance Agreement no. FP-91751101 for her contribution to this work. Any opinions, findings, and conclusions expressed in this material are those of the author(s) and do not necessarily reflect the views of the NSF or EPA. No endorsement is implied by the USDA for any instrument or method mentioned here to the exclusion of other methods which provide similar ability.

References


Table 1. $\kappa$ values of aerosol formed from reactions with OH ($H_2O_2$ as source), NO$_3$ ($N_2O_5$ as source) and HNO$_3$.

<table>
<thead>
<tr>
<th>Amine</th>
<th>Oxidant</th>
<th>RH (%)</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA ($C_3H_9N$)</td>
<td>$H_2O_2$</td>
<td>&lt; 0.1</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>$N_2O_5$</td>
<td>&lt; 0.1</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 22</td>
<td>0.28 ± 0.02</td>
</tr>
<tr>
<td>BA ($C_4H_{11}N$)</td>
<td>$H_2O_2$</td>
<td>&lt; 0.1</td>
<td>0.23 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>$N_2O_5$</td>
<td>&lt; 0.1</td>
<td>0.19 ± 0.04</td>
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<tr>
<td></td>
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<td>12</td>
<td>0.48 ± 0.10</td>
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<td></td>
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<td>23</td>
<td>0.33 ± 0.08</td>
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<tr>
<td></td>
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<td>30</td>
<td>0.49 ± 0.08</td>
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<tr>
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<td>35</td>
<td>0.60 ± 0.10</td>
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<tr>
<td>$C_3H_9N \cdot HNO_3$</td>
<td>&lt; 0.1</td>
<td>0.72 ± 0.04</td>
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<tr>
<td>$C_4H_{11}N \cdot HNO_3$</td>
<td>&lt; 0.1</td>
<td>0.53 ± 0.03</td>
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<tr>
<td>$NH_4NO_3$</td>
<td>&lt; 0.1</td>
<td>0.74*</td>
<td></td>
</tr>
</tbody>
</table>

* Petters and Kreidenweis (2007)
**Table 2.** Mass and volume fraction, density, and hygroscopicity of inorganic/organic components in the humid (RH ~ 22%) TMA-NO$_3$ aerosol.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass fraction ($m$)</th>
<th>Density ($\rho$) (g cm$^{-3}$)</th>
<th>Volume fraction ($\varepsilon$)</th>
<th>Hygroscopicity parameter ($\kappa$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt</td>
<td>0.15</td>
<td>1.25$^a$</td>
<td>0.165</td>
<td>0.72 ± 0.02</td>
</tr>
<tr>
<td>Organics</td>
<td>0.85</td>
<td>1.40$^b$</td>
<td>0.835</td>
<td>0.19 ± 0.00</td>
</tr>
<tr>
<td>Bulk aerosol</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.28 ± 0.02</td>
</tr>
</tbody>
</table>

$^a$ Salo et al. (2011); $^b$ Tang et al. (2013).
Table 3. Values of temperature difference ($\Delta T$), flow rate ($Q$), and the corresponding ss (%) from (NH$_4$)$_2$SO$_4$ calibration of the CCN counter.

<table>
<thead>
<tr>
<th>$\Delta T$ (°C)</th>
<th>Flow Rate, $Q$ (cm$^3$ min$^{-1}$)</th>
<th>ss (%)</th>
<th>(NH$_4$)$_2$SO$<em>4$ $d</em>{p50}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>500</td>
<td>0.37</td>
<td>53.05</td>
</tr>
<tr>
<td>14</td>
<td>250</td>
<td>0.39</td>
<td>49.69</td>
</tr>
<tr>
<td>17</td>
<td>206</td>
<td>0.38</td>
<td>50.85</td>
</tr>
<tr>
<td>21</td>
<td>167</td>
<td>0.37</td>
<td>51.46</td>
</tr>
</tbody>
</table>
Fig. 1. Volume Fraction Remaining (VFR) of secondary aerosol formed from (a) OH photooxidation and (b) amine-N$_2$O$_5$ reactions. For TMA aerosols, VTDMA temperature was set to be 100°C, while for BA 50°C or 35°C because of their higher volatility.
Fig. 2. Fraction of BA$^+$ and NH$_4^+$ mass measured by PILS-IC in the total aerosol mass for the BA$^+$N$_2$O$_5$, experiments under three different relative humidities (RH < 0.1 %, ∼ 10 %, ∼ 30 %).
Fig. 3. $\kappa$ measured at different ss showed inconsistency for secondary aerosol formed from BA + N$_2$O$_5$ at RH ~ 30%.
Fig. 4. Measured $\kappa$ values at $ss \sim 0.38\%$ for butylamine (BA) + N$_2$O$_5$ aerosol formed at RH $\sim 30\%$. Symbols represent various temperature difference ($\Delta T$) between the top and bottom of the CCN counter column.