Atmospheric
Chemistry
and Physics
Discussions

Hygroscopic behavior of atmospheric aerosols containing nitrates and water-soluble organic acids

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Atmospheric
Chemistry
and Physics
Discussions

1 **Abstract**

2 While nitrates have critical impacts on environmental effects of atmospheric aerosols, the effects of coexisting

3 species on hygroscopicity of nitrates remain uncertain. The hygroscopic behaviors of nitrate aerosols (NH_4NO_3,

4 $NaNO_3$, $Ca(NO_3)_2$) and their internal mixtures with water soluble organic acids at varying mass ratios were

5 determined using a hygroscopicity tandem differential mobility analyzer (HTDMA). The nitrate/organic acid

6 mixed aerosols exhibit varying phase behavior and hygroscopic growth depending upon the type of components

7 in the particles. Whereas pure nitrate particles show continuous water uptake with increasing RH, the

8 deliquescence transition is still observed for ammonium nitrate particles internally mixed with organic acids

9 such as oxalic acid and succinic acid with a high deliquescence point. The hygroscopicity of submicron

10 aerosols containing sodium nitrate and an organic acid is also characterized by continuous growth, indicating

11 that sodium nitrate tends to exist in a liquid-like state under dry conditions. It is observed that in contrast to the

12 pure components the water uptake is hindered at low and moderate RH for calcium nitrate particles containing

13 malonic acid or phthalic acid, suggesting the potential effects of mass transfer limitation in highly viscous

14 mixed systems. Our findings improve fundamental understanding of the phase behavior and water uptake of

15 nitrate-containing aerosols in the atmospheric environment.

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Atmospheric
Chemistry
and Physics
Discussions

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1 Introduction

Atmospheric aerosols exert significant impacts on the earth's radiation balance by absorbing or scattering solar radiation and modifying the properties of clouds, which result in large uncertainty in climate forcing (Haywood and Boucher, 2000; Carslaw et al., 2013). The hygroscopic particles can provide liquid water medium for multiphase and aqueous phase chemical processes that influence chemical constituents in the condensed and gas phase (Wang et al., 2016a; Cheng et al., 2016; Hodas et al., 2014; Faust et al., 2017; Tan et al., 2016; Li et al., 2017). It has been established that aerosol liquid water could promote the formation of secondary organic aerosol (SOA) through the partitioning of gas-phase water-soluble organic compounds to the condensed phase and subsequent aqueous-phase processing (Hodas et al., 2014; Faust et al., 2017). The hygroscopic behavior and water content of aerosols in the atmosphere are highly dependent upon the chemical composition, mixing state and ambient relative humidity (RH) (Martin, 2000; Choi and Chan, 2002; Krieger et al., 2012). The atmospheric particulate matter from multiple biogenic and anthropogenic sources is commonly composed of complex inorganic and organic compounds with various physicochemical properties.

The nitrates are ubiquitous and account for a large fraction of inorganic constituents within the atmospheric particulate matter in urban/polluted environments, especially in winter (Huang et al., 2014; Zhang et al., 2015). The majority of nitrates in ambient particles exists as NH_4NO_3, $NaNO_3$ and $Ca(NO_3)_2$ depending on the environmental conditions and chemical formation mechanisms. The formation of nitrates is typically attributed to atmospheric reactions of ammonia, sea salt and mineral dust with nitric acid or nitrogen oxides such as NO_2, NO_3 and N_2O_5 (Zhang et al., 2015). In the urban area, due to the considerable influence of anthropogenic sources the major chemical form of nitrates in fine particulate matter is ammonium nitrate generated via the heterogeneous reaction between HNO_3 and NH_3 in the aerosol phase. Field measurements and laboratory studies have indicated that the mineral dust ($CaCO_3$) and sea salt ($NaCl$) emitted from natural sources could undergo atmospheric aging through the heterogeneous reactions with nitric acid or nitrogen oxides, resulting in the formation of $Ca(NO_3)_2$ and $NaNO_3$ (Zhang et al., 2015). The inorganic salts in the particle phase are generally internally mixed with organic compounds that contribute a large fraction of fine particulate matter. Field measurements have confirmed that organic fraction of the aerosols contains large amounts of water-soluble organic compounds (WSOCs) (Saxena and Hildemann, 1996; Gysel et al., 2004; Decesari et al., 2005), which affect the hygroscopicity of inorganic components. It has been found that water-soluble organic acids such as dicarboxylic acids are representative and important constituents of the WSOCs (Kawamura and Ikushima, 1993; Kawamura et al., 1996; Decesari et al., 2006; Kawamura and Bikkina, 2016). Among the water-soluble organic acids, oxalic acid, malonic acid, succinic acid and phthalic acid are typically identified as the most abundant dicarboxylic acids in atmospheric particles (Kawamura and Bikkina, 2016).

Atmospheric
Chemistry
and Physics
Discussions

1   The phase state of aerosol particles is an important factor in determining the particle's physicochemical

2   properties and climate effects (Kanakidou et al., 2005). Due to its significance, the comprehensive

3   understanding of particle phase in aerosols with varying components could improve the prediction ability of

4   climate models (Kanakidou et al., 2005; Virtanen et al., 2010; Shiraiwa et al., 2017). Unlike sulfates such as

5   ammonium sulfate with distinct phase transition behaviors, the nitrates including ammonium nitrate especially

6   in submicron particles tend to take up water continuously from low RH without obvious phase transitions

7   (Mikhailov et al., 2004; Gibson et al., 2006). Previous observations indicated that pure NH_4NO_3 droplets were

8   difficult to homogeneously crystallize and thus remained in the liquid-like state even under extremely dry

9   conditions (<1% RH) while it could efflorescence with the presence of solid core in the droplets (Lightstone et

10   al., 2000). Soluble inorganic crystalline particles acting as the contact nuclei were found to induce

11   crystallization of aqueous ammonium nitrate (Davis et al., 2015). It was found that the phase state of NH_4NO_3

12   tended to be substantially affected by coexisting species such as ammonium sulfate and succinic acid

13   (Lightstone et al., 2000; Liu et al., 2016). The previous hygroscopic studies have focused on the hygroscopicity

14   of ammonium sulfate and its relevant mixtures with organics such as water-soluble organic acids (Cruz and

15   Pandis, 2000; Choi and Chan, 2002; Prenni et al., 2003; Wise et al., 2003; Badger et al., 2006; Hodas et al.,

16   2015; Wang et al., 2017). However, the overall role of the water-soluble organic acids in hygroscopic growth

17   and phase behavior of the nitrates remains uncertain. Thus, related studies are of importance for understanding

18   of their environmental effects.

19   In this work, the hygroscopic behaviors of internally mixed aerosols composed of atmospherically relevant

20   nitrates and water-soluble organic acids are determined under subsaturation conditions with a hygroscopicity

21   tandem differential mobility analyzer (HTDMA) system. The measured hygroscopic growth of relevant

22   aerosols is compared with predictions from the Zdanovskii-Stokes-Robinson (ZSR) method based on

23   hygroscopicity of individual components. The significant effects of water-soluble organic acids with various

24   hygroscopic characteristics on water uptake behaviors of nitrates have been confirmed, and relevant

25   atmospheric implications are discussed.

26   **2 Experimental section**

27   **2.1 Reagents**

28   Table 1 summarizes chemical properties and manufacturer of nitrates (ammonium nitrate, sodium nitrate and

29   calcium nitrate) and water-soluble organic acids (oxalic, malonic, succinic and phthalic acids) in this study.

30   Aerosol particles were generated from a 0.1 wt% aqueous solution of pure component or mixtures containing

31   nitrates and organic acids at a specific mass ratio. The corresponding solutions were prepared using ultrapure

32   water (EASY Pure® II UF ultrapure water system, resistivity ≥ 18.2 MΩ cm).

2.2 Hygroscopic growth measurements

In this study, the hygroscopicity tandem differential mobility analyzer (HTDMA) system was used to measure the hygroscopic growth of aerosol particles studied. This system has been fully described in our previous studies (Jing et al., 2016; Peng et al., 2016; Jing et al., 2017). Briefly, the HTDMA setup consists of the aerosols' generation and drying section, humidity control apparatus and the particle size selection and detection system. The polydisperse particles were generated from a constant output atomizer containing sample solution, and then passed through a silica gel diffusion dryer combined with a Nafion gas dryer to be dried to RH < 5%. After charged by a neutralizer, the dry particles were transformed into quasi-monodisperse particles with mobility diameter of 100 nm by the first differential mobility analyzer (DMA1). The size-selected aerosols then entered the humidity control apparatus where they were exposed and equilibrated to a given RH in the range of < 5% to 90% with a residence time of 5 s. The size distribution of aerosols after humidification was determined by the second DMA (DMA2) and the condensation particle counter (CPC, MSP 1500). Sheath air in the DMA2 was drawn from the humidity control section to ensure no change in humidity of aerosol flow in the DMA2. The RH of sheath flow was measured at the outlet of DMA2 using a dew point hygrometer (Michell, UK) with an uncertainty of ± 0.8% RH and ± 0.1 K. The sheath and aerosol flow rates in both DMAs were 3.0 and 0.3 liters per minute, respectively. The inversion of HTDMA measurement data was based on a log-normal size distribution approximation (Stolzenburg and McMurry, 2008). All hygroscopicity measurements were conducted at ambient temperature (295 ± 1 K). During the experiment process, no obvious evaporation (no obvious decrease between dry particle size selected by DMA1 and that measured by DMA2) of nitrate-containing particles was observed under our measurement conditions.

The hygroscopic growth factor (GF) is calculated by: $GF = D_{wet}/D_{dry}$, where D_{wet} is the diameter of particles measured by DMA2 at a particular RH and D_{dry} is the diameter of dry particles measured by DMA2 at ≤ 5% RH. Considering the curvature effect for submicron droplets, the RH was converted to water activity a_w in subsequent data analysis by the Köhler equation:

$$RH = a_w \exp(\frac{4M_w \sigma_{sol}}{RT \rho_w D_p}) \qquad (1)$$

Here, M_w is the molar mass of water, σ_{sol} is the surface tension of the droplet, R is ideal gas constant, T is temperature, ρ_w is the density of water, and D_p is the droplet diameter. In this study, the effects of solutes on the surface tension of the droplet were not obvious and thus the surface tension of pure water (0.072 J m^{-2}) was used in estimates by Eq. (1). During the experimental period, hygroscopic growth of ammonium sulfate was measured regularly to validate the measurement reliability of the HTDMA. The RH measurement uncertainty was determined by measuring hydration curves of three inorganic salts such as sodium chloride (NaCl),

Atmospheric
Chemistry
and Physics
Discussions

1   ammonium sulfate [(NH$_4$)$_2$SO$_4$] and potassium chloride (KCl). It was found that the discrepancies between

2   measured deliquescence points and theory predictions for the three salts were within ± 1.5% RH, which was

3   used to estimate the measurement uncertainty in RH. All measured GFs at a given RH are the average values of

4   at least three repeated measurements with the corresponding standard deviation less than 0.02. The measured

5   deliquescence point and GFs of ammonium sulfate agreed well with our previous studies and other reported

6   literature values (Peng et al., 2016; Jing et al., 2017; Sjogren et al., 2007).

7   **3 Results and discussion**

8   **3.1 Water uptake behaviors of single components**

9   The hygroscopic growth of single components including three nitrates is shown in Fig. 1. The three nitrates

10   present gradual hygroscopic growth without prompt deliquescence transitions over the whole RH range studied.

11   The smooth hygroscopic growth suggests the nitrate particles likely remain in a liquid-like or amorphous state

12   at the lowest RH, as also observed by previous studies (Lightstone et al., 2000; Gibson et al., 2006). For

13   example, the early HTDMA studies by Mikhailov et al. (2004) and Svenningsson et al. (2006) have also

14   observed the continuous water-uptake behavior of submicron ammonium nitrate particles without any prompt

15   deliquescence transition. Although crystalline sodium nitrate has a deliquescence point at 74.5% RH (Tang and

16   Munkelwitz, 1994), the prior studies have found that micron and submicron NaNO$_3$ particles formed from

17   aqueous solutions exhibited continuous hygroscopic growth due to initial particles in a metastable or

18   amorphous form even at zero relative humidity (Gysel et al., 2002; Hoffman et al., 2004; Gibson et al., 2006).

19   In this study, the measured growth factor for 100 nm NaNO$_3$ particles is 1.97 at 90% RH in good agreement

20   with the literature value of 1.91 (Gysel et al., 2002). For calcium nitrate, Ca(NO$_3$)$_2$ particles gradually take up

21   water with increasing RH and the measured hygroscopic growth generally matches the subsequent theory

22   prediction based on the assumption that submicron Ca(NO$_3$)$_2$ particles at low RH exist as amorphous hydrates

23   (tetrahydrate, Ca(NO$_3$)$_2$·4H$_2$O) (Gibson et al., 2006). The Aerosol Inorganic-Organic Mixtures Functional

24   groups the Activity Coefficients (AIOMFAC) model is applied to estimate the hygroscopic growth of the three

25   nitrates. The AIOMFAC has been developed to describe the activities of atmospherically relevant aqueous

26   solutions up to high ionic concentrations at room temperature (Zuend et al., 2008; Zuend et al., 2011). As

27   shown in Fig. 1, the measured GFs of the three nitrates over the RH range studied are in fair agreement with the

28   predictions from the AIOMFAC model based on the dehydration process, which also suggests nitrate particles

29   remain noncrystalline even at the lowest RH.

30   For the organic acids studied (seen in Fig. S1, Supplement), oxalic acid (OA) and succinic acid (SA) present

31   no deliquescence transition or any obvious water uptake below 90% RH, which agree well with previous

32   studies (Jing et al., 2016; Peng et al., 2001). The observation of no evaporation losses (no decrease between dry

Atmospheric
Chemistry
and Physics
Discussions

1   particle size selected by DMA1 and that measured by DMA2) for dry OA particles is consistent with other

2   HTDMA studies, suggesting that the generated particles after drying process exist as stable OA dihydrate with

3   low vapor pressure (Prenni et al., 2001; Mikhailov et al., 2009). The GFs of aqueous OA reported by Mikhailov

4   et al. (2009) are applied to estimate ZSR predictions when assuming OA in the mixture contributes to water

5   uptake at high RH. The malonic acid (MA) and phthalic acid (PA) exhibit continuous water uptake behaviors

6   across all RH studied, consistent with the observations in other studies (Prenni et al., 2001; Brooks et al., 2004;

7   Jing et al., 2016).

8   **3.2 Water uptake behaviors of NH_4NO_3/organic acid mixtures**

9   The hygroscopic behaviors of 100 nm NH_4NO_3 particles internally mixed with organic acids at different mass

10 ratios are shown in Figs. 2 and 3. The Zdanovskii-Stokes-Robinson (ZSR) method is used to estimate the

11 hygroscopic growth of internally mixed particles by assuming that each component in the mixed particles takes

12 up water independently (Malm and Kreidenweis, 1997; Stokes and Robinson, 1966). The total water uptake by

13 mixed particles is the sum of water content associated with each pure component, which can be expressed by

14 the following equation:

15
$$GF_{mixed} = \left(\sum_k \varepsilon_k \cdot GF_k^3 \right)^{1/3} \tag{2}$$

16 , where GF_{mixed} and GF_k is the hygroscopic growth factor of the mixed particle and component k, respectively,

17 and ε_k is the volume fraction of component k in the dry particle. The volume fraction ε_k is obtained by:

18
$$\varepsilon_k = \frac{\left(w_k / \rho_k \right)}{\sum_i \left(w_i / \rho_i \right)} \tag{3}$$

19 Here w_k is the mass fraction of component k, and ρ_k is the density of component k. Although ZSR relation

20 does not take into account the interactions between components in the mixture, this simple method has been

21 found to be a valuable tool to predict the water uptake of atmospherically relevant mixtures under high RH

22 conditions (Prenni et al., 2003). In the present study, the ZSR calculations are derived from the hydration curve

23 of nitrates predicted from the AIOMFAC model and the three-parameter fit curve of organic acids (seen in Fig.

24 S1, Supplement).

25 As shown in Fig. 2, the hygroscopic growth of NH_4NO_3/oxalic acid (OA) mixed particles shows various

26 features with varying oxalic acid content. For the 3:1 NH_4NO_3/OA mixed system, the GFs of particles increase

27 gradually with elevated RH and no prompt deliquescence behavior is observed in the RH range studied. The

28 ZSR rule could well describe the hygroscopic growth of mixed particles when taking into account the

29 dissolution of oxalic acid at RH higher than 70%, as indicated by the good agreement between measurements

30 and estimates based on GFs of oxalic acid from Mikhailov et al. (2009). The 1:1 NH_4NO_3/OA mixed particles

Atmospheric
Chemistry
and Physics
Discussions

1   take up no water below 80% RH and exhibit a distinct deliquescence transition at about 86% RH. It can be seen

2   that the ZSR predictions based on our measurements fail to reproduce the hygroscopic growth of NH_4NO_3/OA

3   mixed particles with an equal mass ratio in the whole RH range. After full deliquescence, the water contents

4   associated with the 1:1 NH_4NO_3/OA mixed particles are comparable to the ZSR predictions based on GFs of

5   oxalic acid from Mikhailov et al. (2009), indicating that water uptake of mixed particles is enhanced by

6   dissolution of solid oxalic acid at high RH. It is obvious that the ammonium nitrate in the initial mixed particles

7   exists in a crystalline form rather than an amorphous one as in the pure component particles. The possible

8   reason is that the solid oxalic acid dihydrate seeds formed in the mixed droplets during the drying process could

9   trigger the heterogeneous nucleation of ammonium nitrate. The previous study has reported that the presence of

10   solid succinic acid seeds dramatically lowered the barrier to promote the crystallisation of ammonium nitrate

11   even when succinic acid content was only 25% by mass (Lightstone et al., 2000). In contrast to ammonium

12   nitrate/succinic acid mixtures, the deliquescence transition of ammonium nitrate is not observed for the 3:1

13   NH_4NO_3/OA mixed particles, suggesting that the minor OA fraction could not effectively initiate the

14   crystallisation of ammonium nitrate. The hygroscopic behavior of NH_4NO_3/OA mixed particles also reveals the

15   crystallization of oxalic acid with the presence of hygroscopic NH_4NO_3 at low RH. However, our previous

16   study indicates that the coexisting hygroscopic organics such as levoglucosan and malonic acid could hinder the

17   crystallization of oxalic acid upon dehydration (Jing et al., 2016). It can be concluded that the interactions

18   between NH_4NO_3 and oxalic acid have greater influence on phase state of NH_4NO_3 than oxalic acid.

19   Figure 3 illustrates hygroscopic characteristics of NH_4NO_3 particles internally mixed with malonic acid (MA),

20   succinic acid (SA) and phthalic acid (PA) at equal mass ratio, respectively. The measured hygroscopic growth

21   of NH_4NO_3/MA mixed particles is in fair agreement with ZSR predictions. This suggests that the presence of

22   malonic acid has no effect on the hygroscopic behavior of ammonium nitrate. For NH_4NO_3/SA mixed particles,

23   no water uptake is observed until RH increases to 60%, consistent with the reported deliquescence point of 60.6

24   ± 0.4% for equal mass NH_4NO_3/SA mixed particles using the electrodynamic balance technology (Lightstone et

25   al., 2000). It is obvious that succinic acid could influence phase behavior of ammonium nitrate. The

26   crystallization of ammonium nitrate initiated by heterogeneous nucleation is favored by the presence of solid

27   succinic acid seeds. The ZSR predictions underestimated the water uptake of NH_4NO_3/SA mixed particles

28   above 80% RH. This phenomenon can be attributed to the partial dissolution of succinic acid, which thus

29   contributed to water uptake by mixed aerosols at high RH. The early studies also found the enhanced

30   hygroscopic growth of multicomponent aerosols containing succinic acid compared to ZSR estimates without

31   taking limited solubility of succinic acid into account (Svenningsson et al., 2006; Wang et al., 2016b). The

32   NH_4NO_3/PA mixed particles show continuous water uptake without obvious phase transitions over the whole

1   RH range. At high RH, the ZSR rule could reproduce the GFs of mixed particles while significant deviation

2   between measurements and predictions is observed at low and medium RH. The possible reason is that due to

3   mass transfer limitation the residence time of 5 s appears to be insufficient for 100 nm NH_4NO_3/PA aerosols to

4   reach hygroscopic equilibrium in the low and medium RH range.

5   **3.3 Water uptake behaviors of $NaNO_3$/organic acid mixtures**

6   Figure 4 shows the hygroscopic growth of 100 nm $NaNO_3$ particles internally mixed with oxalic acid, malonic

7   acid, succinic acid and phthalic acid at equal mass ratio, respectively. As can be seen in Fig. 4a, 1:1 $NaNO_3$/OA

8   mixed particles exhibit gradual water uptake without prompt deliquescence transition. The comparisons of

9   measurement results and ZSR predictions suggest that sodium nitrate still remains amorphous and thus

10   contributes to water uptake of mixed particles from low RH, which eventually results in the dissolution of

11   oxalic acid at high RH. In contrast to ammonium nitrate, the crystallization of sodium nitrate does not occur

12   even with the presence of oxalic acid at half mass fraction. For 1:1 $NaNO_3$/MA mixed particles, the continuous

13   hygroscopic growth of this mixed system agrees well with the ZSR predicted curve across all RH studied. The

14   prior study has indicated that the reaction between malonic acid and sodium nitrate within aerosols during the

15   dehydration process could lead to considerable nitrate depletion and formation of organic salts due to the

16   evaporation of HNO_3 (Wang and Laskin, 2014). However, it is clear that this reaction has negligible impacts on

17   the overall hygroscopic behavior of $NaNO_3$/MA aerosols, as indicated by the good agreement between

18   measured growth and ZSR predictions in the RH range studied. It can be explained by the fact that the

19   hygroscopic growth of sodium malonate is comparable to that of malonic acid at each given RH (Wu et al.,

20   2011).

21   In the case of 1:1 $NaNO_3$/SA mixed particles (Fig. 4c), no distinct deliquescence transition was observed

22   upon hydration, which differed from the water uptake behavior of 1:1 NH_4NO_3/SA. Again, it shows sodium

23   nitrate is difficult to crystallize despite the presence of succinic acid that has a high deliquescence point. In

24   addition, the amount of water uptake by mixed particles is significantly larger than predictions from the ZSR

25   rule above 60% RH. The dissolution of succinic acid in aqueous $NaNO_3$ solution should be responsible for

26   enhanced water uptake of mixed particles. As shown in Fig. 4d, the equal mass $NaNO_3$/PA mixed aerosols also

27   present continuous water uptake from low RH. In contrast to 1:1 $NaNO_3$/SA mixed system, the dramatic

28   decrease in amount of water uptake by 1:1 $NaNO_3$/PA mixed system can be observed over the whole RH range

29   compared to ZSR estimates. This discrepancy appears to be caused by mass transfer limitation. It has been

30   found that after drying processing aerosol particles containing an inorganic salt and an organic acid with limited

31   solubility tend to remain phase separation with the organic phase distributed at the outer layer (Peckhaus et al.,

32   2012; Veghte et al., 2014). Zhou et al. (2014) observed the phase separation behavior of ammonium

1 sulfate/phthalic acid mixed particles due to the salting-out effect. Considering phthalic acid with limited

2 solubility, the phase separation behavior may also occur for $NaNO_3$/PA mixed particles upon dehydration. The

3 prior study for ammonium sulfate/succinic acid mixtures showed that mixed particles with core-shell structure

4 had reduced hygroscopic growth relative to the well-mixed particles (Maskey et al., 2014). Similarly, the

5 phthalic acid layer likely inhibits the water transfer from gas phase to $NaNO_3$ phase, thus resulting in the lower

6 growth of particles.

7 **3.4 Water uptake behaviors of $Ca(NO_3)_2$/organic acid mixtures**

8 Due to the interference of precipitation, only hygroscopic growth of 100 nm $Ca(NO_3)_2$ particles internally

9 mixed with malonic acid or phthalic acid at equal mass ratio is given in Fig. 5. The particle size for 1:1

10 $Ca(NO_3)_2$/MA aerosols upon hydration shows slight decrease between 10% and 40% RH and subsequently

11 continuous growth without obvious phase transition in the whole RH range, which distinguishes from

12 hygroscopic growth of pure $Ca(NO_3)_2$ and malonic acid. The similar hygroscopic behavior including the

13 decrease in particle size at low RH was also observed for mixed NH_4NO_3/protein particles (Mikhailov et al.,

14 2004) as well as amorphous oxalic acid and SOA particles derived from methylglyoxal-methylamine aqueous

15 reactions upon hydration below 50% RH (Mikhailov et al., 2009; Hawkins et al., 2014). This specific behavior

16 of particle shrinkage upon hydration typically results from humidity-induced transformation of porous, gel-like

17 structures into more compact sphere for (semi-)solid amorphous particles (Mikhailov et al., 2009). Thus, the

18 hygroscopic characteristics of $Ca(NO_3)_2$/MA aerosols suggest the structure of mixed particles distinguishes

19 from that of pure component particles.

20 The 1:1 $Ca(NO_3)_2$/PA aerosols take up water gradually with exposure of elevated RH. The overestimated

21 water uptake by the ZSR rule could be observed below 80% RH. This substantial deviation between predictions

22 and measurements can be attributed to mass transfer limitation in the aerosols (Chan and Chan, 2005). Due to

23 low molecular diffusivity, organic (semi-)solid amorphous structures at low RH could retard the equilibrium

24 between evaporation and condensation of water from submicron particles on (multi-)second time scales (Booth

25 et al., 2014; Price et al., 2014), thus kinetically inhibiting the hygroscopic growth of particles with insufficient

26 equilibrium time (Mikhailov et al., 2009). When ambient humidity increases to high RH such as 80%, more

27 water content in particles significantly reduces the impacts of mass transfer limitation, as indicated by the

28 general agreement between predictions and measurements above 80% RH in Fig. 5. Although it has been found

29 that nitrate depletions likely occur within $Ca(NO_3)_2$/organic acid aerosols, the reactions between $Ca(NO_3)_2$ and

30 organic acids may have no obvious impacts on the hygroscopic growth in our experiment due to mass transfer

31 limitation. Considering $Ca(NO_3)_2$/organic acid particles in the viscous semisolid state after dehydration (Wang

32 and Laskin, 2014), the low molecular diffusivity in amorphous phases could limit release of HNO_3 from

Atmospheric
Chemistry
and Physics
Discussions

particle phase on (multi-)second time scales. In addition, our previous study also showed that due to the presence of coexisting hygroscopic species the transformation of solid state into viscous semisolid state for NaCl/oxalic acid mixed particles considerably inhibited chloride depletions or HCl evaporation during the dehydration process (Peng et al., 2016).

4 Conclusions and atmospheric implications

Our results reveal that the nitrate/organic acid mixed aerosols exhibit varying phase behavior and hygroscopic growth depending upon the type of components present in the particles. Whereas pure nitrate particles show continuous water uptake with increasing RH, the deliquescence transition is still observed for ammonium nitrate particles internally mixed with organic acids such as oxalic acid and succinic acid with a high deliquescence point. In contrast to ammonium nitrate, hygroscopic nature of submicron sodium nitrate aerosols is characterized by continuous growth even with the presence of oxalic acid or succinic acid, indicating that sodium nitrate particles tend to exist in a liquid-like state under near dry conditions. In the case of calcium nitrate particles containing malonic acid or phthalic acid, the water uptake of mixed aerosols is significantly inhibited in the low and moderate RH range likely due to mass transfer limitation in amorphous solid with high viscosity. Our findings indicate that the coexisting organic acids modify the phase and morphology of nitrate particles in the low and medium RH range, which thus likely result in obvious enhancement or suppression of water uptake with further increasing RH.

The phase state and water uptake of atmospheric particles have crucial impacts on determining the role of aerosols in earth's climate and air quality. The well understanding of the phase state of atmospheric particles could reduce the uncertainty in radiative forcing estimates. The new findings for phase behavior of nitrates aid in further understanding the atmospheric lifetime, optical properties, and cloud formation of nitrates. In addition, these experimental results can serve as a basis for the evaluation and improvement of thermodynamic models for prediction of aerosol's physicochemical properties. The ongoing effort to understand the mechanisms of interactions between water and aerosol particles with varying compositions is of importance in incorporating these processes into global climate models.

Competing interests. The authors declare that they have no conflict of interest.

Author contribution. BJ and MG designed the experiments. BJ and ZW carried them out. BJ performed the data analysis and prepared the manuscript with contributions from all co-authors.

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1   **The Supplement related to this article is available online at supplement.**

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16

17

Atmospheric
Chemistry
and Physics
Discussions

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1   **Table 1.** Chemical properties of substances investigated in this study.

Chemical compounds	Molecular formula	Molar weight [g mol^{-1}]	Density [g cm^{-3}]	Solubility [g 100 cm^{-3} H$_2$O][a]	Manufacturer/Purity
Ammonium nitrate	NH$_4$NO$_3$	80.0	1.72	213	Dtftchem, 99%
Sodium nitrate	NaNO$_3$	85.0	2.26	91.2	Alfa Aesar, ≥99.0%
Calcium nitrate	Ca(NO$_3$)$_2$	164.1	2.5	144	
Calcium nitrate tetrahydrate	Ca(NO$_3$)$_2$·4H$_2$O	236.1	1.82	144	Alfa Aesar, 99.0%
Oxalic acid	C$_2$H$_2$O$_4$	90.0	1.90	9.5	Aldrich, 99.999%
Oxalic acid (dihydrate)	C$_2$H$_2$O$_4$·2H$_2$O	126.1	1.65		
Malonic acid	C$_3$H$_4$O$_4$	104.1	1.62	76	Sigma-Aldrich, 99%
Succinic acid	C$_4$H$_6$O$_4$	118.1	1.57	8.35	Sigma-Aldrich, ≥99.5%
Phthalic acid	C$_8$H$_6$O$_4$	166.1	1.59	0.41[b]	Sigma-Aldrich, ≥99.5%

2   [a] From *CRC Handbook of Chemistry and Physics* at 298 K; [b] From Hartz et al. (2006)

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4

Atmospheric
Chemistry
and Physics
Discussions

1
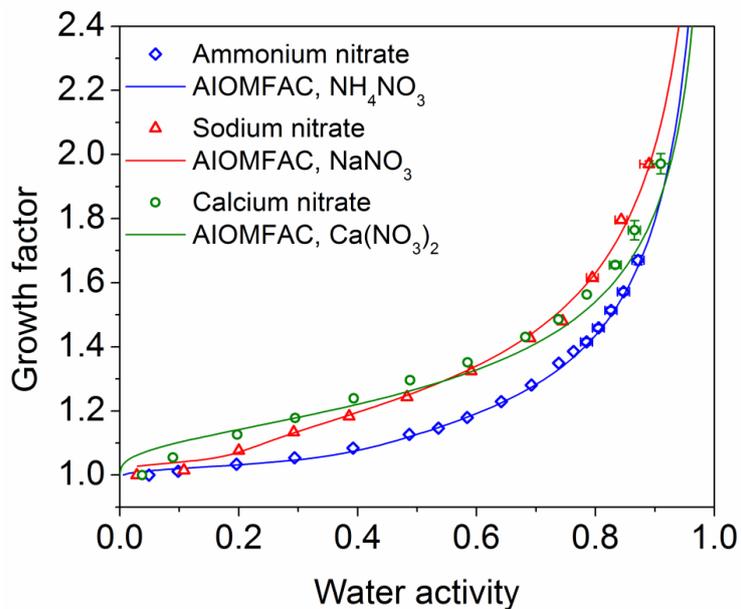
Figure 1. Hygroscopic growth factors of 100 nm NH_4NO_3, $NaNO_3$, $Ca(NO_3)_2$ particles as a function of water activity. The corresponding AIOMFAC-predicted curve associated with measurements is also presented. The error bars representing the standard deviation of multiple measurements are generally not obvious compared to the size of the symbols.

6

1
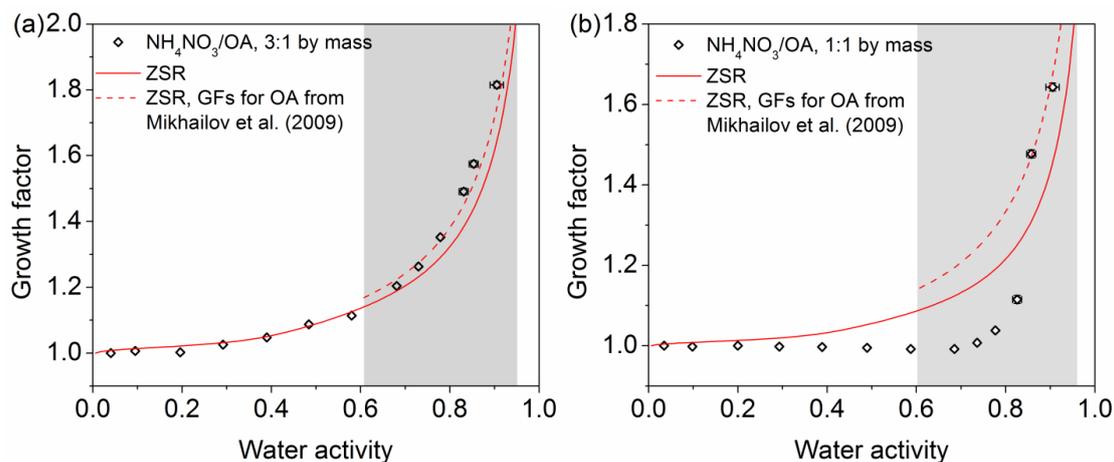
Figure 2. Hygroscopic growth factors of 100 nm NH_4NO_3/oxalic acid (OA) mixed particles with mass ratios of (a) 3:1 and (b) 1:1 as a function of water activity. The ZSR-predicted curves based on GF = 1 for oxalic acid or GFs from Mikhailov et al. (2009) are indicated by red solid and dash line, respectively. The error bars representing the standard deviation of multiple measurements are generally not obvious compared to the size of the symbols. The shading area shows potential water uptake by oxalic acid component under high RH conditions.
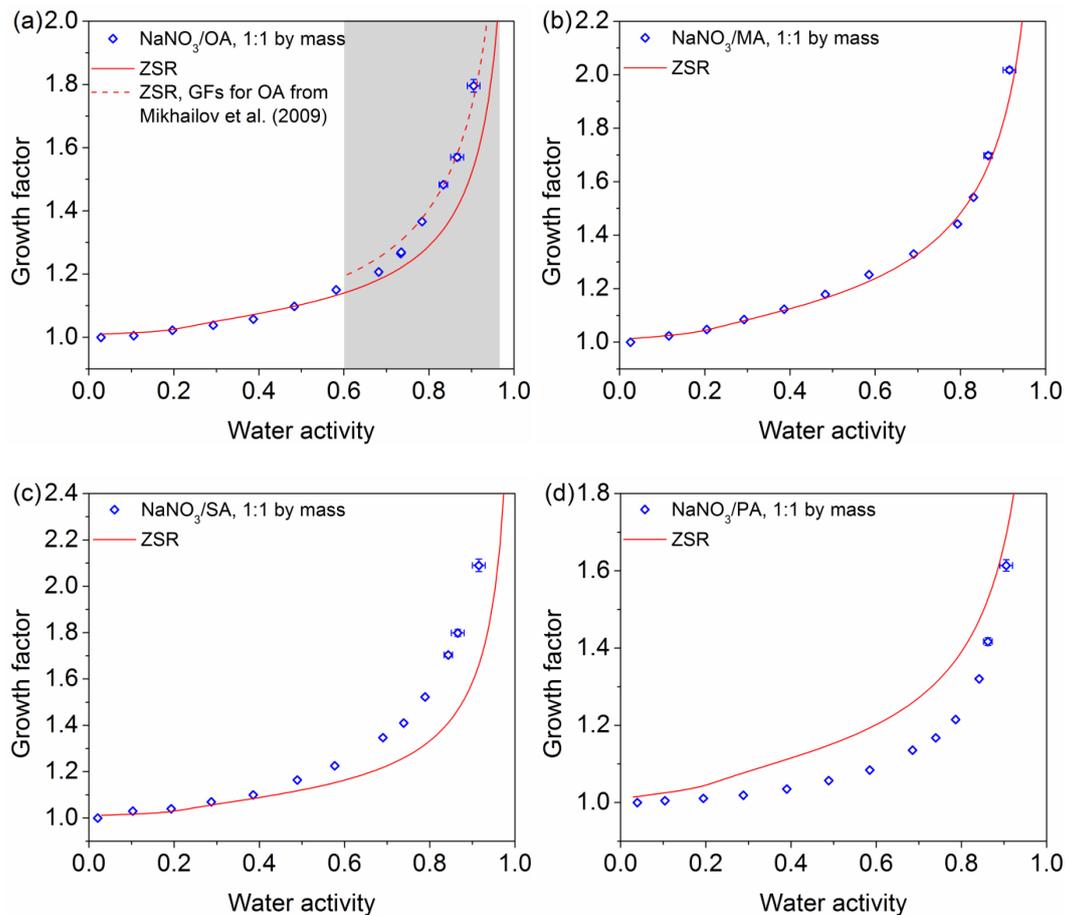
Atmospheric
Chemistry
and Physics
Discussions
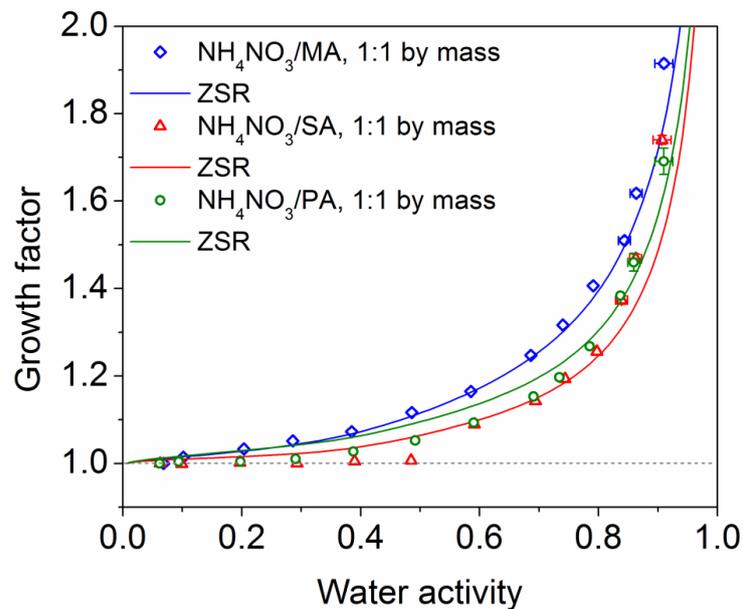
Figure 3. Hygroscopic growth factors of 100 nm internally mixed particles composed of NH_4NO_3/malonic acid (MA), NH_4NO_3/succinic acid (SA) and NH_4NO_3/phthalic acid (PA) with equal mass ratios as a function of water activity. The blue, red and green solid line indicates the hygroscopic growth predicted from the ZSR method. The error bars representing the standard deviation of multiple measurements are generally not obvious compared to the size of the symbols.
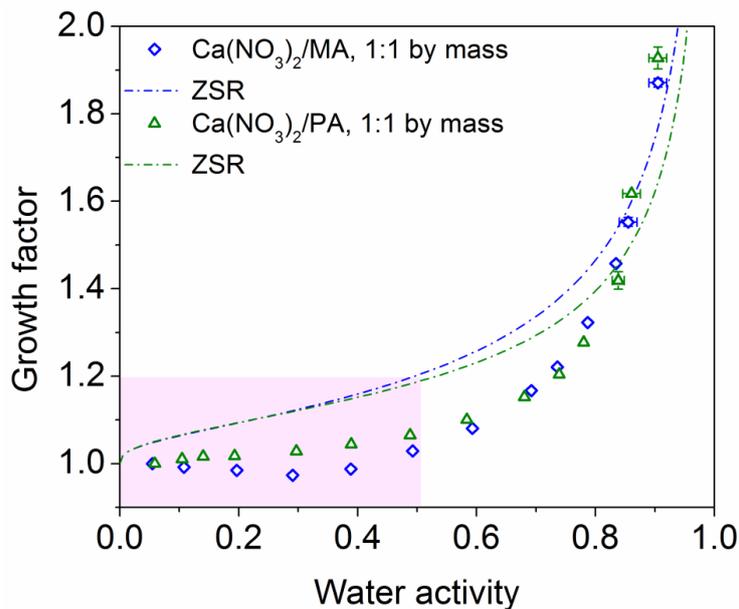
Figure 4. Hygroscopic growth factors of 100 nm internally mixed particles composed of NaNO₃/oxalic acid

(OA) (a), NaNO₃/malonic acid (MA) (b), NaNO₃/succinic acid (SA) (c) and NaNO₃/phthalic acid (PA) (d) with

equal mass ratios as a function of water activity. The red line indicates the hygroscopic growth predicted from

the ZSR method. For the NaNO₃/oxalic acid (OA) mixture, the ZSR-predicted curve based on the GFs for OA

from Mikhailov et al. (2009) is presented as the dash line. The shading area shows potential water uptake by

oxalic acid component. The error bars representing the standard deviation of multiple measurements are not

obvious compared to the size of the symbols.

1

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Figure 5. Hygroscopic growth factors of 100 nm internally mixed particles composed of $Ca(NO_3)_2$ with malonic acid (MA) or phthalic acid (PA) at equal mass ratios as a function of water activity. The blue and green dash dot line indicates the hygroscopic growth predicted from the ZSR method. The error bars representing the standard deviation of multiple measurements are not obvious compared to the size of the symbols. The shading area shows no significant water uptake by the mixed systems under low RH conditions.

8