https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

Effect of mixing structure on the water uptake of mixtures of ammonium sulfate and phthalic acid particles

Weigang Wang[1,4†], Ting Lei[2,3†], Andreas Zuend[5], Hang Su[3], Yafang Cheng[2], Yajun Shi[1], Maofa Ge[1,4,6], Mingyuan Liu[1,4]

[1]State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

[2]Minerva Research Group, Max Planck Institute for Chemistry, Mainz 55128, Germany

[3]Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz 55128, Germany

[4]University of Chinese Academy of Sciences, Beijing 100049, PR China

[5]Department of Atmospheric and Oceanic Sciences, McGill University, Montreal, Quebec, Canada

[6]Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, PR China

† These authors contributed equally to this work

Correspondence to: Weigang Wang (wangwg@iccas.ac.cn) and Maofa Ge (gemaofa@iccas.ac.cn)

Abstract. Aerosol mixing state regulates the interactions between water molecules and particles and thus controls the aerosol activation and hygroscopic growth, which thereby influences the visibility degradation, cloud formation, and its radiative forcing. Current studies on the mixing structure effects on aerosol hygroscopicity, however, is few reported. Here we investigated the effect of phthalic acid (PA) coatings on the hygroscopic behavior of the core-shell mixtures of ammonium sulfate (AS) with PA using a coating-hygroscopicity tandem differential mobility analyzer (coating-HTDMA). The slow increase in the hygroscopic growth factor of core-shell particles is observed

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

with increasing thickness of coating PA prior to the DRH of AS. At RH above 80 %, a decrease in hygroscopic growth factor of particles occurs as the thickness of PA shell increases, which indicates that the increase of PA mass fractions leads to a reduction of the overall core-shell particle hygroscopicity. In addition, the use of the ZSR relation leads to the underestimation for the measured growth factors of core-shell particles without consideration of the morphological effect of core-shell particles. For the AS/PA well mixed particles, a shift of deliquescence relative humidity (DRH) of AS to lower relative humidity (RH) is observed due to the presence of PA in the well-mixed particles. The predicted hygroscopic growth factor using the ZSR relation is consistent with the measured hygroscopic growth factor of the well-mixed particles. Moreover, we compared and discussed the influence of mixing states on the water uptake of AS/PA aerosol particles. It is found that the hygroscopic growth factor of the core-shell particles is slightly higher than that of the well-mixed particles with the same mass fractions of PA at RH above 80%. For our observation of AS/PA particles may contribute to a growing field of knowledge regarding the influence of coating properties and mixing structure on water uptake.

1 Introduction

The ability of aerosol particles to absorb and maintain water molecules, called hygroscopicity, is one of the most important physico-chemical properties of atmospheric aerosol particles with profound implications (Shi et al., 2012; Lei et al., 2014, 2018; Gupta et al., 2015; Hodas et al., et al., 2015; Zawadowicz et al., 2015; Martin et al., 2017). It might determine the phase state (Mu et al., 2018), size (Peng et al., 2001; Choi et al., 2002), mixing state, optical properties, and chemical reactivity of atmospheric aerosols exposed to the environment of the different relative humidities

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

(Heintzenberg et al., 2001; Rudich et al., 2003; Spindler et al., 2007; Abo Riziq et al., 2007, 2008; Eichler et al., 2008). Moreover, the change of these properties after water absorption on aerosol particles can strongly affect the cloud formation, aerosol radiative forcing, global climate, and even human health (Cheng et al., 2008; Reutter et al., 2009; Rose et al., 2011; Stock et al., 2011; Liu et al., 2012, 2013; Tie et al., 2017). Therefore, the interaction between water molecules and aerosol particles is crucial for a better understanding of the aerosol-cloud-climate effects in the atmosphere (Sjogren et al., 2007; Zamora et al., 2011; Jing et al., 2016).

Atmospheric aerosols contain a complex mixture of inorganic and organic compounds in the different mixing structures, e.g., externally mixed, internally mixed (Ganguly et al., 2006). The internally mixed aerosol particles may divided into homogeneous and heterogeneous internally mixed aerosol particles (Lang-Yona et al., 2009), which could, in turn, strongly influence the water uptake, optical properties, and the cloud condensation nuclei (CCN) ability of the particles (Lesins et al., 2002; Falkovich et al., 2004; Zhang et al., 2005; Schwarz et al., 2006; Su et al., 2010). Most of earlier studies on the hygroscopic behavior of multi-components aerosol focus on the well mixed particles generated from homogeneously internally mixed solutions (Miñambres et al., 2010; Shi et al., 2014; Gupta et al., 2015; Jing et al., 2016; Lei et al., 2014; 2018) For example, Choi and Chan (2002) studied on the effects of glycerol, succinic acid, malonic acid, citric acid, and glutaric acid on the hygroscopic properties of sodium chloride and AS in the well mixed aerosol particles, respectively using an eletrodynamic balance. They observed that the deliquescence and efflorescence of sodium chloride and AS were affected by the presence of different organic components in the mixed aerosol particles. Concerning the hygroscopicity of the heterogeneity of internally mixed aerosol particles, such as core-shell particles, there are several studies on

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

investigating their interaction with water molecules (Ciobanu et al., 2009; Song et al., 2012; Shiraiwa et al., 2013; Hodas et al., 2015; Song et al., 2018). However, to date, few laboratory studies on the influence of organic coatings on the hygroscopic behavior of seed particles and the difference of mixing state effects on the hygrosocpicity of aerosol particles (Zhang et al., 2008; Pagels et al., 2009; Xue et al., 2009; Lang-Yona et al., 2010; Ditas et al., 2018). E.g., A HTDMA study on the organic coating effects on the hygroscopicity of AS core was studied by Maskey et al. (2014). They observed a shift of DRH of AS to lower RH for the core-shell particles due to presence of levoglucosan coatings. They further compared water absorption on AS/levoglucosan core-shell particles and the AS/succinic acid core-shell particles. They suggests that difference organic coatings lead to changes in the hygroscopic properties of core-shell particles. Chan et al. (2006) investigated hygroscopicity of AS coated with different mass fractions of glutaric acid during two continuous humidification and dehumidification cycles using a Raman spectra and an electrodynamic balance. They observed different hygroscopic behavior and morphology of aerosol particles between the two humidification and dehumidification cycles due to the different mixing states. Therefore, to investigate organic coating effect on the hygroscopicity of seed aerosol particles and further to study on difference of mixing states effects on the hygroscopic behavior of aerosol particles are crucial for estimation the direct and indirect radiative effect of aerosol particles on the Earth's climate (Saxena et al., 1995; Ansari et al., 2000; Maskey et al., 2014).

PA is ubiquitous in rural mountains and marine atmosphere in Asia (Wang et al., 2011). It is mainly produced by the photo-oxidation of volatile organic compounds (VOCs), such as xylene, and naphthalene (Kawamura and Ikushima, 1993; Schauer et al., 1996; Zhang et al., 2016). PA has also been identified as a significant contributor to the urban organic compounds (Rogge et al., 1993). PA

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

particles are generally used as a tracer for the secondary organic aerosol (SOA) in atmospheric fine particles (Schauer et al., 2000, 2002). Recently, Zhang et al. (2016) reported the importance of atmospheric PA aerosol particles in the visibility degradation and the formation of CCN. The organic PA can have profound effect on light scattering, hygroscopictiy, and phase transition properties of multicomponent atmospheric aerosols. However, these physico-chemical properties of PA have been little documented in the literature (Brooks et al., 2004; Liu et al., 2016). Here we summarized a few studies on the hygroscopicity of the PA-containing aerosol particles. Brooks et al. (2004) investigated continuous hygroscopic growth of PA aerosol particles in the humidification process using a HTDMA technique. Hori et al. (2003) and Huff Hartz et al. (2006) measured the high CCN activity of PA in spite of its low solubility. Also, the liquid-liquid phase separations (LLPS) with aerosol particles consisting organic and inorganic components were observed by many groups (Ciobanu et al., 2009; Betram et al., 2011; Song et al. 2012a, 2012b; You et al., 2014). For example, Song et al. (2012a, 2012b) investigated that LLPS occurs in the mixed dicarboxylic acids containing 5, 6, and 7 carbon using an optical microscopy and micro-Raman spectroscopy, and further established that occurrence of LLPS of aerosol particles has an average elemental oxygen-to-carbon (O:C) ratio of the organic fraction of less than 0.8. Subsequently, the occurrence of liquid-liquid phase separation in the internally mixed aerosols consisting of AS and PA was performed by Zhou et al. (2014) during the dehumidification processes using the Raman spectra. You et al. (2014) further found that the LLPS of aerosol particles with a different O: C ratio of 0.5<O: C<0.8 depends on the types of organic functional groups and inorganic salts presented. Therefore, these studies suggest that the LLPS in the mixed organic and inorganic components aerosol particles is influenced by the amounts of organic and inorganic aerosol components and types.

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

In this work, we investigated the effect of the different thickness of coating PA and the core size on the water uptake of core-shell particles containing AS, and further studied the effect of the mixing states on the hygroscopic behavior of PA /AS aerosol particles using a HTDMA technique. For example, we compared the hygroscopic behavior of well-mixed AS/PA particles with that of core-shell AS/PA particles with the same PA mass fractions. In addition, we used the Zdanovskii-Stokes-Robinson (ZSR) relation and the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) model (Zuend et al., 2008; 2011) to predict the hygroscopic growth factor (GF) of mixed aerosol particles in the different mixing structure. Moreover, the AIOMFAC-based model with a version of the liquid-liquid equilibrium (LLE) algorithm was employed in our study to predict the phase compositions of liquid and solid phases for a given composition of a mixture (Zuend and Seinfeld. 2013).

2 Experimental and modeling methods

2.1 HTDMA setup and experimental protocol

A HTDMA setup is employed to measure the aerosol nanoparticle hygroscopic growth factor (g_f) and phase transition in the RH range from 5% to 90 %. Here, g_f is defined as the ratio of mobility diameter of aerosol particles after humidification (D_m(RH)) to that dry condition (D_m(<5% RH)). Figure 1 shows a schematic diagram of the HTDMA setup. It is comprised of four main components, including three differential mobility analyzers (DMA), a condensation particle counter (CPC), a humidification system, and a coating system. The more detail information on the HTDMA setup, calibration, and verification have been described elsewhere (Lei et al., 2014; 2018; Jing et al., 2016; Liu et al., 2016). In our study, the particle-sizing, the aerosol/sheath flow rates, and DMA voltage

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

supply have been calibrated every month, respectively. The uncertainty of aerosol/sheath flow rates are kept within ±1% around the reference values. The deviations of the measured DMAs voltage from set-point values is less than ±1%. The sizing agreement of DMAs between measured diameter of polystyrene latex (PSL) spheres and their nominal diameter (100±3 nm) is within ±1%. The chemical substances and related to physical properties are available in the Supporting Information Table S1. The solutions used in our measurements are prepared with distilled and de-ionized millo-Q water (resistivity of 18.2 MΩ cm at 298 K).

2.1.1 Homogeneously internally mixed AS/PA Aerosol particles

Briefly, poly-disperse aerosol particles were atomized from homogeneous bulk solutions with different mass fractions of PA and AS (Fig. 1), assuming that the compositions of aerosol particles remain the same as that of the solutions used in the atomizer (MSP 1500, MSP). The resulting particles were dried and subsequently charged through a dryer and then a neutralizer, respectively. A mono-disperse distribution of particles with a desired diameter were selected by the first differential mobility analyzer (DMA1) with RH below 5 %. After particle sizing, the aerosol particles were exposed to a humidification mode (5%→90%) in the Nafion conditioner tubes. The number size distributions of humidified aerosol particles were then measured by a DMA3 coupled with a CPC. To have a precise control of the aerosol RH, the flow rates of the humid and dry air were adjusted with a proportional-integral-derivative (PID) system. Also, to ensure the sufficient water equilibrium with aerosol particles, the difference between RH2 and RH3 (RH in the sheath flow) was within 2 % during the experiment.

2.1.2 Heterogeneously internally mixed AS/PA aerosol aerosols

The seed aerosol particles were generated from an aqueous solution of AS (0.05 wt%) by an atomizer.

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

After a passage through a silica gel diffusion dryer and a neutralizer, the seed aerosol particles with a certain diameter (100, 150, 200nm, respectively) were firstly selected by a DMA1 and then exposed to organic vapors in a coating system. To be specific, the coating system contains a controlled silicone oil bath vaporizer, a reservoir of organic compound, and a condenser. The seed AS particles passed through a sealed flask immersed in a silicone oil bath. The sealed flask was filled with the PA powder. The PA vapors were enriched into the aerosol flow by heating. The resulting organic vapors were condensed onto the seed particles after cooling to an ambient environment through a condenser. Similarly, this system for coating organic components on the particles has been proved to be efficient by Abo Riziq et al. (2008). The coated particles of certain sizes were then selected by the DMA2 to determine the thickness of organic components (D_{total} = D_{core} + coating). After core-shell particle-sizing, aerosols pre-humidified in a Nafion tube and flowed into the second Nafion humidifier at the set RH2 to reach equilibrium at the RH condition. Finally, the conditioning core-shell particle was detected by a DMA3 and a CPC at ambient temperature. The uncertainty of thickness of coating PA was ± 1.0 nm, considering the fluctuation in temperature and uncertainty of sizing measurements by DMAs.

2.2 Theory and modeling methods

2.2.1 GF data fit

We use the following expression to predict the hygroscopic growth factor of individual components.

$$GF = \left[1 + (a + b * a_w + c * a_w^2)\frac{a_w}{1-a_w}\right]^{\frac{1}{3}} \quad (1)$$

Here it is assumed that water activity (a_w) is equal to the water saturation ratio (a_w = RH / 100 %). The coefficients a, b, and c are determined by fitting Eq. (1), and their values are shown in Table 1 according to the measured GF data against RH. The equation (1) is expected to fit the continuous

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

water uptake behavior of particles (Brooks et al., 2004; Kreidenweis et al., 2015).

2.2.2 GF predictions by ZSR

We use the Zdanovskii-Stokes-Robinson (ZSR) relation to calculate the hygroscopic growth factor of mixed particles, GF_{mixed}. The GF of a mixture can be estimated from the GF_j of the pure components j and their respective volume fractions, $\mathcal{E}_j$, in the mixture (Malm and Kreidenweis, 1997).

$$\mathrm{GF_{mix}} = \left[\sum_j \varepsilon_j \left(\mathrm{GF_j}\right)^3\right]^{\frac{1}{3}} \quad (2)$$

$$\varepsilon_{AS} = \frac{\frac{4}{3}\pi R_{AS}^3}{\frac{4}{3}\pi R_{core-shell}^3} \quad (3)$$

3 Results and discussion

3.1 Hygroscopic growth of homogeneously internally mixed aerosol particles

Figure 2 shows the measured hygroscopic growth factors of the AS, PA, and well-mixed AS with different mass fractions of PA particles with dry diameter 100nm against RH, respectively. During the hydration mode, there is no change in size until a slow increase occurs at 60% RH in the case of well-mixed AS/PA aerosol particles. This increase may occur because the PA uptakes a small amount of water. However, an abrupt increase in the hygroscopic growth factor is observed at 75% RH for well-mixed particles containing 50wt, 75wt % PA, of which the growth factor is higher than that of pure PA aerosol particles (1.09 ± 0.01 nm from measurements shown in Fig. 2) at the same RH. An interesting, yet contrasting phenomenon is that water uptake for well-mixed particles containing 50wt % PA components is relatively higher than that of mixtures containing 75wt % PA at 75% RH. One possible reason is that the full deliquescence of AS in the well-mixed particles with 50wt % PA components is completed at 75 % RH, while AS in the mixtures containing 75wt % PA components

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

is partially deliquescent. A decrease in the hygroscopic growth factor of well-mixed AS/PA particles with increasing mass fractions of PA is observed at RH above 80 %. For example, the measured growth factors for internal mixtures containing 25wt, 50wt, 75wt % PA are 1.36, 1.28, 1.19 at 80% RH, respectively, lower than the growth factor of 1.45 for pure deliquesced AS particles (value from measurements shown in Fig. 2) at the same RH. Also, the measured hygroscopic growth factors within experimental uncertainty were in good agreement with the results from the well-mixed particles performed by Hämeri et al. (2002). In addition, with increasing mass fractions of PA in the well-mixed particles, the smoothing of the hygroscopic growth factor curves is obvious, indicating that the PA aerosol particles have a significant effect on the water uptake of well-mixed AS/PA particles such as a shift or suppression of DRH of AS in the mixed particles. For example, in the case of 1:3 mixtures of AS:PA (by mass), 75wt% PA in the well-mixed particles suppresses the deliquescence of AS, i.e., AS in the well-mixed particles slowly dissolve into the liquid phase due to continuous water uptake of PA prior to the deliquescence relative humidity of AS (80% RH). This similar phenomenon was observed by previous studies (e.g., Hämeri et al., 2002; Qiu and Zhang, 2013). For example, Qiu and Zhang (2013) observed that mixture particles consisting of dimethylaminium sulfate and AS exhibited a moderate growth by water uptake in the RH range of 40%-70% RH. The calculated growth factors from a model based on the ZSR relation agree well with the hygroscopic growth factors of well-mixed AS/PA particles when accounting for measurement uncertainty. A possible reason for this good agreement is that the measured growth factors referring to the water uptake contribution by PA in the ZSR relation are obtained from the fitted growth curve of pure PA particles (as shown in Fig. 2. Fitted expression, Eq. (1)). Thus, in the case of well-mixed AS/PA, relatively good agreement with the experimental growth factors of

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

222 mixtures with 25, 50, and 75 wt % PA demonstrates that individual components independently
223 absorb water in proportion to their volume. However, the discrepancy between measured growth
224 factor of well-mixed AS/PA particles at 75 % RH and the predicted growth factors by using the ZSR
225 relation may be due to the molecule interaction between organic molecular and completely or
226 partially dissolved AS ions. A similar phenomenon was reported for well-mixed mixtures of AS +
227 levoglucosan in the previous study by Lei et al (2014, 2018).

228 **3.2 Hygroscopic growth of core-shell structured aerosol particles**

229 Figure 3 shows the measured hygroscopic growth of core-shell structured particles as a function of
230 RH. Here, we investigated the hygroscopic behavior of samples of various seed particle sizes (AS
231 particle dry diameter of 100, 150, 200nm) and coating (PA coating of 10, 20, 30, 50nm), respectively.
232 The core-shell structured particles start to absorb a small amount of water at RH lower than the
233 DRH of AS due to the organic coating. A similar behavior has been observed for core-shell
234 structured particles containing AS and palmitic acid by Garland et al. (2005), where early water
235 uptake and reduced hygroscopic growth after deliquescence of AS (compared to pure AS aerosols)
236 were reported. A reduction of the hygroscopic growth factors of core-shell particles becomes
237 obvious as the thickness of the PA shell increases after the deliquescence of core-shell particles. For
238 example, the measured growth factor value at 80% RH is 1.45, 1.40, 1.32, and 1.28 for core-shell
239 particles containing 100nm AS and 10, 20, 30, 50nm coating PA shell, respectively. The kinetic
240 limitation on the core-shell particles is expected to increase considerably with increasing the
241 thickness of the coating PA shells, which retards the transport rate of water molecules across core-
242 shell aerosol particles/air interface. In addition, the measured hygroscopic growth factor of core-
243 shell AS/PA mixtures is predicted by the ZSR relation, which is based on the hygroscopic growth

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

244 factors of AS and PA derived from the E-AIM predictions for AS and the fitted GF curve (Eq. 1).
245 The ZSR-based predictions are lower than that of core-shell aerosol particles at RH in the range of
246 5-90%. The underprediction of the ZSR relation was also observed in the literatures (Chan et al.,
247 2006; Sjogren et al., 2007). Sjogren et al. (2006) observed a strong higher water uptake of mixtures
248 consisting of AS and adipic acid with different mass rations (1:2, 1:3, and 1:4) at RH above 80 %
249 compared with ZSR relation in the hydration condition. They assumed that adipic acid is more likely
250 to enclose the water-soluble AS in veins and cavities, which results in easy uptake of water and a
251 negative curvature of the solution meniscus at the opening of the vein compared to a flat or convex
252 particle surface. Thence, in the case of AS/PA core-shell particles, one potential reason for the
253 underestimation of the measured growth factor by ZSR relation is the morphology effect on the
254 core-shell structured AS/PA particle. To be specific, for the core-shell aerosol particles consisting of
255 PA and AS, especially at 80% RH, it shows a considerable amount of water uptake due to the
256 dissolution of the AS core. This dissolution of AS may form completely or partially mixed AS/PA
257 solution droplets. The resulting effect of the arrangement and restructuring of core-shell structured
258 particles may change the hygroscopicity and mixing state of the core-shell particles at RH above
259 80% (Chan et al., 2006; Sjogren et al., 2007). Another morphological effect could be that
260 morphology of a somewhat porous polycrystalline AS core could lead to a larger amount of AS in
261 the particles at RH prior to deliquescence of AS – to appear as a 100-200 nm mobility diameter –
262 hence a thinner than 10-50 PA coating to bring it to a near spherical shape of 110-250 nm core-shell
263 particles (Zelenyuk et al., 2006).
264 Figure 4 shows that the experimental water absorption of the varying size of AS core coated with
265 50-nm PA shell in the hydration condition. In the case of 50nm-PA shell coated with a certain size

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

of the AS seed (100, 150, 200nm) with respect to 68wt, 55wt, 46 wt % PA in the core-shell particles, It exhibits an increase in hygroscopic growth factor of core-shell particles at RH below 80 % as the size of AS core decreases. However, a decrease in hygroscopic growth factor of core-shell mixtures is observed at RH above 80 % with decreasing the size of the AS core. This indicates that the 50nm-PA shell in the core-shell particles have predominantly contributed to the hygroscopic growth of core-shell particles at low RH. At high RH (e.g., after AS deliquescence), however, 50-nm PA coating shows a weak kinetic limitations for water uptake by core-shell particles as the size of AS core increases. For example, the measured growth factor value is 1.28, 1.34, and 1.40 at 80% RH for 100-200 nm AS core in the mixed particles, respectively. The discrepancy between measured hygroscopic growth factors and predicted hygroscopic growth factors of core-shell particles by ZSR relation, as discussed in Sect. 3.2, is due to the morphology effect. For ZSR prediction, it assumes volume fraction of AS components is constant according to the ratio of volume of AS core in the sphere to the volume of core-shell sphere based on Eq. (3). Without considering morphology effect, the ZSR prediction results in an underestimation of hygroscopic growth factors of core-shell particles.

3.3 Comparison of heterogeneously and homogeneously internally mixed AS/PA aerosol particles

Figure 5 shows the hydration curves of different AS cores coated with the different mass fractions of PA loading (shown in the Supporting Information Table S2) in comparison with those of the well-mixed with the same PA mass fractions particles, pure AS particles, and pure PA particles in the range of 5 – 90% RH. The effect of the coating PA on core-shell particles becomes more pronounced than that of PA in the well-mixed particles at RH below 70% as shown in Fig 5a-b, which leads to

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

higher amounts of water absorption at low RH. However, compared to Fig 5a-b, Fig. 5c shows the hygroscopic growth factors of well mixed AS/PA is slightly higher than that of AS/PA core-shell particles with 46% wt PA. At 75% RH, the measured growth factor value of core-shell particles is lower than that of homogeneously internally mixed mixtures in the PA mass fraction range from 68wt to 46wt % due to the mass transfer limitations of water vapor transport to the AS core in the core-shell particles. For the well mixed AS/PA particles, however, partial dissolution of AS into the liquid AP phase may lead to more water uptake by well mixed particles. For example, for the core-shell mixtures with 68wt % PA loading, the experimental growth factor value is 1.09 at 75% RH, relative to the growth factor of 1.17 of well-mixed mixtures AS/PA. After an abrupt increase in particle diameter of mixed particles, the core-shell AS/PA particles uptake slightly more water than well-mixed AS/PA with the same mass fractions of PA as RH increases above 80%. Core-shell particle morphology may experience the restructuring and associate size change of particles. A similar hygroscopic behavior was observed in previous papers (Chan et al., 2006; Sjogren et al., 2007; Maskey et al., 2014). Chan et al. (2006) observed for hygroscopicity of 49wt % glutaric acid coated on AS core during two continuous hydration cycles: the experimental growth factor of the fresh core-shell of AS and glutaric acid in the first hydration cycle is a bit higher than those in second hydration cycle with the same mass fractions of glutaric acid. They suggested that the mixing state has changed from core-shell to well-mixed state during the humidification process. Also, a slightly higher growth factor of core-shell particles than that of well-mixed particles was found when comparing the hygroscopic growth factors of 49wt % glutaric acid coated on AS core with that of well-mixed mixtures of AS with the same mass fractions of glutaric acid from different papers (Choi et al., 2002; Chan et al., 2006). However, a contrasting observation was observed in the previous

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

study (Maskey et al., 2014). Maskey et al. (2014) investigated the hygroscopic behavior of the internal mixtures consisting AS coated with either succinic acid or levoglucosan in the different mixing state with the same volume fractions of organic compounds. The growth factor of core-shell particles consisting of AS and succinic acid is lower than that of the well-mixed particles, while experimental values for core-shell of AS/levoglucosan particles are close to those of the well-mixed mixtures. The possible reasons for the difference between our study and results from Maskey et al. (2014) are physical properties of the organic components, such as hygrosocpicity, viscosity, volatility, gas/liquid/solid diffusion coefficient of water vapor, and water uptake coefficients. Thence, different kinds of organic compounds have a different effect in the hygroscopic growth of mixtures, including the core-shell and the well-mixed state. For example, no hygroscopic growth was observed up to 99 % RH for pure succinic acid particles (shown in Fig. S1a). Peng et al. (2001) measured the DRH of succinic acid at 99% RH using a bulk solution at 24 °C. Also, Henning et al. (2002) observed no hygroscopic growth factors of soot/succinic acid core-shell particles in the hydration mode using a HTDMA. In the case of AS/succinic acid core-shell particles, No water uptake by AS coated succinic acid shell was observed before 80% RH, while there is a gradual increase in water absorption of core-shell particles prior to the deliquescence of AS with different mass fraction of PA components as shown in Fig 5a-c. This suggested the physical state of shell is solid and liquid for Maskey et al. (2014) and our measurements, respectively. At RH above 80%, the kinetic limitation on the water vapor uptake through solid shell into the core is more obvious than that through liquid shell into the core (i.e., liquid diffusion coefficient of water vapor is the range of 10^{-10} to 10^{-9}, solid diffusion coefficient of water vapor is the range of 10^{-13}-10^{-14} at 25°C). This can lead to different hygroscopic behavior of core-shell particles. In the case of

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

AS/levoglucosan measured by Maskey et al. (2014), they found that the slightly higher growth factors for the well-mixed particles is than core-shell aerosol particles (88nm AS core coating 12nm levoglucosan). The mass fraction of levoglucosan in the core-shell particles is ~ 29wt %. In our study, AS coated with PA with mass fraction range is between 46wt to 68wt %. Using the lower mass fraction of PA (e.g., 29wt %), compared to mass fraction range of 46-68wt %, it may occur lower hygroscopic growth factors of AS/PA core-shell particles than that of well mixed particles. The low mass fraction of PA will be explored in future. In addition, by using the ZSR relation to predict the hygroscopic growth factors of the internal mixture in the different mixing structures with the same mass fractions of organic compounds, the measured growth factors of well-mixed AS/PA particles agree well with the calculated growth factors by the ZSR relation comparing with that of core-shell AS/PA particles.

4 Summary and conclusion

Due to different sources and aging process of aerosol particles in the atmosphere, atmospheric aerosol particles tend to exist in different mixing structures, such as externally mixed, homogeneous mixed (e.g., well-mixed and core-shell structure). In this work, PA is used as a representative organic component generated from various sources, such as vehicles, biomass burning, photo-oxidation to investigate hygroscopic behavior of AS/PA aerosol particles with different mixing states. Continuous water absorption by pure PA aerosol particles has an important contribution in smoothing of hygroscopic curve of AS/PA well-mixed mixtures with increasing mass fraction of PA components. In addition, the ZSR relation is a good estimation of experimental hygroscopic growth factors of AS/PA well-mixed particles. Furthermore, A coating-HTDMA technique study on the PA

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

354 coating effects on the hygroscopicity of AS core is investigated. PA coating increase the water
355 uptake by core-shell at RH prior to the AS deliquescence but decrease hygroscopic growth of core-
356 shell particles at high RH. Finally, we and compared and discussed the difference of influence of
357 mixing structures on the hygroscopicity of AS/PA aerosol particles. In addition, in this study, using
358 an E-AIM model, Fitted Expression Eq. (1), and the ZSR relation is to predict the measured
359 hygroscopic growth factors of pure components, well-mixed, and core-shell particles, respectively.
360 According to filed studies reported in the previous literature, a variety of organic aerosol particles
361 were characterized in the atmosphere. Thence, the effect of various organic substances on the
362 hygroscopic behavior cycle of the organic/inorganic core-shell particles need to be further
363 investigated. Currently, suppression or delay of the DRH and ERH of core-shell particles to some
364 extent depends on the different types of organic compound coatings, such as molecular structure,
365 viscosity, solubility and hygroscopicity. Also, for the certain organic compounds such as PA, a
366 difference in the hygroscopic behavior of mixing states is more likely to depend on the difference
367 of influence of kinetic limitations. Moreover, in order to understand which models suitable to
368 explain these potential atmospheric relevant core-shell aerosol hygroscopicities, and whether they
369 contain any rules related to functional groups of the organic components, it is significant to explore
370 the possibility of modeling combining with the experimental measurements. Understanding the
371 contribution of different organics coating to hygroscopic behavior of the core-shell mixtures as well
372 as discussion of the extent to which kinetic limitations or organic physico-chemical properties is
373 expected to have contributed to difference in the hygroscopicity in the different mixing structure,
374 which may lead toward a more mechanistic understanding of how water uptake can be linked to the
375 mixing states in the atmosphere.

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

This work focus on the water uptake by these aerosol particles in the different mixing states. Atmospheric aerosol particles may undergo the humidity cycles depend on the ambient RH history. A hysteresis effect with solid-liquid phase transition of core-shell aerosol particles may occur as RH decreases in the ambient air. Also, more attention to the residence time will be paid on core-shell aerosol particles to reach equilibrium in the whole of RH range. These changes related to the hygroscopic behavior of core-shell aerosol particles studies will be a topic in the future.

Author contributions: W.G.W designed and led the study. W.G.W and T.L assembled the coating-HTDMA. T.L performed the experiments and prepared the manuscript with contributions from all co-authors. All co-authors discussed the results and commented on manuscript.

Data availability

The data used in this study are available upon request from the corresponding author.

Acknowledgement

This project was supported by The National Key Research and Development Program of China (2017YFC0209500), and the National Natural Science Foundation of China (41822703, 91744204, 91844301).

Reference

Abo Riziq, A., A., Trainic, M., Erlick, C., Segre, E., and Rudich, Y.: Extinction efficiencies of coated absorbing aerosols measured by cavity ring down aerosol spectrometry, Atmos. Chem. Phys., 8, 1823-1833, 2008.

Abo Riziq, A., Erlick, C., Dinar, E., and Rudich, Y.: Optical properties of absorbing and non-

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

398 absorbing aerosols retrieved by cavity ring down (CRD) spectroscopy, Atmos. Chem. Phys., 7,
399 1523-1536, 2007.
400 Ansari, A. S. and Pandis, S. N.: Water Absorption by Secondary Organic Aerosol and Its Effect on
401 Inorganic Aerosol Behavior, Environmental Science & Technology, 34, 71-77, 2000.
402 Bertram, A. K., Martin, S. T., Hanna, S. J., Smith, M. L., Bodsworth, A., Chen, Q., Kuwata, M., Liu,
403 A., You, Y., and Zorn, S. R.: Predicting the relative humidities of liquid-liquid phase separation,
404 efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and
405 water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental
406 ratio of the organic component, Atmos. Chem. Phys., 11, 10995-11006, 2011.
407 Brooks, S. D., DeMott, P. J., and Kreidenweis, S. M.: Water uptake by particles containing humic
408 materials and mixtures of humic materials with ammonium sulfate, Atmospheric Environment, 38,
409 1859-1868, 2004.
410 Chan, M. N., Lee, A. K. Y., and Chan, C. K.: Responses of ammonium sulfate particles coated with
411 glutaric acid to cyclic changes in relative humidity: Hygroscopicity and Raman characterization,
412 Environmental Science & Technology, 40, 6983-6989, 2006.
413 Cheng, Y. F., Wiedensohler, A., Eichler, H., Heintzenberg, J., Tesche, M., Ansmann, A., Wendisch,
414 M., Su, H., Althausen, D., Herrmann, H., Gnauk, T., Brüggemann, E., Hu, M., and Zhang, Y. H.:
415 Relative humidity dependence of aerosol optical properties and direct radiative forcing in the surface
416 boundary layer at Xinken in Pearl River Delta of China: An observation based numerical study,
417 Atmospheric Environment, 42, 6373-6397, 2008.
418 Choi, M. Y. and Chan, C. K.: The Effects of Organic Species on the Hygroscopic Behaviors of
419 Inorganic Aerosols, Environmental Science & Technology, 36, 2422-2428, 2002.

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

420 Ciobanu, V. G., Marcolli, C., Krieger, U. K., Weers, U., and Peter, T.: Liquid−Liquid Phase
421 Separation in Mixed Organic/Inorganic Aerosol Particles, The Journal of Physical Chemistry A, 113,
422 10966-10978, 2009.
423 Cruz, C. N. and Pandis, S. N.: Deliquescence and Hygroscopic Growth of Mixed Inorganic−Organic
424 Atmospheric Aerosol, Environmental Science & Technology, 34, 4313-4319, 2000.
425 Eichler, H., Cheng, Y. F., Birmili, W., Nowak, A., Wiedensohler, A., Brüggemann, E., Gnauk, T.,
426 Herrmann, H., Althausen, D., Ansmann, A., Engelmann, R., Tesche, M., Wendisch, M., Zhang, Y.
427 H., Hu, M., Liu, S., and Zeng, L. M.: Hygroscopic properties and extinction of aerosol particles at
428 ambient relative humidity in South-Eastern China, Atmospheric Environment, 42, 6321-6334, 2008.
429 Falkovich, A. H., Schkolnik, G., Ganor, E., and Rudich, Y.: Adsorption of organic compounds
430 pertinent to urban environments onto mineral dust particles, Journal of Geophysical Research:
431 Atmospheres, 109, n/a-n/a, 2004.
432 Ganguly, D., Jayaraman, A., Rajesh, T. A., and Gadhavi, H.: Wintertime aerosol properties during
433 foggy and nonfoggy days over urban center Delhi and their implications for shortwave radiative
434 forcing, Journal of Geophysical Research: Atmospheres, 111, 2006.
435 Garland, R. M., Wise, M. E., Beaver, M. R., DeWitt, H. L., Aiken, A. C., Jimenez, J. L., and Tolbert,
436 M. A.: Impact of palmitic acid coating on the water uptake and loss of ammonium sulfate particles,
437 Atmos. Chem. Phys., 5, 1951-1961, 2005.
438 Gupta, D., Kim, H., Park, G., Li, X., Eom, H. J., and Ro, C. U.: Hygroscopic properties of NaCl and
439 NaNO₃ mixture particles as reacted inorganic sea-salt aerosol surrogates, Atmos.
440 Chem. Phys., 15, 3379-3393, 2015.
441 Hämeri, K., Charlson, R., and Hansson, H.-C.: Hygroscopic properties of mixed ammonium sulfate

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

442 and carboxylic acids particles, AIChE Journal, 48, 1309-1316, 2002.

443 Heintzenberg, J., Maßling, A., and Birmili, W.: The connection between hygroscopic and optical

444 particle properties in the atmospheric aerosol, Geophysical Research Letters, 28, 3649-3651, 2001.

445 Hodas, N., Zuend, A., Mui, W., Flagan, R., and Seinfeld, J.: Influence of particle-phase state on the

446 hygroscopic behavior of mixed organic–inorganic aerosols, Atmospheric Chemistry and Physics,

447 15, 5027-5045, 2015.

448 Hori, M., Ohta, S., Murao, N., and Yamagata, S.: Activation capability of water soluble organic

449 substances as CCN, Journal of Aerosol Science, 34, 419-448, 2003.

450 Huff Hartz, K. E., Tischuk, J. E., Chan, M. N., Chan, C. K., Donahue, N. M., and Pandis, S. N.:

451 Cloud condensation nuclei activation of limited solubility organic aerosol, Atmospheric

452 Environment, 40, 605-617, 2006.

453 Jing, B., Tong, S., Liu, Q., Li, K., Wang, W., Zhang, Y., and Ge, M.: Hygroscopic behavior of

454 multicomponent organic aerosols and their internal mixtures with ammonium sulfate, Atmospheric

455 Chemistry and Physics, 16, 4101-4118, 2016.

456 K., C. M. N. a. C. C.: Mass transfer effects in hygroscopic measurements of aerosol particles,

457 Atmospheric Chemistry and Physics, 2005. 2005.

458 Kawamura, K. and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the

459 urban atmosphere, Environmental Science & Technology, 27, 2227-2235, 1993.

460 Kreidenweis, S. M., Koehler, K., DeMott, P. J., Prenni, A. J., Carrico, C., and Ervens, B.: Water

461 activity and activation diameters from hygroscopicity data - Part I: Theory and application to

462 inorganic salts, Atmospheric Chemistry and Physics, 5, 1357-1370, 2005.

463 Lang-Yona, N., Abo-Riziq, A., Erlick, C., Segre, E., Trainic, M., and Rudich, Y.: Interaction of

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

464 internally mixed aerosols with light, Physical Chemistry Chemical Physics, 12, 21-31, 2010.

465 Lei, T., Zuend, A., Cheng, Y., Su, H., Wang, W., and Ge, M.: Hygroscopicity of organic surrogate
466 compounds from biomass burning and their effect on the efflorescence of ammonium
467 sulfate in mixed aerosol particles, Atmos. Chem. Phys., 18, 1045-1064, 2018.

468 Lei, T., Zuend, A., Wang, W. G., Zhang, Y. H., and Ge, M. F.: Hygroscopicity of organic compounds
469 from biomass burning and their influence on the water uptake of mixed organic ammonium sulfate
470 aerosols, Atmospheric Chemistry and Physics, 14, 1-20, 2014.

471 Lesins, G., Chylek, P., and Lohmann, U.: A study of internal and external mixing scenarios and its
472 effect on aerosol optical properties and direct radiative forcing, Journal of Geophysical Research:
473 Atmospheres, 107, AAC 5-1-AAC 5-12, 2002.

474 Liu, Q., Jing, B., Peng, C., Tong, S., Wang, W., and Ge, M.: Hygroscopicity of internally mixed
475 multi-component aerosol particles of atmospheric relevance, Atmospheric Environment, 125, 69-
476 77, 2016.

477 Liu, X., Gu, J., Li, Y., Cheng, Y., Qu, Y., Han, T., Wang, J., Tian, H., Chen, J., and Zhang, Y.: Increase
478 of aerosol scattering by hygroscopic growth: Observation, modeling, and implications on visibility,
479 Atmospheric Research, 132, 91-101, 2013.

480 Liu, X., Zhang, Y., Cheng, Y., Hu, M., and Han, T.: Aerosol hygroscopicity and its impact on
481 atmospheric visibility and radiative forcing in Guangzhou during the 2006 PRIDE-PRD campaign,
482 Atmospheric Environment, 60, 59-67, 2012.

483 Martin, A. C., Cornwell, G. C., Atwood, S. A., Moore, K. A., Rothfuss, N. E., Taylor, H., DeMott,
484 P. J., Kreidenweis, S. M., Petters, M. D., and Prather, K. A.: Transport of pollution to a remote
485 coastal site during gap flow from California's interior: impacts on aerosol composition, clouds, and

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

radiative balance, Atmos. Chem. Phys., 17, 1491-1509, 2017.

Maskey, S., Chong, K. Y., Kim, G., Kim, J.-S., Ali, A., and Park, K.: Effect of mixing structure on the hygroscopic behavior of ultrafine ammonium sulfate particles mixed with succinic acid and levoglucosan, Particuology, 13, 27-34, 2014.

Miñambres, L., Sánchez, M. N., Castaño, F., and Basterretxea, F. J.: Hygroscopic Properties of Internally Mixed Particles of Ammonium Sulfate and Succinic Acid Studied by Infrared Spectroscopy, The Journal of Physical Chemistry A, 114, 6124-6130, 2010.

Pagels, J., Khalizov, A. F., McMurry, P. H., and Zhang, R. Y.: Processing of Soot by Controlled Sulphuric Acid and Water Condensation—Mass and Mobility Relationship, Aerosol Science and Technology, 43, 629-640, 2009.

Peng, C., Chan, M. N., and Chan, C. K.: The Hygroscopic Properties of Dicarboxylic and Multifunctional Acids: Measurements and UNIFAC Predictions, Environmental Science & Technology, 35, 4495-4501, 2001.

Qiu, C. and Zhang, R.: Multiphase chemistry of atmospheric amines, Physical Chemistry Chemical Physics, 15, 5738-5752, 2013.

Rogge, W. F., Mazurek, M. A., Hildemann, L. M., Cass, G. R., and Simoneit, B. R. T.: Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation, Atmospheric Environment. Part A. General Topics, 27, 1309-1330, 1993.

Rose, D., Gunthe, S. S., Su, H., Garland, R. M., Yang, H., Berghof, M., Cheng, Y. F., Wehner, B., Achtert, P., Nowak, A., Wiedensohler, A., Takegawa, N., Kondo, Y., Hu, M., Zhang, Y., Andreae, M. O., and Poschl, U.: Cloud condensation nuclei in polluted air and biomass burning smoke near the mega-city Guangzhou, China -Part 2: Size-resolved aerosol chemical composition, diurnal cycles,

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

508 and externally mixed weakly CCN-active soot particles, Atmospheric Chemistry and Physics, 11,
509 2817-2836, 2011.
510 Rudich, Y.: Laboratory Perspectives on the Chemical Transformations of Organic Matter in
511 Atmospheric Particles, Chemical Reviews, 103, 5097-5124, 2003.
512 Saxena, P., Hildemann, L. M., McMurry, P. H., and Seinfeld, J. H.: Organics alter hygroscopic
513 behavior of atmospheric particles, Journal of Geophysical Research: Atmospheres, 100, 18755-
514 18770, 1995.
515 Schauer, J. J. and Cass, G. R.: Source Apportionment of Wintertime Gas-Phase and Particle-Phase
516 Air Pollutants Using Organic Compounds as Tracers, Environmental Science & Technology, 34,
517 1821-1832, 2000.
518 Schauer, J. J., Fraser, M. P., Cass, G. R., and Simoneit, B. R. T.: Source Reconciliation of
519 Atmospheric Gas-Phase and Particle-Phase Pollutants during a Severe Photochemical Smog
520 Episode, Environmental Science & Technology, 36, 3806-3814, 2002.
521 Schauer, J. J., Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R.
522 T.: Source apportionment of airborne particulate matter using organic compounds as tracers,
523 Atmospheric Environment, 30, 3837-3855, 1996.
524 Schwarz, J. P., Gao, R. S., Fahey, D. W., Thomson, D. S., Watts, L. A., Wilson, J. C., Reeves, J. M.,
525 Darbeheshti, M., Baumgardner, D. G., Kok, G. L., Chung, S. H., Schulz, M., Hendricks, J., Lauer,
526 A., Kärcher, B., Slowik, J. G., Rosenlof, K. H., Thompson, T. L., Langford, A. O., Loewenstein, M.,
527 and Aikin, K. C.: Single-particle measurements of midlatitude black carbon and light-scattering
528 aerosols from the boundary layer to the lower stratosphere, Journal of Geophysical Research:
529 Atmospheres, 111, n/a-n/a, 2006.

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

530 Shi, Y. J., Ge, M. F., and Wang, W. G.: Hygroscopicity of internally mixed aerosol particles
531 containing benzoic acid and inorganic salts, Atmospheric Environment, 60, 9-17, 2012.
532 Shiraiwa, M., Zuend, A., Bertram, A. K., and Seinfeld, J. H.: Gas-particle partitioning of
533 atmospheric aerosols: interplay of physical state, non-ideal mixing and morphology, Physical
534 Chemistry Chemical Physics, 15, 11441-11453, 2013.
535 Sjogren, S., Gysel, M., Weingartner, E., Baltensperger, U., Cubison, M. J., Coe, H., Zardini, A. A.,
536 Marcolli, C., Krieger, U. K., and Peter, T.: Hygroscopic growth and water uptake kinetics of two-
537 phase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures, Journal of
538 Aerosol Science, 38, 157-171, 2007.
539 Song, M., Ham, S., Andrews, R. J., You, Y., and Bertram, A. K.: Liquid–liquid phase separation in
540 organic particles containing one and two organic species: importance of the average
541 O : C, Atmos. Chem. Phys., 18, 12075-12084, 2018.
542 Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation and
543 morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, Atmospheric
544 Chemistry and Physics, 12, 2691-2712, 2012a.
545 Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation in
546 aerosol particles: Dependence on O:C, organic functionalities, and compositional complexity,
547 Geophysical Research Letters, 39, 2012b.
548 Spindler, C., Riziq, A. A., and Rudich, Y.: Retrieval of Aerosol Complex Refractive Index by
549 Combining Cavity Ring Down Aerosol Spectrometer Measurements with Full Size Distribution
550 Information, Aerosol Science and Technology, 41, 1011-1017, 2007.
551 Stock, M., Cheng, Y. F., Birmili, W., Massling, A., Wehner, B., Müller, T., Leinert, S., Kalivitis, N.,

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

552 Mihalopoulos, N., and Wiedensohler, A.: Hygroscopic properties of atmospheric aerosol particles
553 over the Eastern Mediterranean: implications for regional direct radiative forcing under clean and
554 polluted conditions, Atmos. Chem. Phys., 11, 4251-4271, 2011.
555 Su, H., Rose, D., Cheng, Y. F., Gunthe, S. S., Massling, A., Stock, M., Wiedensohler, A., Andreae,
556 M. O., and Pöschl, U.: Hygroscopicity distribution concept for measurement data analysis and
557 modeling of aerosol particle mixing state with regard to hygroscopic growth and CCN activation,
558 Atmos. Chem. Phys., 10, 7489-7503, 2010.
559 Tie, X., Huang, R.-J., Cao, J., Zhang, Q., Cheng, Y., Su, H., Chang, D., Pöschl, U., Hoffmann, T.,
560 Dusek, U., Li, G., Worsnop, D. R., and O'Dowd, C. D.: Severe Pollution in China Amplified by
561 Atmospheric Moisture, Scientific Reports, 7, 15760, 2017.
562 Wang, G., Kawamura, K., Xie, M., Hu, S., Li, J., Zhou, B., Cao, J., and An, Z.: Selected water-
563 soluble organic compounds found in size-resolved aerosols collected from urban, mountain and
564 marine atmospheres over East Asia, Tellus B, 63, 371-381, 2011.
565 Wex, H., Hennig, T., Salma, I., Ocskay, R., Kiselev, A., Henning, S., Massling, A., Wiedensohler,
566 A., and Stratmann, F.: Hygroscopic growth and measured and modeled critical super-saturations of
567 an atmospheric HULIS sample, Geophysical Research Letters, 34, n/a-n/a, 2007.
568 Xue, H., Khalizov, A. F., Wang, L., Zheng, J., and Zhang, R.: Effects of dicarboxylic acid coating
569 on the optical properties of soot, Physical Chemistry Chemical Physics, 11, 7869-7875, 2009.
570 You, Y., Smith, M. L., Song, M., Martin, S. T., and Bertram, A. K.: Liquid–liquid phase separation
571 in atmospherically relevant particles consisting of organic species and inorganic salts, International
572 Reviews in Physical Chemistry, 33, 43-77, 2014.
573 Zamora, I. R., Tabazadeh, A., Golden, D. M., and Jacobson, M. Z.: Hygroscopic growth of common

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

574 organic aerosol solutes, including humic substances, as derived from water activity measurements,
575 Journal of Geophysical Research: Atmospheres, 116, n/a-n/a, 2011.
576 Zawadowicz, M. A., Proud, S. R., Seppalainen, S. S., and Cziczo, D. J.: Hygroscopic and phase
577 separation properties of ammonium sulfate/organics/water ternary solutions, Atmos. Chem. Phys.,
578 15, 8975-8986, 2015.
579 Zelenyuk, A., Cai, Y., and Imre, D.: From Agglomerates of Spheres to Irregularly Shaped Particles:
580 Determination of Dynamic Shape Factors from Measurements of Mobility and Vacuum
581 Aerodynamic Diameters, Aerosol Science and Technology, 40, 197-217, 2006.
582 Zhang, Q., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J.-L.: Time- and size-
583 resolved chemical composition of submicron particles in Pittsburgh: Implications for aerosol
584 sources and processes, Journal of Geophysical Research: Atmospheres, 110, n/a-n/a, 2005.
585 Zhang, R., Khalizov, A. F., Pagels, J., Zhang, D., Xue, H., and McMurry, P. H.: Variability in
586 morphology, hygroscopicity, and optical properties of soot aerosols during atmospheric processing,
587 Proceedings of the National Academy of Sciences, 105, 10291-10296, 2008.
588 Zhang, Y.-L., Kawamura, K., Watanabe, T., Hatakeyama, S., Takami, A., and Wang, W.: New
589 directions: Need for better understanding of source and formation process of phthalic acid in
590 aerosols as inferred from aircraft observations over China, Atmospheric Environment, 140, 147-149,
591 2016.
592 Zhou, Q., Pang, S.-F., Wang, Y., Ma, J.-B., and Zhang, Y.-H.: Confocal Raman Studies of the
593 Evolution of the Physical State of Mixed Phthalic Acid/Ammonium Sulfate Aerosol Droplets and
594 the Effect of Substrates, The Journal of Physical Chemistry B, 118, 6198-6205, 2014.
595 Zuend, A., Marcolli, C., Luo, B. P., and Peter, T.: A thermodynamic model of mixed organic-

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020


Atmospheric Chemistry and Physics Discussions

596 inorganic aerosols to predict activity coefficients, Atmospheric Chemistry and Physics, 8, 4559-
597 4593, 2008.
598 Zuend, A., Marcolli, C., Peter, T., and Seinfeld, J. H.: Computation of liquid-liquid equilibria and
599 phase stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic
600 aerosols, Atmospheric Chemistry and Physics, 10, 7795-7820, 2010.
601 Zuend, A. and Seinfeld, J. H.: A practical method for the calculation of liquid–liquid equilibria in
602 multicomponent organic–water–electrolyte systems using physicochemical constraints, Fluid Phase
603 Equilibria, 337, 201-213, 2013.
604
605
606
607
608
609
610
611
612
613
614
615
616
617

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

618

619 **Tables**

620 **Table 1.** Coefficients of the fitted growth curve parameterization to measured growth

621 factor data using Eq. (1)

Chemical Compound	a	b	c
Phthalic Acid	0.083116	0.291473	-0.353544

622

623

624

625

626

627

628

629

630

631

632

633

634

635

636

637

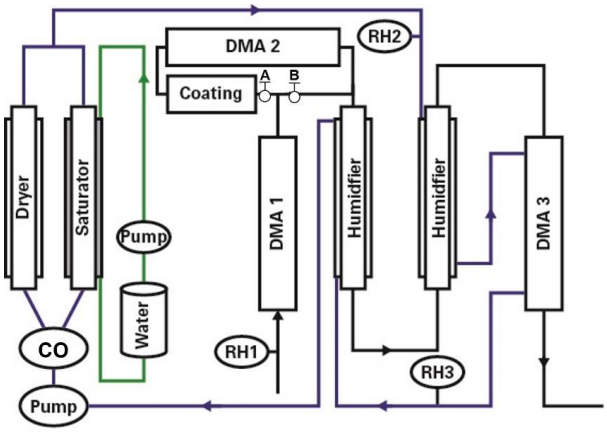
https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

638

639 **Figures**

640



641

642 **Figure 1.** Schematic diagram of the coating-hygroscopicity tandem differential mobility analyzer. Here,
643 CO: critical orifice; DMA: differential mobility analyzer; RH1 and RH2 (measured RH sensor) represent
644 the RH of aerosol and humidified flow in the inlet of DMA1 and humidifier, respectively. RH3 (measured
645 by dew point mirror) represent the RH of excess air. Valve B is open and valve A is closed to the
646 homogeneous internally mixed-mode experiment. Valve A is open and Valve B is closed to the coating-
647 mode experiment. Black line: aerosol line; Blue line: sheath line; Green line: MilliQ water.

648

649

650

651

652

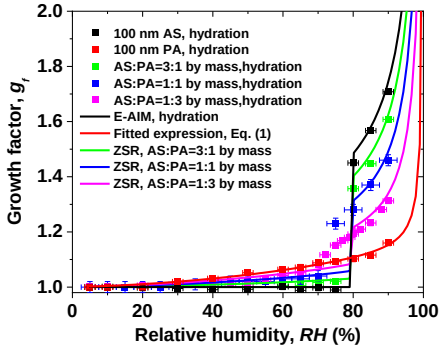
653

654

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

655



656

657 **Figure 2.** Hygroscopic growth factor for 100 nm (dry diameter, RH < 5 %) aerosol particles containing:
658 ammonium sulfate (AS), phthalic acid (PA), and well-mixed mixtures of PA and AS with different mass
659 ratio of AS to PA. In comparison, the E-AIM model, the Fitted expression Eq. (1), and the ZSR relation
660 predicted growth factors of AS, PA, and well mixed particles with different mass fractions of PA,
661 respectively.

662

663

664

665

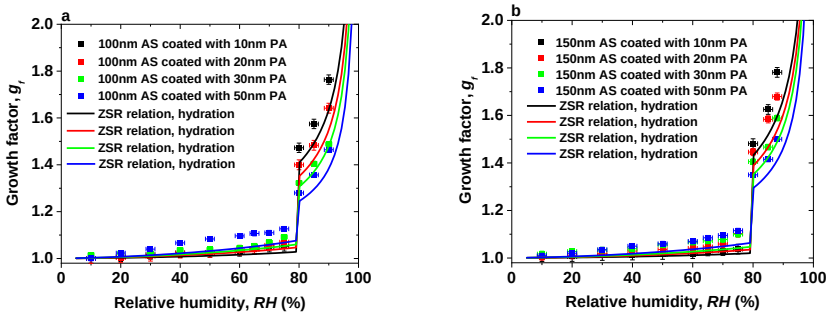
666

667

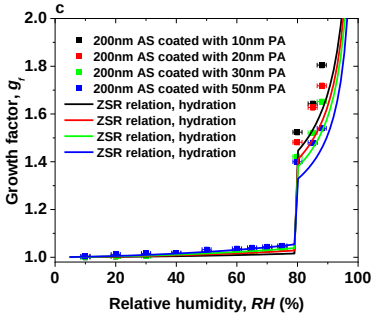
https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions

668



669



670 **Figure 3.** Hygroscopic growth factor for core-shell of ammonium sulfate (AS) and phthalic acid (PA)

671 aerosol particles. In comparison, the ZSR relation predicted growth factor of core-shell aerosol particles

672 (**a**) 100-nm AS core (**b**) 150-nm AS core (**c**) 200-nm AS core.

673

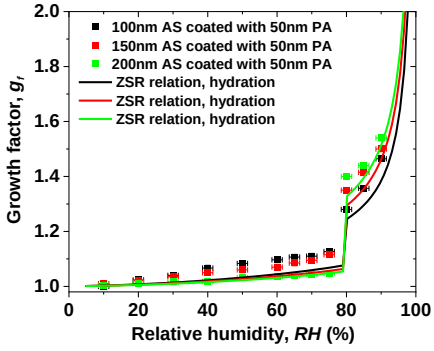
674

675

676

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

Atmospheric Chemistry and Physics Discussions



677

678 **Figure 4.** Hygroscopic growth factor for 100-200 nm ammonium sulfate (AS) core with coating 50 nm

679 phthalic acid (PA). In comparison, the ZSR relation predicted growth factor of core-shell aerosol particles

680 with different AS cores.

681

682

683

684

685

686

687

688

689

https://doi.org/10.5194/acp-2020-632
Preprint. Discussion started: 28 July 2020

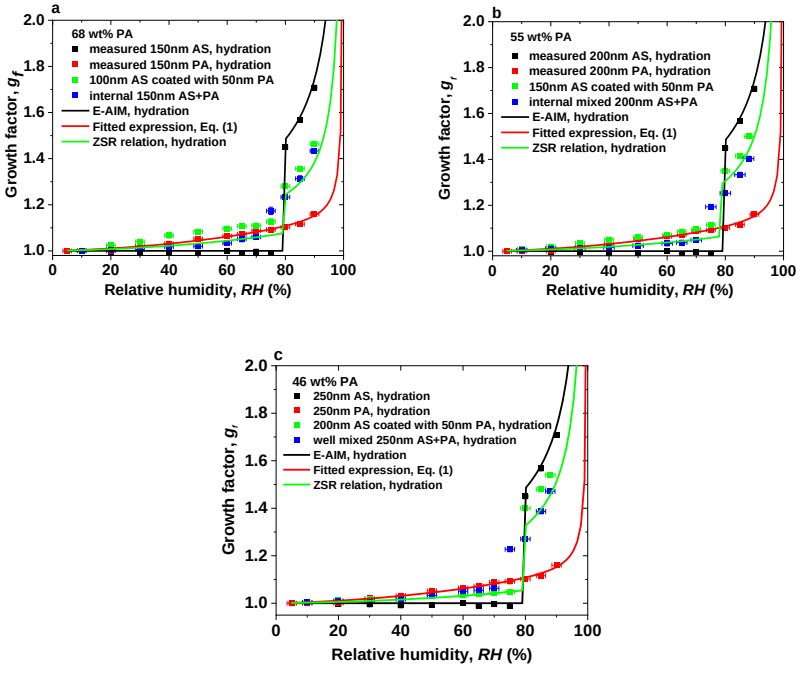


Figure 5. Hygroscopic growth factor for core-shell and well-mixed aerosol particles with the same dry mass fractions of phthalic acid (PA) containing: (a): 68 wt % PA, (b): 55 wt % PA, (c): 46 wt % PA. In comparison, the E-AIM model, the Fitted expression Eq. (1), and the ZSR relation predicted growth factors of ammonium sulfate (AS), PA, and internally mixed particles with different mass fractions of PA, respectively.