

Author's response

Response to editor:

We thank for the editor's constructive comments. We repeat the comments in bold font, followed by our response in italic font. The related changes in the manuscript have been highlighted in yellow.

Thank you for responding to my comments. However, I do not feel your responses have resolved my concerns or the referees concerns, and the modifications have led to sections in the manuscript that are confusing and contradictory. These issues need to be resolved before I am able to accept the manuscript for publication. See specific comments below:

1) Regarding justification for the formation of oxalic acid dihydrate. Based on the previous studies, I am fine with the assumption that oxalic acid dihydrate forms at low relative humidities in single component oxalic acid particles. However, I wonder about the validity of this assumption for particles containing oxalic acid and levoglucosan. You used previous studies of single component oxalic acid particles to argue that the oxalic acid dihydrate will form in your particles containing oxalic acid and levoglucosan. However, even though the dihydrate forms in single component oxalic acid particles, the dihydrate may not form in the two component oxalic acid-levoglucosan particles. The presence of the levoglucosan may completely shut off any crystallization. Just to be clear, I am suggesting the possibility that mixed levoglucosan and oxalic particles remain in a liquid (or amorphous solid) state even at the lowest RHs studied. In fact, I wonder if figure 4c provides some justification for this. In 4c there doesn't appear to be any indication of crystallization even at the lowest relative humidity. The spectra in figure 4c were recorded with larger particles, so with smaller particles, as used in the HTDMA experiments, crystallization would be even less likely, suggesting that at the lowest RHs studied mixtures of oxalic acid and levoglucosan will be in the liquid state. Please discuss this possibility in your manuscript.

Reply: Thanks for the editor's comment. We agree that a dihydrate refers to a crystalline material. We also notice that the word "dihydrate" used in previous HTDMA studies is limited to describe the oxalic acid composition rather than the crystalline phase (Prenni et al., 2001; Mikhailov et al., 2009). The editor also agreed that oxalic acid dihydrate forms at low

relative humidities in single component oxalic acid particles. Measurements using the HTDMA in early studies indicated substantial water uptake by oxalic acid particles during the humidification after 40% RH (Prenni et al., 2001; Mikhailov et al., 2009). In fact, it cannot be expected that during the humidification the oxalic acid dihydrate could take up water below its deliquescence point 97%. Thus, a reasonable explanation is that the oxalic acid particles are composed of “dihydrate” but not in a crystalline phase. Mikhailov et al. (2009) also suggested that the oxalic acid composition could be described as “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule”. Previous HTDMA studies have shown that the submicron oxalic acid particles under dry conditions are most likely composed of “dihydrate” irrespective of various phase state. For example, Prenni et al. (2001) observed continual hygroscopic growth of oxalic acid particles with increasing relative humidity, suggesting the initial particles were not completely dry but rather concentrated solution droplets. They reported that the measured hygroscopic growth agreed well with Köhler model calculations assuming that the initially generated particles consisted of oxalic acid “dihydrate”. Mikhailov et al. (2009) also found that the solid amorphous oxalic acid particles under dry conditions consisted of oxalic acid “dihydrate”, as indicated by Köhler model calculations. It can be seen that the submicron oxalic acid particles tend to consist of “dihydrate” or “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule”. Although oxalic acid has a high enough vapor pressure, no evaporation losses were observed in previous HTDMA studies (Prenni et al., 2001; Mikhailov et al., 2009), as well as in our study. The most plausible explanation for the high stability of the investigated oxalic acid particles is that they were not anhydrous but composed of “dihydrate” or “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule” (Mikhailov et al., 2009). As for 100 nm levoglucosan/oxalic acid mixed particles, there is also no evaporation losses observed in our study, as indicated by no reduction in particle size during measurements at $RH < 5\%$. The similar phenomenon was also observed for other mixed systems containing oxalic acid. It indicates oxalic acid in the submicron mixed particles under dry conditions may be composed of “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule”.

We have realized that the use of the word “dihydrate” in the manuscript may cause some confusion. We would like to add corresponding description “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule” after the word “dihydrate” in the manuscript, which has been highlighted in yellow.

We agree that mixed levoglucosan and oxalic particles may remain in a liquid state even at the lowest RHs studied. We would like to add corresponding discussion in the last paragraph of section 4.2.1 in the manuscript.

Related changes in the revised manuscript:

Page 16 line 12, we add “The carbonyl stretching band at 1750 cm^{-1} is close to that in the liquid phase, indicating the Lev/OA (1:1, mass) mixture appears to be partially in a liquid phase. The spectra in Fig. 4c were recorded with larger particles, thus crystallization would be even less likely within smaller particles used in the HTDMA experiments, suggesting that mixtures of oxalic acid and levoglucosan may be in the liquid state even at the lowest RHs studied.”

References

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Poeschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmos. Chem. Phys., 9, 9491-9522, doi:10.5194/acp-9-9491-2009, 2009.

Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Sherman, D. E., Russell, L. M., and Ming, Y.: The effects of low molecular weight dicarboxylic acids on cloud formation, J. Phys. Chem. A, 105, 11240-11248, doi:10.1021/jp012427d, 2001.

2) “Anhydrous OA” is used throughout the manuscript but it is not always clear if the authors are referring to “amorphous anhydrous OA” or “crystalline anhydrous OA”. Please go through the manuscript and make sure it is clear what type of anhydrous state you are referring to (i.e. crystalline or amorphous).

Reply: Thanks for your suggestion. We have made some modification through the manuscript where it is necessary to indicate the phase state of anhydrous oxalic acid (OA). The

corresponding changes have been highlighted in yellow.

3) Issues that are now confusing in the manuscript after changes have been made:

a. Section 4.2.1. The authors indicate that “no deliquescence behavior is observed and the continuous water uptake starting at low RH indicates the initial particles appear to be in a liquid state and retain water.” Later they say that “OA in the initial mixed particles may exist in a liquid state and contributes to water uptake by mixed particles in the subsequent humidification”. This discussion is consistent with my comment (1) above. However, later the authors also state, “Considering hygroscopic species such as levoglucosan could retain some water at low RH, it can be expected that oxalic acid in the submicron mixed particles is also composed on stable dihydrate”. Since a dihydrate is a crystalline form, these statements are contradictory and confusing. How do the authors reconcile these contradictory statements? Please adjust the manuscript to remove this contradiction.

b. Section 4.2.1., the authors state “oxalic acid particles under dry conditions are most likely composed of dihydrate irrespective of various phase state”. What does “irrespective of various phase state” refer to? Since they are referring to the dihydrate there is only one phase state?

c. Section 4.2.1. In the newly added text, the authors state “Mikhailov also found that the solid amorphous oxalic acid particles under dry conditions consisted of oxalic acid dihydrate”. A solid amorphous oxalic acid particle cannot consist of oxalic acid dihydrate, since a dihydrate refers to a crystalline material while an amorphous material refers to a non-crystalline material.

Reply: Thanks for the editor’s comment. The detailed response can be seen in comment 1. We have realized that the use of the word “dihydrate” in the manuscript may cause some confusion. We would like to add corresponding description after the word “dihydrate” in the manuscript.

Related changes in the revised manuscript:

Page 14 line 4, this paragraph was changed into “Previous HTDMA studies have shown that the submicron oxalic acid particles under dry conditions are most likely composed of

“dihydrate” irrespective of various phase state. For example, Prenni et al. (2001) observed continual hygroscopic growth of oxalic acid particles with increasing relative humidity, suggesting the initial particles were not completely dry but rather concentrated solution droplets. They reported that the measured hygroscopic growth agreed well with Köhler model calculations assuming that the initially generated particles consisted of oxalic acid “dihydrate”. Mikhailov et al. (2009) also found that the solid amorphous oxalic acid particles under dry conditions consisted of oxalic acid “dihydrate”, as indicated by Köhler model calculations. It can be seen that the submicron oxalic acid particles tend to consist of “dihydrate”, i.e., “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule”. In fact, the formation of anhydrous oxalic acid usually requires very dry conditions and cannot be expected in HTDMA measurement (Mikhailov et al., 2009). Although oxalic acid has a high enough vapor pressure, no evaporation losses were observed in previous HTDMA studies (Prenni et al., 2001; Mikhailov et al., 2009), as well as in our study. The most plausible explanation for the high stability of the investigated OA particles is that they were not anhydrous but composed of “dihydrate” or “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule” (Mikhailov et al., 2009). As for 100 nm levoglucosan/oxalic acid mixed particles, there is also no evaporation losses observed in our study, as indicated by no reduction in particle size during measurements at $RH < 5\%$. The similar phenomenon was also observed for other mixed systems containing oxalic acid. Thus, it indicates oxalic acid in the submicron mixed particles under dry conditions may also exist in a “dihydrate” form, i.e., “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule”.

Hygroscopic behavior of multicomponent organic aerosols and their internal mixtures with ammonium sulfate

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Abstract

Water soluble organic compounds (WSOCs) are important components of organics in the atmospheric fine particulate matter. Although WSOCs play an important role in the hygroscopicity of aerosols, water uptake behavior of internally mixed WSOC aerosols remains limited characterization. Here, the hygroscopic properties of single component such as levoglucosan, oxalic acid, malonic acid, succinic acid and phthalic acid and multicomponent WSOC aerosols mainly involving oxalic acid are investigated with the hygroscopicity tandem differential mobility analyzer (HTDMA). The coexisting hygroscopic species including levoglucosan, malonic acid and phthalic acid have strong influence on the hygroscopic growth and phase behavior of oxalic acid, even suppress its crystallization completely during the drying process. The phase behaviors of oxalic acid/levoglucosan mixed particles are confirmed by infrared spectra. The discrepancies between measured growth factors and predictions from Extended Aerosol Inorganics Model (E-AIM) with UNIFAC method and Zdanovskii-Stokes-Robinson (ZSR) approach increase at medium and high relative humidity (RH) assuming oxalic acid in a solid state. For the internal mixture of oxalic acid with levoglucosan or succinic acid, there is enhanced water uptake at high RH compared to the model predictions based on reasonable oxalic acid phase assumption. Organic mixture has more complex effect on the hygroscopicity of ammonium sulfate than single species. Although hygroscopic species such as levoglucosan accounts for a small fraction in the multicomponent aerosols, they may still strongly influence the hygroscopic behavior of ammonium sulfate by changing phase state of oxalic acid which plays the role of “intermediate” species. Considering the abundance of oxalic acid in the atmospheric aerosols, its mixtures with hygroscopic species may significantly promote water uptake under high RH conditions and thus affect the cloud condensation nuclei (CCN) activity, optical properties and chemical reactivity of atmospheric particles.

1 Introduction

Atmospheric aerosols can strongly affect the Earth's climate and atmospheric processes (Ramanathan et al., 2001). As one of the most important physicochemical properties, the hygroscopic properties determine the size, concentration, and phase state of aerosol particles and thus contribute to radiative forcing on the climate system, including both the direct forcing by absorbing or scattering light and indirect forcing through activation of cloud condensation nuclei (CCN) (Haywood and Boucher, 2000; Kanakidou et al., 2005). In addition, the water uptake of atmospheric aerosols influences their atmospheric lifetimes, reactivity, air quality and even human health (Pandis et al., 1995; Krueger et al., 2003; Chan and Yao, 2008; Poschl, 2005; Schneidemesser; et al., 2015).

For the atmospheric fine particulate matter, the organic components can usually occupy 20-90% by mass (Kanakidou et al., 2005; Zhang et al., 2007), a large fraction of which is composed of water soluble organic compounds (WSOCs) (Saxena and Hildemann, 1996; Graham et al., 2002; Decesari et al., 2005). Hygroscopic properties of aerosols are mainly affected by their chemical composition. Therefore, water soluble organic compounds can significantly alter aerosols' hygroscopicity (Saxena et al., 1995; Mircea et al., 2005). Compared with the thorough study on hygroscopic properties of atmospheric inorganic components, the knowledge on the hygroscopic behavior of WSOCs still remains relatively limited (Kanakidou et al., 2005; Jimenez et al., 2009; Hallquist et al., 2009). Due to complexity of organic matter, it is difficult to conduct a comprehensive investigation on the hygroscopic behavior of all the organic compounds. To solve this problem, a set of identified model organic compounds have been proposed to represent the WSOCs (Fuzzi et al., 2001; Mayol-Bracero, 2002; Decesari et al., 2006). According to the approach suggested by Fuzzi et al. (2001), the WSOCs can be generally separated into three categories based on acid/base character: (i) neutral compounds, (ii) mono-/di-carboxylic acids, and (iii) polycarboxylic acids such as humic-like organic polymers. Levoglucosan as a tracer of biomass burning products (Simoneit et al., 1999), is often selected to represent the neutral compounds (Decesari et al., 2006; Svenningsson et al., 2006). Dicarboxylic acids are ubiquitous in the atmosphere and have been identified as significant components of the organic matter in urban and remote atmospheric aerosols (Chebbi and Carlier, 1996; Mochida et al., 2003; Kundu et al., 2010).

Field measurements have shown that oxalic acid is usually the dominant dicarboxylic acid in aerosol particles, followed by malonic and succinic acids, phthalic acid (Hegde and Kawamura, 2012; Kawamura et al., 2013).

The hygroscopic properties of levoglucosan and the low molecular weight dicarboxylic acids have been investigated widely with different measurement methods in the past several years (Peng et al., 2001; Prenni et al., 2001; Brooks et al., 2002; Braban et al., 2003; Mochida and Kawamura, 2004; Parsons et al., 2004b; Chan et al., 2005; Yeung and Chan, 2010; Zamora et al., 2011; Ma et al., 2013; Minambres et al., 2013; Ghorai et al., 2014). Most studies have focused on hygroscopicity of aerosol particles containing only single organic component or its mixture with inorganic salt (Lightstone et al., 2000; Cruz and Pandis, 2000; Hameri et al., 2002; Prenni et al., 2003; Wise et al., 2003; Braban and Abbatt, 2004; Parsons et al., 2004a; Ling and Chan, 2008; Zardini et al., 2008; Pope et al., 2010; Peckhaus et al., 2012; Ghorai et al., 2014). It was found that water uptake and phase behavior of the organic aerosols has great uncertainty. The hygroscopicity of WSOCs is dependent on their composition, mixed state and phase state. Even for the same single component WSOC, differences still existed in measurements of hygroscopic growth with various measurement technologies (Zamora et al., 2011). Previous HTDMA measurements showed that oxalic acid particles had obvious water uptake upon hydration below 90% relative humidity (RH) while it was not observed in the electrodynamic balance (EDB) measurements (Prenni et al., 2001; Peng et al., 2001). This discrepancy could be attributed to initial physical state of aerosol particles, which has considerable influence on water uptake behaviors of atmospheric aerosols (Martin, 2000; Mikhailov et al., 2009). Due to complex interactions among organic mixtures, organic aerosol fractions are more likely to form liquid or amorphous rather than crystalline phases (Mikhailov et al., 2009; Marcolli et al., 2004; Cappa et al., 2008). Considering the potential impact of the interactions between organic species on their hygroscopicity, it needs further study on the hygroscopic behaviors of multicomponent organic aerosols and their mixtures with ammonium sulfate (Marcolli et al., 2004; Moore and Raymond, 2008). Additionally, measurements for the hygroscopic growth of internally mixed organic aerosols can be used to assess the prediction reliability of relevant thermodynamic models (Peng et al., 2001).

In this study, the hygroscopic behaviors of multicomponent organic aerosol particles were investigated with a hygroscopicity tandem differential mobility analyzers (HTDMA) system. Levoglucosan, oxalic acid, malonic acid, succinic acid, and phthalic acid were chosen as the surrogates of WSOC. The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used to reveal information about molecular interactions and phase transitions in the aerosol particles. Several model methods were applied to predict the water uptake of these organic aerosols including Extended Aerosol Inorganics Model (E-AIM, available at <http://www.aim.env.uea.ac.uk/aim/aim.php>) in combination with the UNIFAC (Universal Quasi-Chemical Functional Group Activity Coefficient) method, Zdanovskii-Stokes-Robinson (ZSR) method, and Ideal solution model. Additionally, the nonideality and CCN activity of WSOC aerosols were evaluated. Finally, the influence of organic mixture on the water uptake behavior of ammonium sulfate was determined.

2 Experiment and method

2.1 Hygroscopic growth measurements

The hygroscopicity tandem differential mobility analyzer (HTDMA) used here has been described in previous studies (Lei et al., 2014; Liu et al., 2016). The schematic of HTDMA system is shown in Fig. 1, mainly including three parts: (1) the aerosol particles generation and drying section; (2) the particles size selection and humidity control apparatus; (3) the detection system for number size distributions of the humidified aerosols. The wet aerosol particles were produced from a constant output atomizer (1500, MSP) containing aqueous solutions of the organic compounds. Chemical properties and mixture composition of the substances investigated were listed in Table 1 and 2. Each pure component or mixture was completely dissolved in ultrapure water (EASY Pure® II UF ultrapure water system, 18.2 MΩ cm) to form a dilute solution with concentration of around 0.1 wt %. The nebulized aerosols were subsequently dried to RH<5% in silica gel diffusion dryers coupled with a Nafion gas dryer (Perma Pure Inc., USA).

The initial polydisperse aerosol particles were then charged and passed through the first differential mobility analyzer (DMA1), where nearly monodisperse aerosol particles with the desired initial particle diameter of 100 nm were selected. The size-selected particles then

entered into a humidification system consisting of two Nafion conditioner tubes. The aerosols were prehumidified in the first Nafion conditioner tube and accomplished humidification in the second Nafion tube at a desired relative humidity. The residence time of aerosol particles at a given RH before entering into DMA2 was about 5 s in the humidification section. The size distribution of humidified aerosol particles was measured by the second differential mobility analyzer (DMA2) and a condensation particle counter (CPC, MSP 1500). The inversion of HTDMA measurement data was based on a log-normal size distribution approximation (Stolzenburg and McMurry, 2008). The ratio of sheath air to aerosol flow rate was maintained at 10:1 for both DMAs. In our system, sheath air flows were recirculated in a closed-loop arrangement to ensure relative humidity in the humidification section and DMA2 was equal. A dew point hygrometer (Michell, UK) was used to monitor the relative humidity of sheath flow in the DMA2, with an uncertainty of ± 0.08 % RH. All experiments were performed at ambient temperature (297 ± 1 K). In our measurements for organic mixtures, no obvious reduction of particle diameter was observed during measurements in DMA2 at $\text{RH} < 5\%$, indicating the evaporation of organics was suppressed in the mixtures.

Hygroscopic growth factor (GF), indicating water uptake ability of aerosol particles, is defined as the ratio of particle mobility diameter at a specific RH to the mobility diameter measured in DMA2 at $\text{RH} < 5\%$. All results are the average of at least three measurements and uncertainty in our measured growth factors are within 0.02. The results of instrument performance evaluation can be seen in Fig. S1 in Supplement.

2.2 Infrared absorption measurements

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy is a valuable tool to probe the hygroscopic process of aerosol particles. The ATR horizontal cell apparatus (Pike Technologies) was similar to our previous studies (Zhang et al., 2014) and a Ge crystal instead of ZnSe was used as the substrate due to acidity of oxalic acid. Aerosol particles produced from aqueous samples (2.0 wt%) in a constant output atomizer passed through the silica gel diffusion dryer and then deposited on the Ge crystal substrate, resulting in a homogeneously dispersed sample. To obtain enough signal-to-noise level spectrum, the aerosol particles used for infrared measurements did not experience size selection. The upper

limit of particle size was below 2 μm . The RH inside the ATR cell was controlled by a nitrogen flow which was mixed by dry nitrogen with nitrogen saturated with water vapor. A humidity probe accurate to $\pm 2\%$ (HMP 237, Vaisala) was placed at the exit of the cell to monitor the RH. To ensure hygroscopic equilibration, each RH was maintained 30 min before making measurement. Infrared spectra at various RHs during humidification were measured in the spectral range from 4000 to 750 cm^{-1} with 4 cm^{-1} resolution by averaging 64 scans using a Thermo Nicolet 6700 FTIR spectrometer equipped with a high-sensitivity mercury cadmium telluride (MCT) detector. All spectra reported here were referenced to the background signal of the blank Ge crystal under dry conditions and gas water lines have been subtracted.

3 Modeling methods

3.1 Hygroscopic growth treatment

To minimize the Kelvin curvature effect for submicron particles measured in the HTDMA, the relative humidity (RH) was converted to water activity (a_w) by Köhler equation:

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

Here, σ_{sol} is the surface tension of droplet, M_w is the molar mass of water, R is the ideal gas constant, T is the temperature, ρ_w is the density of water, D_p is the droplet diameter. The surface tension of droplet is set to be that of pure water (0.072 J m^{-2}). Although organics in the droplet may reduce its surface tension, a_w error caused by approximation was negligible compared with the uncertainty of the RH measurement.

According to the expression proposed by Kreidenweis et al. (2005), continuous water uptake behavior of individual species can be well described with a polynomial fit equation:

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

The coefficients a , b and c obtained by Eq. (2) fitting to GF- a_w measurement data are given in Table 3.

3.2 Hygroscopic growth prediction

The ZSR method is widely used to estimate hygroscopic growth of internally mixed particles by assuming independent water uptake of the pure components in the particles at a given RH (Prezzi et al., 2003; Brooks et al., 2004; Zamora and Jacobson, 2013). This method has been successfully applied to predict water uptake of various mixed systems containing inorganic salts and organic species in the atmosphere. The hygroscopic growth factor (GF_{mix}) of the mixed particles can be calculated by ZSR relation (Stokes and Robinson, 1966; Malm and Kreidenweis, 1997), as following:

$$GF_{mix} = \left(\sum_k \varepsilon_k GF_k^3 \right)^{1/3} \quad (3)$$

Where GF_k is the hygroscopic growth factor of pure component k , ε_k is the respective volume fraction in the dry mixture. This equation is derived by assumption that water content of mixture is equal to sum of water uptake of pure components. The volume fraction (ε_i) of component i is calculated as:

$$\varepsilon_i = \frac{(w_i / \rho_i)}{\sum_k (w_k / \rho_k)} \quad (4)$$

Where w_i is the mass fraction of species i , ρ_i is the respective density. Despite its simple assumption that each component in the mixture takes up water independently, the ZSR rule usually could well describe the hygroscopic growth of mixed particles with all components in the aqueous phase. For liquid particles, the large discrepancies between ZSR predictions and measurements can be attributed to the chemical interactions between components (Chan and Chan, 2003; Zardini et al., 2008).

The Extended Aerosol Inorganics Model (E-AIM) developed by Wexler and Clegg (2002), can be used to treat the solution thermodynamics including prediction of the water activity, phase state, and equilibrium partitioning of the atmospheric inorganic aerosol systems. E-AIM was later extended to include organic components by combining with the widely applied Universal Quasi-Chemical Functional Group Activity Coefficient (UNIFAC) model (Fredenslund et al., 1975; Hansen et al., 1991; Wittig et al., 2003). The UNIFAC model based on functional group contributions can predict water activity coefficients for aqueous organic

mixtures with various compositions. Due to hydrogen bonding interactions between polar groups, standard UNIFAC model is not suitable for organic compounds with two highly polar functional groups separated by less than three or four carbon atoms, especially low molecular weight dicarboxylic acids (Peng et al., 2001). Peng et al. (2001) had revised UNIFAC parameters involving interactions between hydroxyl/carboxyl groups and water to accurately predict water activity for several individual dicarboxylic acids. Here the UNIFAC model with parameters modified by Peng et al. (2001) was used for WSOCs studied in this work. Considering the measured GFs are calculated from the lowest RH~4%, the predicted GFs from E-AIM are also obtained from the same lowest RH. It should be noted that the residual water in the particles at the lowest RH~4% are so slight that it could hardly result in significant difference between the predicted GFs from the lowest RH(~4%) or dry condition (0% RH).

For the ideal solution, the water activity a_w is equal to the mole fraction of water in the solution (Raoult's law), seen in Eq. (5). Based on the ideal solution assumption, this model may fail to predict water activity of solutions containing electrolyte components or organic compounds with non-ideal interaction. Previous investigations have demonstrated the ideal solution model was a useful tool to predict the hygroscopic growth of atmospheric organics such as humic-like substances, levoglucosan and oxalic acid (Gysel et al., 2004; Mochida and Kawamura, 2004; Mikhailov et al., 2009).

$$a_w = \frac{n_w}{n_w + n_s} \quad (5)$$

where n_w , n_s are the mole numbers of water and solute, respectively.

Considering aerosol droplets may be deviated from ideal solution due to large solute concentrations and complex interactions between solutes, the van't Hoff factor i was used to evaluate non-ideality of solution (Low, 1969; Pruppacher et al., 1998). The van't Hoff factor is equal to the numbers of dissociated ions per solute molecule, usually defined as following form:

$$a_w^{-1} = 1 + i \frac{n_s}{n_w} \quad (6)$$

where n_s is the sum of the mole number of all the solutes and n_w is the mole number of water in solution.

3.3 Single hygroscopicity parameter κ

According to κ -Köhler theory proposed by Petters and Kreidenweis (2007), a single hygroscopicity parameter κ for describing the hygroscopic growth ability of aerosol particles, can be obtained based on hygroscopic growth measurements under subsaturated conditions (Carrico et al., 2008):

$$\kappa = \frac{(GF^3 - 1)(1 - a_w)}{a_w} \quad (7)$$

Where a_w is the water activity and GF is the respective hygroscopic growth factor. For organic compounds with continuous water uptake under subsaturated conditions, it was found that the κ -value based on the GF measurements from HTDMA around 90% RH can be used to assess the CCN activity of aerosols (Petters and Kreidenweis, 2007; Chan et al., 2008).

4 Results and discussion

4.1 Hygroscopic growth of individual component aerosols

Hygroscopic behaviors of dicarboxylic acids including oxalic acid (OA), malonic acid (MA), succinic acid (SA) and phthalic acid (PA) for 100 nm initial aerosol particles are presented in Fig. 2. For MA and PA with significant hygroscopic growth, predictions from E-AIM and ideal solution model are also shown. As can be seen from Fig. 2a, the GF of OA particles does not increase below 30% RH and then keeps around 1.02 until 90% RH. The slight increase of GF suggests water absorption on the surface of OA particles. No significant hygroscopic growth or deliquescence behavior for OA is observed in the 5-90% RH range studied, consistent with previous studies by EDB and other methods (Peng et al., 2001; Brooks et al., 2002; Braban et al., 2003; Ma et al., 2013). Theory prediction and bulk measurements also show the deliquescence point of OA is greater than 97% RH (Peng et al., 2001; Zamora et al., 2011). Measurements using the HTDMA in early studies indicated substantial water uptake by OA particles during hydration above 45% RH (Prenni et al., 2001; Mikhailov et al., 2009). The phase state of the particles can strongly influence their

hygroscopic growth. Mikhailov et al. (2009) demonstrated that initial state of OA particles generated in their measurement should be amorphous, resulting in gradual water uptake at lower RH. OA particles generated in the present study may be crystalline due to dry conditions and electric charge effects (Mikhailov et al., 2009), thus accounting for no significant water uptake prior to deliquescence point. Although OA has a high vapor pressure, no evaporation losses for OA particles are observed in agreement with earlier HTDMA studies, suggesting that the initial particles under dry conditions consisted of OA “dihydrate”, i.e., “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule” (Prenni et al., 2001; Mikhailov et al., 2009). It has been found that crystalline anhydrous OA particles could transform into OA dihydrate during hydration between 10-30% RH (Braban et al., 2003). If the initial particles are composed of crystalline anhydrous OA, then the GF of around 1.17 can be obtained based on the transition from anhydrous form to dihydrate one. Obviously, this is not the case in the present study.

As shown in Fig. 2b, MA exhibits continuous water uptake with increasing RH and no phase transition is observed, in agreement with previous EDB and HTDMA measurements (Peng et al., 2001; Prenni et al., 2001). Such hygroscopic behavior indicates MA particles are in a liquid state and still retain some water even at RH~5 % (Peng et al., 2001). Predictions from UNIFAC model based on liquid MA assumption have a good agreement with measured GF above 50% RH while slightly overestimate hygroscopic growth at lower RH. Contrarily, the ideal solution model underestimates the hygroscopic growth of MA above 40% RH. As for SA (Fig. 2c), no hygroscopic growth is observed even at 90% RH, similar behavior also reported by Prenni et al. (2001) and Svenningsson et al. (2006). According to EDB and bulk measurements, the deliquescence relative humidity (DRH) of SA can reach up to 99% RH due to its limited solubility (Peng et al., 2001; Zamora et al., 2011). The hygroscopic growth of submicron PA particles is given in Fig. 2d. The PA particles take up water gradually without phase changes in the RH range studied. Our results suggest initial PA particles may still retain water at the lowest RH, similar to other organic species such as citric acid and malic acid (Peng et al., 2001). The overall trend of the growth curve is consistent with measurements reported by Brooks et al. (2004) and Hartz et al. (2006). Considering the molecular structure of PA, the UNIFAC model with the parameters modified by Peng et al. (2001) was used here.

The UNIFAC model underestimates hygroscopic growth at the moderate and high RH while predictions from ideal solution model are close to the measured GFs. It should be noted that Peng et al. (2001) corrected UNIFAC model interaction parameters only based on water activity data for solutions of seven dicarboxylic acids, mainly straight chain carboxylic acids. Therefore, more water activity data for complex model organic compounds may be helpful for further UNIFAC parameter modification.

4.2 Hygroscopic growth of multicomponent organic aerosols

For organic aerosols containing OA, theoretical growth curves derived from E-AIM are based on various OA phase assumption, i.e., solid and liquid phase, indicated by solid and dashed lines, respectively. In the ZSR approach, the GFs of OA in a solid phase are set equal to 1 and hygroscopic growth curve of OA in a liquid phase is obtained from UNIFAC model (i.e. dehydration curve). To better reproduce the measured GFs, model calculations assuming OA “dihydrate” and anhydrous OA **within various phase** are presented in Figs. 3a, 5a-7a and 3b, 5b-7b, respectively.

4.2.1 Levoglucosan and oxalic acid (Lev/OA)

The hygroscopic behaviors of organic aerosols containing levoglucosan and OA at different mass ratios are shown in Fig. 3. For the 1:1 mixed Lev/OA particles (Fig. 3a, b), no deliquescence behavior is observed and the continuous water uptake starting at low RH~10 % indicates the initial particles appear to be in a liquid state and retain some water. Both ZSR relation and E-AIM based on OA solid phase assumption strongly underestimate the hygroscopic growth of Lev/OA particles in the whole RH range. ZSR approach assumes independent water uptake of components and no interactions exist in the mixtures. Thus, interactions between individual components of mixed particles can determine whether this simple method will deviate from measured GFs for multicomponent aerosols. Measurements with the HTDMA have demonstrated that levoglucosan particles could retain water even at RH lower than 10% (Mochida and Kawamura, 2004; Mikhailov et al., 2009). The supersaturated levoglucosan solution may inhibit the formation of OA crystalline during the generation of initial particles. Parsons et al. (2004a) also found that levoglucosan could reduce the deliquescence or crystallization relative humidity of ammonium sulfate. Thus, OA

in the initial mixed particles may exist in a liquid state and contributes to water uptake by mixed particles in the subsequent humidification (Prenni et al., 2001; Mikhailov et al., 2009), which leads to enhanced hygroscopic growth compared to predictions assuming solid oxalic acid in the mixture.

As shown in Fig. 3a, water uptake predictions from ZSR relation and E-AIM are obviously elevated, assuming OA exists in the liquid phase over the whole RH range studied. However, differences between measured GFs and predicted values based on OA “dihydrate” assumption are still outside the measurement uncertainty at high RH above 60%. In the early study by Prenni et al. (2003), it indicated that ZSR rule could well describe the hygroscopic growth of internally mixed particles containing ammonium sulfate and oxalic acid based on the “dihydrate” assumption. The discrepancy in the present study may be caused by the potential interactions between levoglucosan and oxalic acid in the droplets, which may promote hygroscopicity of particles at high RH. The hydrogen bonding between levoglucosan and oxalic acid may enhance the dissociation of OA at high RH, as suggested by the van't Hoff factor of 1:1 Lev/OA mixture ($i = 1.71$ considerably larger than 1, seen in Fig. 10a). The increasing dissociation of OA could produce more ions at a given RH, leading to reduction of water activity of the Lev/OA droplets (Varga et al., 2007), as indicated by Eq. (6). Considering the relative humidity is kept constant at a specific value during the measurement, more water vapor from gas phase would condensate on the droplets to promote the water activity which reaches thermodynamic equilibrium with the RH, as determined by Köhler equation. Consequently, the Lev/OA mixture shows more water uptake compared to model predictions irrespective of OA phase assumption.

Previous HTDMA studies have shown that the submicron oxalic acid particles under dry conditions are most likely composed of “dihydrate” irrespective of various phase state. For example, Prenni et al. (2001) observed continual hygroscopic growth of oxalic acid particles with increasing relative humidity, suggesting the initial particles were not completely dry but rather concentrated solution droplets. They reported that the measured hygroscopic growth agreed well with Köhler model calculations assuming that the initially generated particles consisted of oxalic acid “dihydrate”. Mikhailov et al. (2009) also found that the solid amorphous oxalic acid particles under dry conditions consisted of oxalic acid “dihydrate”, as

indicated by Köhler model calculations. It can be seen that the submicron oxalic acid particles tend to consist of “dihydrate”, i.e., “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule”. In fact, the formation of anhydrous oxalic acid usually requires very dry conditions and cannot be expected in HTDMA measurement (Mikhailov et al., 2009). Considering hygroscopic species such as levoglucosan could retain some water at low RH, it can be expected that oxalic acid in the submicron mixed particles is also composed of stable dihydrate. It has been found in the emulsion freezing experiments that crystallization of oxalic acid occurred in a dihydrate form within the aqueous malonic acid + oxalic acid or M5(malic acid, malonic acid, maleic acid, glutaric acid and methylsuccinic acid) + oxalic acid solution droplets (Zobrist et al., 2006; Wagner et al., 2015). Although oxalic acid has a high enough vapor pressure, no evaporation losses were observed in previous HTDMA studies (Prezzi et al., 2001; Mikhailov et al., 2009), as well as in our study. The most plausible explanation for the high stability of the investigated OA particles is that they were not anhydrous but composed of “dihydrate” or “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule” (Mikhailov et al., 2009). As for 100 nm levoglucosan/oxalic acid mixed particles, there is also no evaporation losses observed in our study, as indicated by no reduction in particle size during measurements at RH<5%. The similar phenomenon was also observed for other mixed systems containing oxalic acid. Thus, it indicates oxalic acid in the submicron mixed particles under dry conditions may also exist in a “dihydrate” form, i.e., “non-stoichiometric hydrates containing about two water molecules per oxalic acid molecule”.

For comparison, predicted growth curves from three models according to anhydrous OA assumption are given in Fig. 3b. The ZSR method based on OA liquid phase assumption can well describe water uptake of Lev/OA mixtures (1:1, mass) in the 5-90% RH range. The predictions from E-AIM assuming OA present in a liquid phase, are close to measured GFs but still lower due to its underestimation for water contents of levoglucosan at high RH (Fig. S2, Supplement). The growth curves from ideal solution model differ from measurements regardless of OA composition assumption, caused by nonideality of solution.

To further explore the effects of composition on hygroscopicity, the hygroscopic growth of Lev/OA (1:3, 3:1, mass) mixtures with only ZSR predicted curves are shown in Figs. 3c, d. In

the Lev/OA (1:3, mass) case, it can be observed that predictions based on liquid anhydrous OA assumption are in good agreement with measured GFs above 70% RH. Below 40% RH, the mixed particles show no obvious water uptake and the consistence of measurements with predictions based on OA inert mass assumption suggests OA in this mixture may exist in solid phase. Levoglucosan in the particles can take up water gradually with increasing RH, resulting in formation of aqueous solution. Solid OA can be partially dissolved in aqueous levoglucosan and contribute to water uptake at medium 40-70% RH. By compared with ZSR calculations, it can be concluded that OA finishes full deliquescence after 60% RH. As for the Lev/OA (3:1, mass) case, it can be seen that the discrepancies between measurements and predictions based on liquid “dihydrate” assumption decrease at high RH compared to those for other mixing ratios due to the minor oxalic acid composition. Previous studies on aerosol particles containing binary components indicated that organic species such as malonic acid, citric acid contributing to water uptake at low RH could induce partial deliquescence of ammonium sulfate and lower its deliquescence point (Choi and Chan, 2002b; Prenni et al., 2003; Zardini et al., 2008). Svenningsson et al. (2006) have investigated the hygroscopic growth of organic mixtures composed of levoglucosan, succinic acid and fulvic acid and found that experimental values could be reproduced by ZSR approach as long as limited solubility of succinic acid was taken into consideration.

Infrared spectra of equal mass levoglucosan and oxalic acid mixture are used to confirm the interactions between species and phase transitions. The ATR-IR spectra of pure levoglucosan, OA particles and Lev/OA (1:1, mass) mixture recorded at various RHs are presented in Fig. 4. For levoglucosan aerosols, the spectrum at 2% RH shows a broad absorption between 3570 and 3050 cm^{-1} assigned to O-H stretch. The absorbance of the O-H stretch increases at higher RH and a new infrared feature occurs at 1646 cm^{-1} contributed by condensed phase water. The spectrum of OA particles at 2% RH shows an anhydrous feature with a sharp carbonyl stretching band at 1723 cm^{-1} . When RH increases to 30%, the twin bands in the region 3600-3300 cm^{-1} indicate the transformation of anhydrous **crystalline** form to dihydrate one. No obvious liquid water feature can be observed with further humidification up to 91% RH. Our infrared measurement for OA particles is consistent with observation by Braban et al. (2003) while deviates from the H-TDMA results in Fig. 2a. This may be caused by the size

effect considering the IR absorption in the present study is mainly contributed by larger micron particles. As with the Lev/OA (1:1, mass) mixture, features from both levoglucosan and OA components are present. In the 2% RH spectrum the carbonyl stretching band from OA is split into peaks at 1750 cm^{-1} and 1724 cm^{-1} , which suggests strong interaction between OA and levoglucosan. The carbonyl stretching band at 1750 cm^{-1} is close to that in the liquid phase, indicating the Lev/OA (1:1, mass) mixture appears to be partially in a liquid phase. The spectra in Fig. 4c were recorded with larger particles, thus crystallization would be even less likely within smaller particles used in the HTDMA experiments, suggesting that mixtures of oxalic acid and levoglucosan may be in the liquid state even at the lowest RHs studied. Above 30% RH, the carbonyl stretching band shifts to 1743 cm^{-1} in agreement with the C=O feature from aqueous OA (Hug and Bahnemann, 2006). Meanwhile, the increase of absorption between $3570\text{-}3050\text{ cm}^{-1}$ and feature at 1646 cm^{-1} confirm obvious water uptake by mixture particles. The IR results also indicate levoglucosan could strongly influence phase state of OA, resulting in more water uptake at low RH.

4.2.2 Levoglucosan and phthalic acid (Lev/PA)

Figure 5 shows the hygroscopic growth of 100 nm initial particles containing levoglucosan and phthalic acid with equal mass ratio. Continuous water uptake without phase transition can be observed. Both ZSR and ideal solution model could well describe the hygroscopic behavior of this mixture within experiment uncertainty, indicating that the droplets behave like ideal solution. The E-AIM (UNIFAC) underestimates water uptake at high RH due to strong interactions between polar groups on the solute molecule (Peng et al., 2001). Choi and Chan (2002a) used the EDB to measure the water activity of binary organic mixtures by equal molar ratio including maleic acid and malic acid, malonic acid and glutaric acid. They found that both ZSR and modified UNIFAC could accurately predict the measurements for these mixtures which did not experience phase transition, similar to results observed with the HTDMA by Moore and Raymond (2008).

4.2.3 Oxalic acid and malonic acid (OA/MA)

Figure 6 shows the hygroscopic growth of 100 nm initial particles containing oxalic acid and malonic acid with equal mass ratio. The hygroscopic growth of OA/MA (1:1, mass)

mixed particles displays a smooth nature. Previous particle measurements showed that MA could strongly affect the deliquescence behavior of coexisting species like ammonium sulfate or glutaric acid (Choi and Chan, 2002a; Ling and Chan, 2008). It was reported that MA could substantially suppress the crystallization of glutaric acid in the equal molar mixed particles (Choi and Chan, 2002a). Due to the influence of MA, the OA may also exist in a liquid state at low RH thus the mixed particles still contain some water retained from these two components and take up water continuously from low RH. Assuming the oxalic acid in the initial particles composed of “dehydrate”, predictions from ZSR and E-AIM based on OA liquid phase assumption are relatively consistent with measured hygroscopic growth while deviate a lot based on solid assumption (Fig. 6a). As for the anhydrous OA case, the deviations between predictions from ZSR and E-AIM based on OA liquid phase assumption and measurements increase at low RH while minimize at high RH. And the growth curve from ideal solution model is more close to the experiment data.

4.2.4 Oxalic acid and succinic acid (OA/SA)

Figure 7 displays the hygroscopic behavior of 100 nm initial particles containing oxalic acid and succinic acid with equal mass ratio. Based on ZSR assumption, it can be expected that no water uptake by this mixture would occur over the RH range studied, as indicated by ZSR-calculated curve. However, the obvious hygroscopic growth of OA/SA mixture after 70% RH can be observed and the GF is up to 1.28 at 90% RH. No model curves are in good agreement with experiment results within measurement uncertainty in the entire RH range. The predicted DRH from modified UNIFAC model is 96% RH for equal mass OA/SA mixture. The ATR-IR spectra of micron mixed particles during hydration also suggest no water uptake below 92% RH (seen in Fig. 8). However, the submicron OA/SA mixed particles present continuous growth without distinct deliquescence transition from 70% RH. SA has been proved to be nonhygroscopic under subsaturation condition by various measurement methods. The water uptake by the submicron OA/SA mixed particles may be attributed to OA which may form amorphous rather than crystalline phase in the initial mixed particles with submicron size (Mikhailov et al., 2009). The amorphous OA tends to take up water at lower RH than its crystalline counterpart thus contributing to the gradual hygroscopic growth of OA/SA mixed particles below DRH, which could not be predicted by thermodynamic

methods.

Infrared spectra of equal mass oxalic acid and succinic acid mixture are used to explore the hygroscopic behaviors. The ATR-IR spectra of pure OA, SA particles and OA/SA (1:1, mass) mixture recorded at various RHs are presented in Fig. 8. For pure SA aerosols, the spectra at various RHs show no difference and no liquid water feature can be observed. In the spectra of OA/SA (1:1, mass) mixture, the occurrence of absorption in the region $3600\text{-}3300\text{ cm}^{-1}$ indicates the transformation of anhydrous form to dihydrate. However, no obvious condensed phase water feature is detected even at 90% RH. The difference between HTDMA and IR measurements may be caused by size effects which have influence on the hygroscopic behaviors of aerosols (Laskina et al., 2015; Cheng et al., 2015).

4.2.5 Oxalic acid and phthalic acid (OA/PA)

Figure 9 shows the hygroscopic growth of 100 nm initial particles containing oxalic acid and phthalic acid with equal mass ratio. Although PA is less hygroscopic than MA, the OA/PA mixed particles show a similar growth trend with that of OA/MA. It is obvious that the ZSR and E-AIM substantially underestimate the water content of particles at medium and high RH without taking deliquescence of OA into account. Due to the presence of hygroscopic species such as phthalic acid, the crystallization of OA in the mixed particles could be suppressed during the drying process leading to OA in a liquid state in the initial particles. Thus, oxalic acid could contribute to water uptake by mixed particles from low RH (Hemming and Seinfeld, 2001), resulting in enhanced hygroscopic growth compared to predictions assuming solid oxalic acid in the mixture. We also measured hygroscopic growth of aerosols consisting of levoglucosan, oxalic acid and phthalic acid (Lev/OA/PA) with equal mass ratio and found the similar hygroscopic behavior with Lev/OA or OA/PA mixtures, shown in Fig. S3 in Supplement.

4.3 Evaluation of organic droplet nonideality

To describe the dissociation and nonideality of submicron organic aerosol droplets, the van't Hoff factor i is used to assess the degree of deviation from ideality. For the organics, a van't Hoff factor of 1 usually suggests that the solution behaves as an ideal solution. Based on the Eq. (6), van't Hoff factor i is obtained from the slope of the linear fit by a_w^{-1} versus n_s/n_w

for each aerosol droplet. The calculated van't Hoff factor i as well as corresponding R-squared values are given in Fig. 10. For mixtures containing oxalic acid, van't Hoff factor i is calculated based on various OA composition in initial particles, OA “dihydrate” and anhydrous OA, shown in Fig. 10a, b, respectively.

The van't Hoff factors for OA, SA and their mixture are not included since no full deliquescence occurs in the measured RH range. The resulting i for levoglucosan, MA and PA is 1.35, 1.38 and 1.20 respectively, consistent with the literature values of 1.05, 1.29 for levoglucosan (Zamora and Jacobson, 2013; Mikhailov et al., 2009), and 1.37 for MA (Wise et al., 2003). It seems that the three single component aerosol droplets deviate slightly from ideal solution. Assuming OA “dihydrate”, i for most organic mixtures is close to 1 while for Lev/OA with the mass ratio of 1:1, 1:3 it is considerably larger than 1, suggesting the mixtures deviate substantially from an ideal solution. For anhydrous OA assumption case, only i (0.62) for OA/PA mixture deviates a lot from 1. In the case of Lev/OA (1:1, 1:3 by mass), i for mixtures assuming OA “dihydrate” is 1.71, 1.58, respectively, larger than that of the pure component [e.g., i for OA “dihydrate” is 0.98 (Mikhailov et al., 2009)].

4.4 CCN activity of multicomponent WSOC aerosols

Previous studies have confirmed organics may play important role in cloud formation by acting as cloud condensation nuclei (CCN) (Suda et al., 2014; Xu et al., 2014). Here we use the single hygroscopicity parameter κ to evaluate the hygroscopicity and CCN activity of WSOC aerosol particles (Petters and Kreidenweis, 2007). This parameter usually can be derived from hygroscopic growth measurements at RH~90% with the HTDMA or from critical supersaturation measurements under supersaturated conditions (Petters and Kreidenweis, 2007). It has been shown values of κ estimated from the two methods agree well within 30%, especially for organics with continuous hygroscopic growth (Petters and Kreidenweis, 2007; Chan et al., 2008; Petters et al., 2009). For aerosol particles containing OA, it is convenient to use the κ capturing all solute properties to describe the hygroscopicity without taking OA composition assumption into account, indicated by Eq. (7).

It has been found κ for organic aerosols may correlate with the ratio of oxygen to carbon atoms (O/C) in dry particles while deviations from this relationship were also reported

(Jimenez et al., 2009; Duplissy et al., 2011; Rickards et al., 2013). The single hygroscopicity parameter κ evaluated from the HTDMA data at 90% RH is plotted as a function of O/C ratio, seen in Fig. 11. The κ -values for SA and its mixture with OA are not included. For OA, the κ -value (0.484) is obtained from UNIFAC-predicted GF, consistent with literature values 0.48, 0.504 (Rickards et al., 2013; Kreidenweis et al., 2008). The κ -values for other pure components are also in good agreement with reported values. As shown in Fig. 11, the general trend indicates the possible relationship between κ -value and O/C ratio for WSOC aerosols. To further assess the effects of coexisting species on hygroscopicity of mixed particles, the κ -values derived from HTDMA measurements for pure levoglucosan, oxalic acid and their mixtures at various mass ratios as well as the corresponding ZSR predictions assuming anhydrous OA or OA “dihydrate” in a liquid state are shown in Fig. 12. It can be observed that the hygroscopicity of three Lev/OA mixtures is similar and more close to that of OA compared to levoglucosan. Predictions from ZSR rule significantly underestimate κ -values derived from GF measurements, regardless of OA composition assumption. The enhanced hygroscopicity of Lev/OA mixed particles is likely due to the fact that the decreasing water activity of droplets resulting from interactions between levoglucosan and oxalic acid controls the water condensation on the droplets. The similar enhancement effects on hygroscopicity were also observed in aerosol particles containing ammonium sulfate and fulvic acid due to complex chemical interactions (Chan and Chan, 2003).

4.5 Effect of organic mixture on hygroscopicity of ammonium sulfate (AS)

The organic mixture of oxalic acid with levoglucosan is selected to determine the influences of multicomponent organics on the hygroscopic properties of ammonium sulfate (AS). As shown in Fig. 13, the hygroscopic growth measurements for equal mass mixture of AS with OA are also presented for comparison. It can be seen that 1:1 AS/OA mixture does not show any hygroscopic growth until reaching its deliquescence point 77% RH consistent with literature values for eutonic mixtures (Brooks et al., 2002). Based on OA dihydrate assumption, the E-AIM predictions agree well with measured growth factors. It should be noted that the deliquescence point predicted by E-AIM is 73% RH slightly lower than the experiment result. The ZSR relation underestimates water uptake of AS/OA mixture after complete deliquescence without taking OA dissolution into consideration.

For the 2:1:1 AS/OA/Lev mixed aerosols, a smoothing of hygroscopic growth behavior can be observed without obvious phase transitions occurring. Both E-AIM and ZSR method underestimate the hygroscopic growth above 30% RH. In the previous study, the binary mixture containing AS and levoglucosan still showed phase transitions even when organic fraction accounted for up to 50% (Lei et al., 2014). A possible explanation for present phenomenon is that levoglucosan could suppress crystallization of OA resulting in more water uptake at low RH which enhances partial dissolution of AS. For both equal mass mixtures of AS/OA and AS/Lev, the hygroscopic growth of particles can be well described by E-AIM (seen in Fig.13a and Lei et al., 2014). However, this is not the case for AS/OA/Lev mixture. It is clear that the organic mixture has more complex effect on the hygroscopicity of ammonium sulfate than single organic species. Although levoglucosan only accounts for a small fraction in the mixture, it still strongly influences the hygroscopic behavior of AS by changing phase state of OA which plays the role of “intermediate” species.

5 Conclusion and Atmospheric Implications

In this study, the hygroscopic properties of single component and multicomponent water-soluble organic compounds mainly involving oxalic acid are investigated with the HTDMA. The hygroscopic behavior of oxalic acid in our measurements differs from previous HTDMA data but agrees with EDB and other methods results. The hygroscopic growth of other single component aerosol particles including levoglucosan, malonic acid, succinic acid and phthalic acid, are in good agreement with previous studies. The most of multicomponent organic aerosols show continuous water uptake behavior without obvious phase transition from low RH except for the OA/SA mixture. For equal mass mixed organic aerosols containing oxalic acid, the coexisting hygroscopic species such as levoglucosan, malonic acid and phthalic acid have strong influence on the phase behavior of oxalic acid, even suppress its crystallization completely during the drying process. Oxalic acid in a liquid state in the initial particles could contribute to water uptake by mixed particles from low RH, which leads to enhanced hygroscopic growth compared to predictions assuming solid oxalic acid in the mixture. The enhanced water uptake of Lev/OA mixed particles is likely due to the change in water activity of droplets resulting from interactions between levoglucosan and oxalic acid. As for oxalic acid/succinic acid mixed particles, the amorphous OA may be responsible for

the unexpected water uptake at high RH below the DRH.

Model methods including E-AIM (UNIFAC), ZSR approach and ideal solution model are used to predict the hygroscopic growth of single component and multicomponent organic aerosol particles. The discrepancies between measurements and predictions from E-AIM and ZSR approach increase at medium and high RH assuming the OA in a solid state. For ZSR method, it can describe the hygroscopic growth of aerosol particles containing OA in a liquid state at high RH based on anhydrous OA composition assumption except for OA/SA. However, it should be noted that the OA in the initial submicron particles is more likely to exist in a “dihydrate” form rather than an anhydrous one. Consequently, the substantial underestimation of hygroscopic growth of Lev/OA mixed particles at high RH by the ZSR relation based on “dihydrate” assumption may be caused by the chemical interactions such as hydrogen bonding between solutes, also indicated by the van't Hoff factor i and the single hygroscopicity parameter κ -value. Comparisons between measurement results and thermodynamic predictions assess the reliability of the aerosol models for predicting hygroscopic properties of atmospheric WSOC with various chemical properties. Predictions from E-AIM (UNIFAC) considerably underestimated water content of some mixed aerosols at high RH, suggesting model parameters may need to be further modified so that it can more reliably predict thermodynamic properties of atmospheric organic aerosols. Due to low disassociation, most WSOC mixtures studied have a van't Hoff factor close to 1 except for Lev/OA (1:1,1:3 mass), influenced by OA composition assumption. By comparing the single hygroscopicity parameter κ -values with ZSR predictions, it also indicates the hygroscopicity of mixtures containing oxalic acid and levoglucosan is significantly enhanced under high RH conditions.

These findings suggest that the presence of coexisting hygroscopic species has a great impact on the phase behaviors and hygroscopic growth of oxalic acid which has a high deliquescence point. Organic mixture has more complex effect on the hygroscopicity of ammonium sulfate than single species. Although hygroscopic species such as levoglucosan account for a small fraction in the multicomponent aerosols, they may still strongly influence the hygroscopic behavior of AS by changing phase state of OA which plays the role of “intermediate” species. Considering the abundance of oxalic acid in the atmospheric aerosols,

its mixtures with hygroscopic species may promote water uptake under high RH conditions and thus affect the cloud condensation nuclei (CCN) activity, optical properties and chemical reactivity of atmospheric particles.

The Supplement related to this article is available online.

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Table 1. Chemical properties of investigated organic species.

Substance	Chemical Formula	MW(g mol ⁻¹)	ρ (g cm ⁻³)	Supplier/Purity
Ammonium sulfate	(NH ₄) ₂ SO ₄	132.1	1.77	Alfa Aesar, 99.95%
Levoglucozan	C ₆ H ₁₀ O ₅	162.1	1.62	Aldrich, 99%
Oxalic acid	C ₂ H ₂ O ₄	90	1.9	Aldrich, 99.999%
Oxalic acid (dihydrate)	C ₂ H ₂ O ₄ · 2H ₂ O	126	1.65	-
Malonic acid	C ₃ H ₄ O ₄	104.1	1.62	Sigma-Aldrich, 99%
Succinic acid	C ₄ H ₆ O ₄	118.1	1.57	Sigma-Aldrich, ≥99.5%
Phthalic acid	C ₈ H ₆ O ₄	166.1	1.59	Sigma-Aldrich, ≥99.5%

Table 2. Chemical composition and O/C ratio of mixtures used in experiments.

Mixture	Mass ratio	O/C ratio
Levoglucozan (Lev) + oxalic acid (OA)	1:1	1.27
Levoglucozan (Lev) + oxalic acid (OA)	1:3	1.58
Levoglucozan (Lev) + oxalic acid (OA)	3:1	1.03
Levoglucozan (Lev) + phthalic acid (PA)	1:1	0.64
Oxalic acid (OA) + malonic acid (MA)	1:1	1.62
Oxalic acid (OA) + succinic acid (SA)	1:1	1.40
Oxalic acid (OA) + phthalic acid (PA)	1:1	0.97
Levoglucozan (Lev) + oxalic acid (OA) + phthalic acid (PA)	1:1:1	0.93

Table 3. The three-parameter fit values for the the hygroscopic growth of the investigated organic aerosol particles with the Eq. (2).

Substance	a	b	c	R ²
Levoglucozan	0.4315	-0.4929	0.2789	0.9997
Malonic acid	0.2512	0.2493	-0.1236	0.9959
Phthalic acid	0.4368	-0.6003	0.2737	0.9910

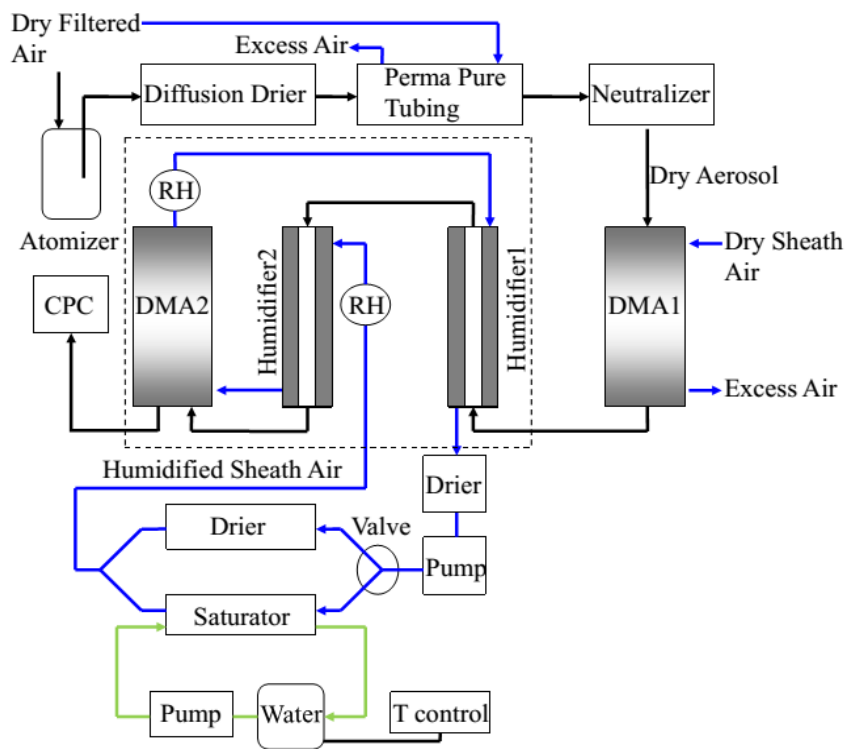


Figure 1. Schematic setup of the hygroscopicity tandem differential mobility analyzer (HTDMA) system.

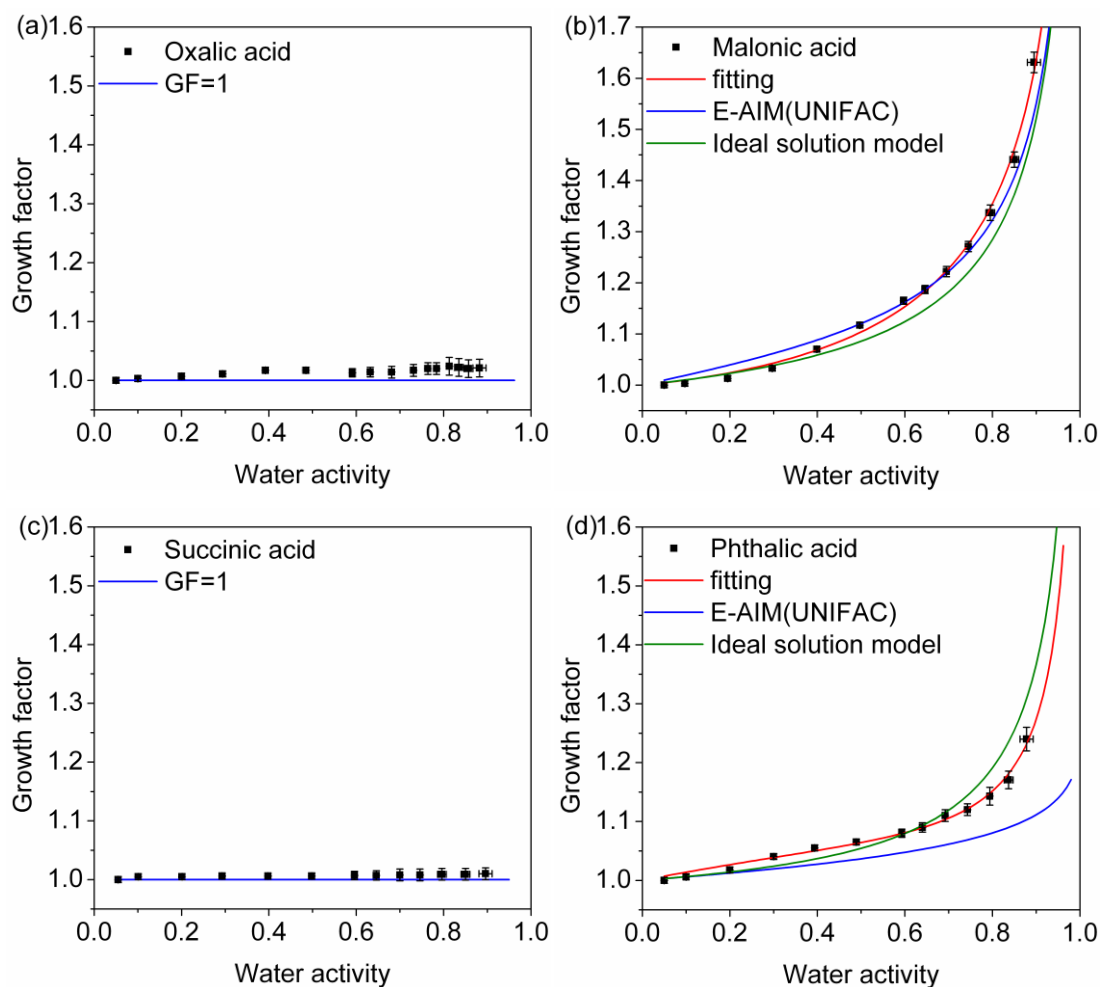


Figure 2. Hygroscopic growth factors of (a) oxalic acid, (b) malonic acid, (c) succinic acid and (d) phthalic acid particles as a function of water activity. Initial particle diameter is about 100 nm. For malonic acid and phthalic acid, the fit to the measurements with Eq. (2) is shown. Predictions from the E-AIM (UNIFAC) and ideal solution model are also included. The uncertainty in our measured growth factors is within 0.02.

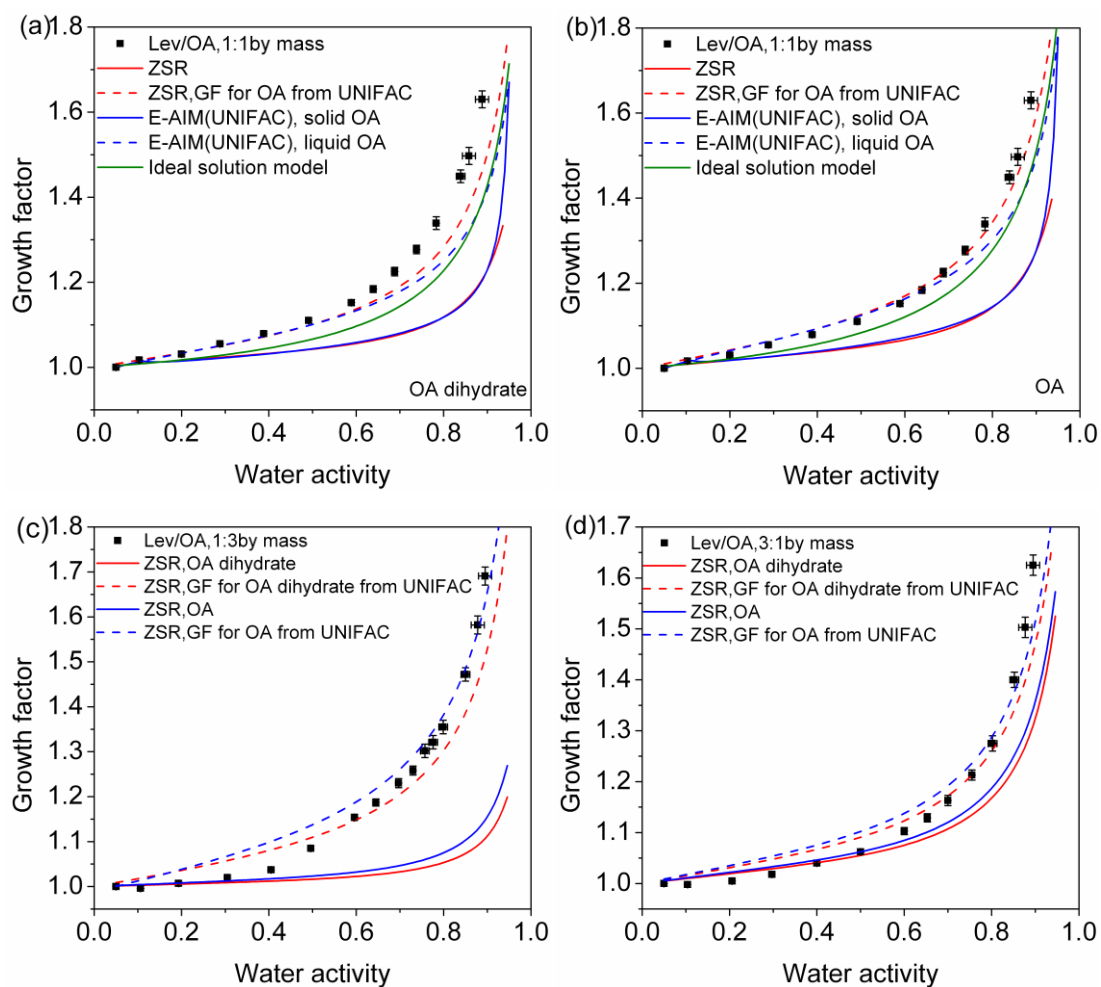


Figure 3. Hygroscopic growth factors of aerosols containing levoglucosan and oxalic acid (Lev/OA) with various mass ratio (a) and (b) 1:1, (c) 1:3, (d) 3:1 as a function of water activity. Initial particle diameter is about 100 nm. Predictions from the ZSR, E-AIM (UNIFAC) and ideal solution model are included in (a) and (b), assuming oxalic acid “dihydrate” and anhydrous oxalic acid in the initial particles under dry conditions, respectively. The dashed lines are calculated based on liquid oxalic acid (OA) assumption. For (c) 1:3, (d) 3:1 mass ratio, only ZSR-predicted curves are shown on the basis of different OA assumption. The uncertainty in our measured growth factors is within 0.02.

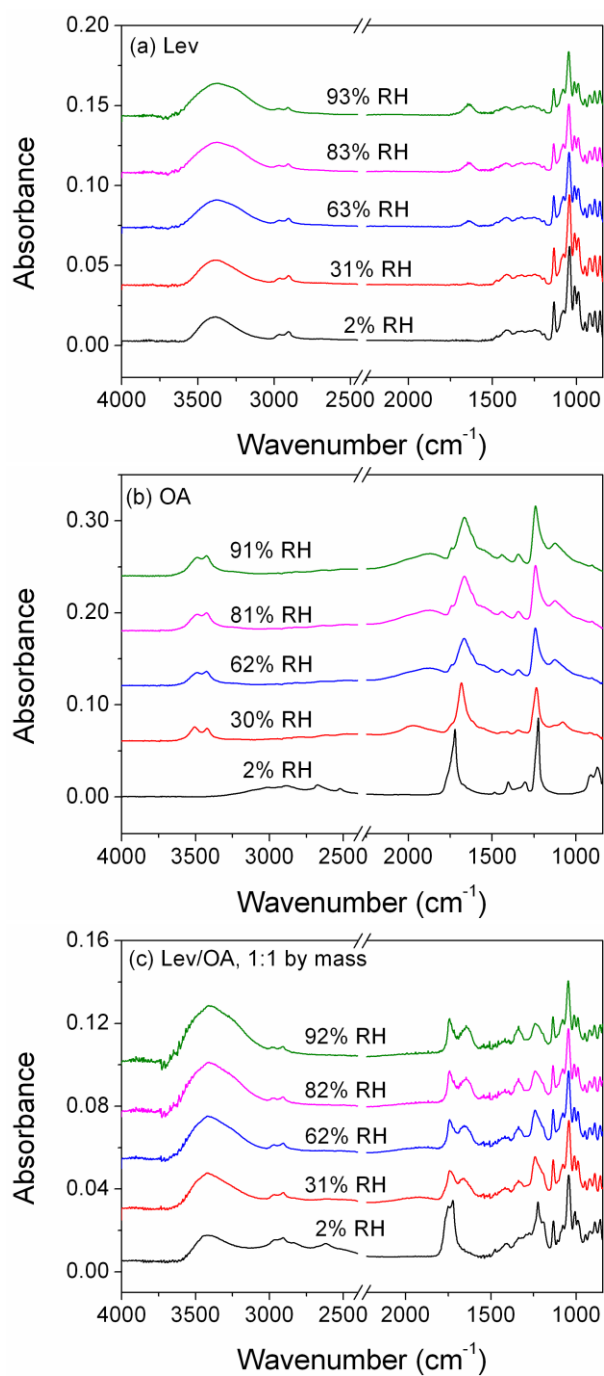


Figure 4. ATR-FTIR absorbance spectra of aerosol particles upon hydration with RH for (a) levoglucosan, (b) oxalic acid and (c) levoglucosan/oxalic acid mixture (1:1, by mass). Features from gas-phase water have been subtracted. Gas-phase CO_2 absorptions have been removed and the spectra have been offset for clarity.

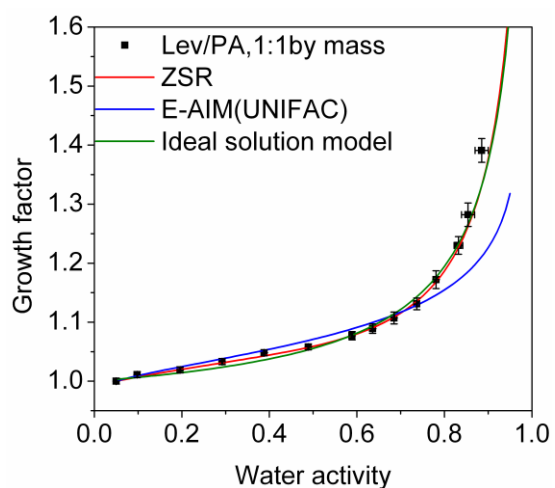


Figure 5. Hygroscopic growth factors of aerosols consisting of levoglucosan and phthalic acid (Lev/PA) at a mass ratio of 1:1 as a function of water activity. Initial particle diameter is about 100 nm. Predictions based on the ZSR, E-AIM (UNIFAC) and ideal solution model are also included. The uncertainty in our measured growth factors is within 0.02.

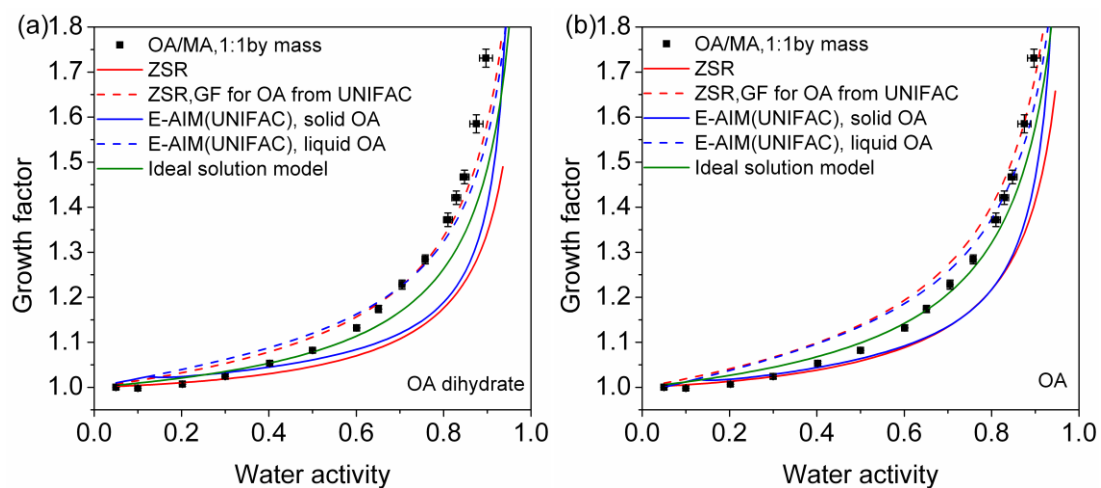


Figure 6. Hygroscopic growth factors of aerosols containing oxalic acid and malonic acid (OA/MA) at a mass ratio of 1:1 as a function of water activity. Initial particle diameter is about 100 nm. Predictions from the ZSR, E-AIM (UNIFAC) and ideal solution model are also included, assuming (a) oxalic acid “dihydrate”, (b) anhydrous oxalic acid in the initial particles under dry conditions. The dashed lines are calculated based on liquid oxalic acid (OA) assumption. The uncertainty in our measured growth factors is within 0.02.

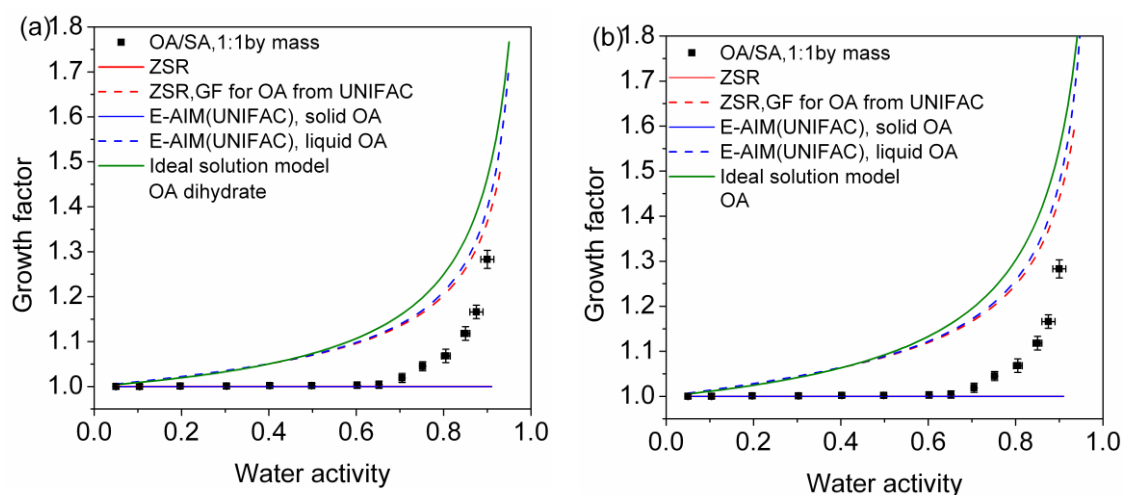


Figure 7. Hygroscopic growth factors of aerosols consisting of oxalic acid and succinic acid (OA/SA) at a mass ratio of 1:1 as a function of water activity. Initial particle diameter is about 100 nm. Predictions from the ZSR, E-AIM (UNIFAC) and ideal solution model are also included, assuming (a) oxalic acid “dihydrate”, (b) anhydrous oxalic acid in the initial particles under dry conditions. The dashed lines are calculated based on liquid oxalic acid (OA) assumption. The uncertainty in our measured growth factors is within 0.02.

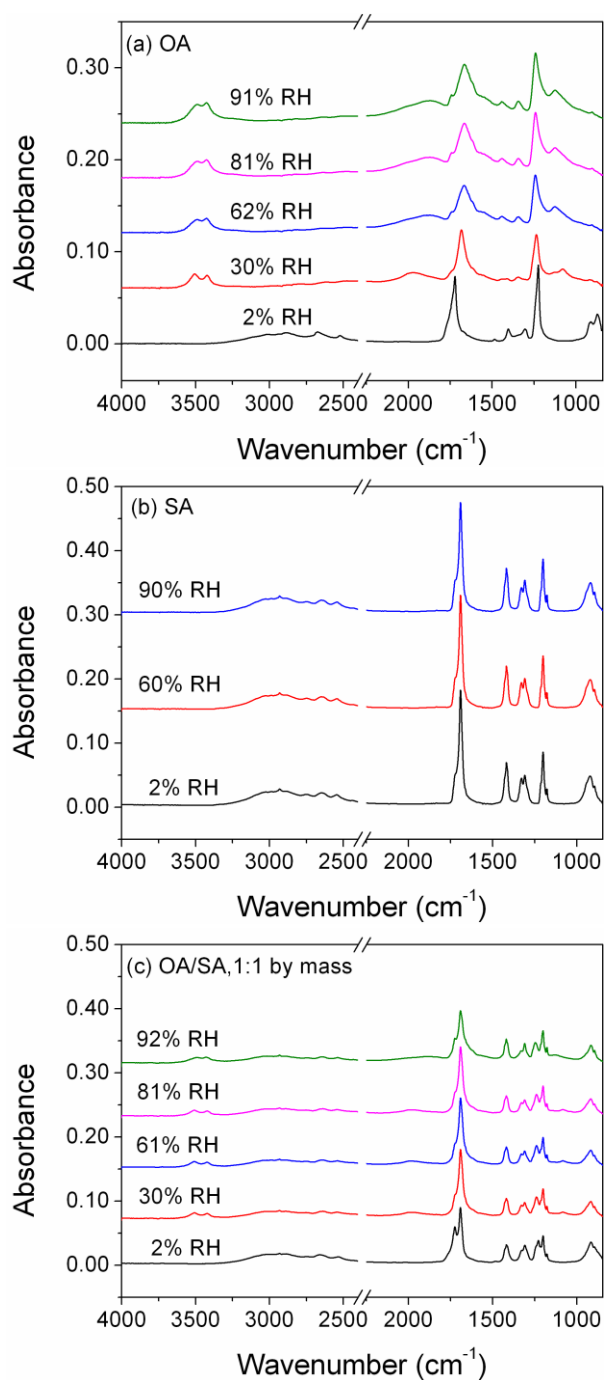


Figure 8. ATR-FTIR absorbance spectra of aerosol particles upon hydration with RH for (a) oxalic acid, (b) succinic acid and (c) oxalic acid/succinic acid mixture (1:1, by mass). Features from gas-phase water have been subtracted. Gas-phase CO₂ absorptions have been removed and the spectra have been offset for clarity.

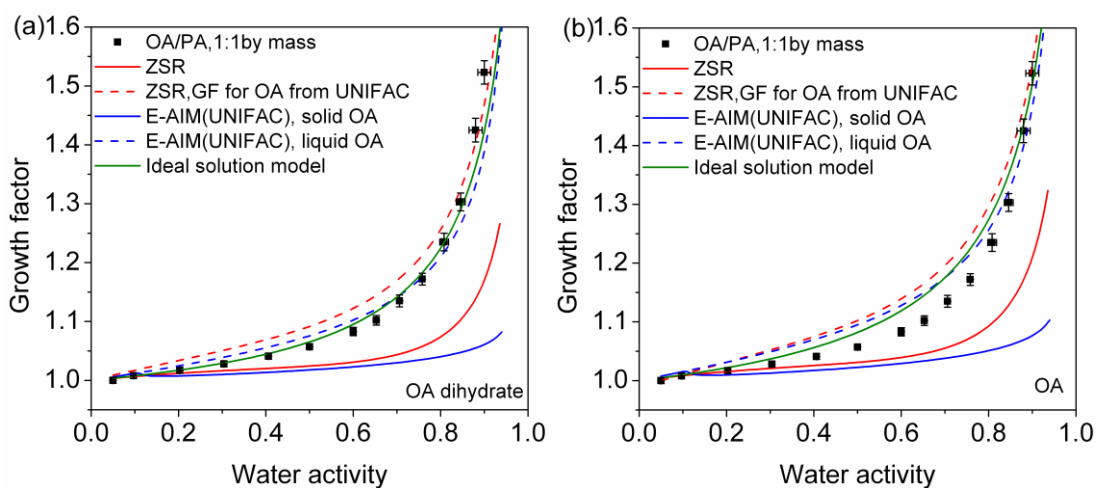


Figure 9. Hygroscopic growth factors of aerosols consisting of oxalic acid and phthalic acid (OA/PA) at a mass ratio of 1:1 as a function of water activity. Initial particle diameter is about 100 nm. Predictions from the ZSR, E-AIM (UNIFAC) and ideal solution model are also included, assuming (a) oxalic acid “dihydrate”, (b) anhydrous oxalic acid in the initial particles under dry conditions. The dashed lines are calculated based on liquid oxalic acid (OA) assumption. The uncertainty in our measured growth factors is within 0.02.

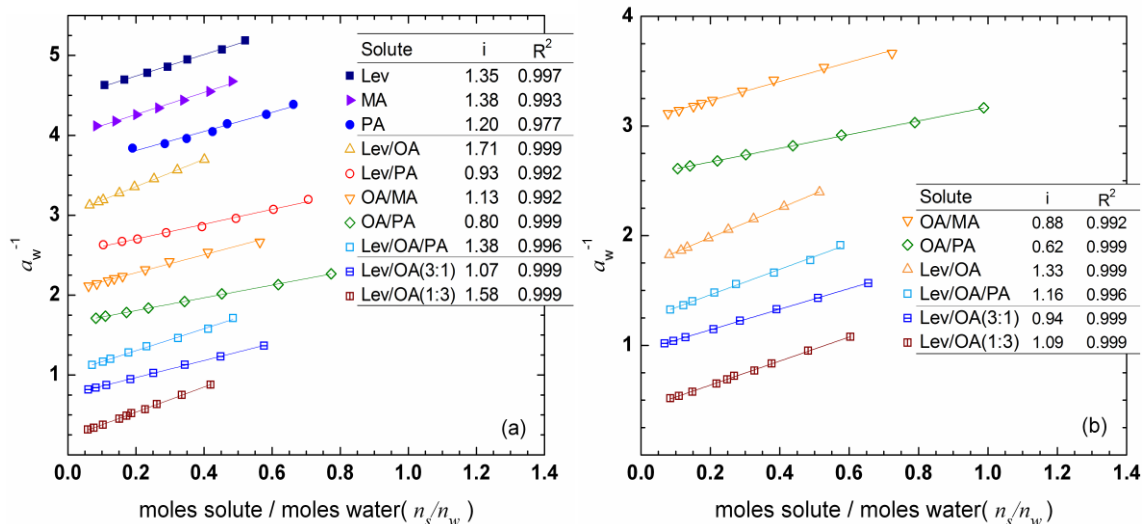


Figure 10. The inverse of the water activity (a_w^{-1}) as a function of the ratio of mole number of total solute to mole number of water (n_s/n_w) for all organic droplets. The slope of the fit line is equal to the van't Hoff factor (i). The R-squared values for the fit are also listed. Each data set was offset by $a_w^{-1} = 0.3$ from the previous one for clarity. Calculations for aerosols containing oxalic acid are based on assumption of (a) oxalic acid "dihydrate" and (b) anhydrous oxalic acid. All the mixtures are by equal mass composition except specially noted.

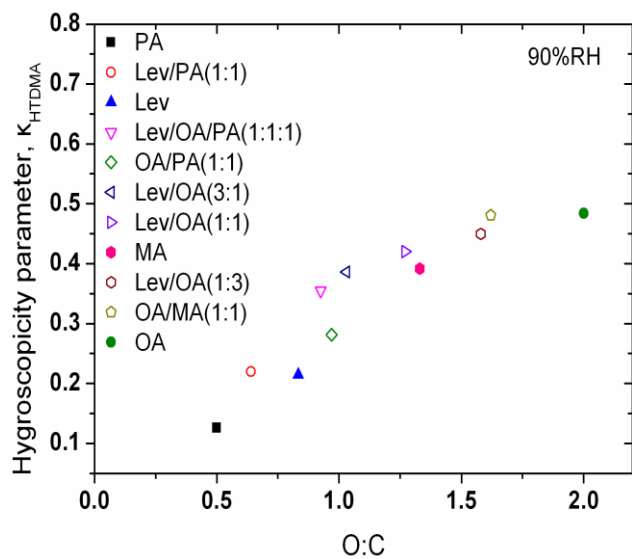


Figure 11. Relationship between O:C and hygroscopicity parameter κ derived from HTDMA measurements at 90% RH for all the organic aerosol particles in this study.

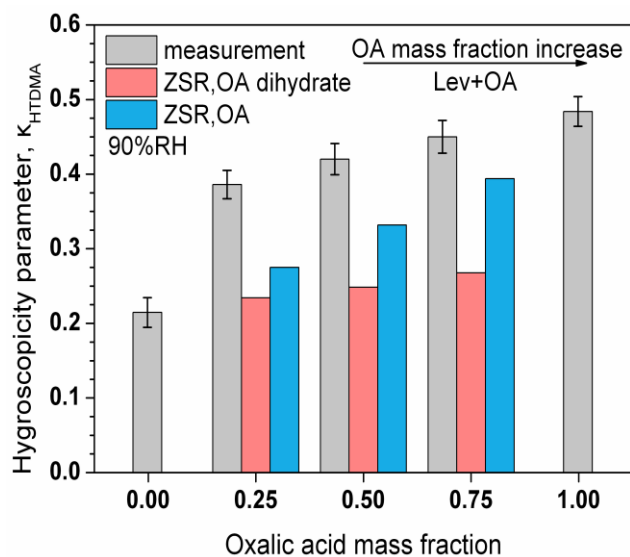


Figure 12. The κ results derived from HTDMA measurements at 90% RH for aerosols containing oxalic acid (OA) and levoglucosan (Lev) in varying mass proportions. ZSR-predicted κ values are also shown by assuming liquid oxalic acid “dihydrate” or liquid anhydrous oxalic acid in the initial mixtures under dry conditions. The κ value of oxalic acid is obtained from the UNIFAC.

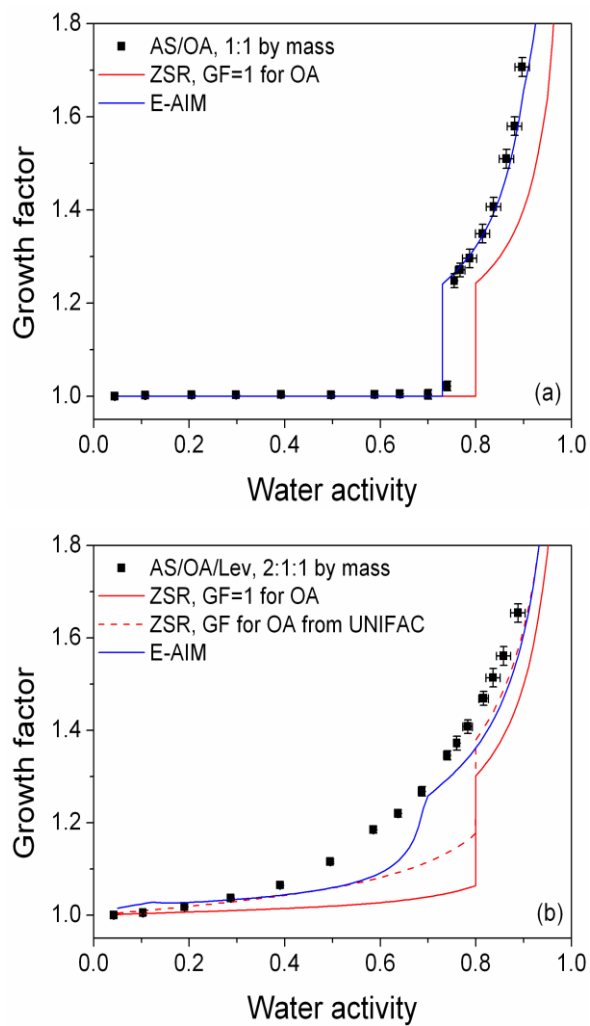


Figure 13. Hygroscopic growth factors of 1:1 AS/OA (a), 2:1:1 AS/OA/Lev (b) as a function of water activity. Initial particle diameter is about 100 nm. Predicted growth curves from the ZSR and E-AIM assuming oxalic acid “dihydrate” are indicated by red and blue lines respectively. The uncertainty in our measured growth factors is within 0.02.