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Water uptake of multicomponent organic mixtures and their influence on hygroscopicity of inorganic salts

Yuanyuan Wang^{1,2,3}, Bo Jing^{1,2,3}, Yucong Guo², Junling Li², Shengrui Tong²,
Yunhong Zhang^{1,*}, Maofa Ge^{2,*}

1. The Institute of Chemical Physics, School of Chemistry, Beijing Institute of Technology, Beijing 100081, China

2. Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

The hygroscopic behaviors of atmospherically relevant multicomponent water soluble organic compounds (WSOCs) and their effects on ammonium sulfate (AS) and sodium chloride were investigated using a hygroscopicity tandem differential mobility analyzer (HTDMA) in the relative humidity (RH) range of 5%–90%. The measured hygroscopic growth was compared with predictions from the Extended-Aerosol Inorganics Model (E-AIM) and Zdanovskii–Stokes–Robinson (ZSR) method. The equal mass multicomponent WSOCs mixture containing levoglucosan, succinic acid, phthalic acid and humic acid showed gradual water uptake without obvious phase change over the whole RH range. It was found that the organic content played an important role in the water uptake of mixed particles. When organic content was dominant in the mixture (75%), the measured hygroscopic growth was higher than predictions from the E-AIM or ZSR relation, especially under high RH conditions. For mass fractions of organics not larger than 50%, the hygroscopic growth of mixtures was in good agreement with model predictions. The influence of interactions between inorganic and organic components on the hygroscopicity of mixed particles was related to the salt type and organic content. These results could contribute to understanding of the hygroscopic behaviors of multicomponent aerosol particles.

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Introduction

In the atmosphere, the interaction between water vapor and aerosol particles has a significant influence on many atmospheric processes. The water uptake of aerosol particles could affect their dry and wet deposition, atmospheric visibility, human health, solar radiation and heterogeneous chemical reactions (Pandis et al., 1995; Poschl, 2005). Atmospheric aerosol particles are generally complex mixtures containing

numerous inorganic salts and organic materials, which significantly contribute to the hygroscopic growth of particles. The hygroscopic properties of inorganic salts present in the atmosphere have been well known (Ansari and Pandis, 1999; Colberg et al., 2003). However, the hygroscopic behaviors of organics have not been well characterized due to the kinds of species and uncertainties in hygroscopicity and phase transitions (Decesari et al., 2000; Mader et al., 2004). Field measurements have shown that a large mass fraction of total

* Corresponding authors.

E-mail addresses: yhz@bit.edu.cn (Y. Zhang), gemaofa@iccas.ac.cn (M. Ge).

³ These authors contributed equally to this work.

atmospheric fine particles is organic matter, in which water soluble organic compounds (WSOCs) are the major hygroscopic constituents (Decesari et al., 2005; Saxena and Hildemann, 1996). The water soluble organic fraction can affect the water uptake behaviors of mixed particles (Gysel et al., 2004).

According to the method proposed by Fuzzi et al. (2001), complex WSOCs can be divided into three different classes: (1) neutral compounds; (2) mono-/di-carboxylic acids; and (3) polycarboxylic acids (PA). Decesari et al. (2001) found that PA constituted up to 40% of total WSOCs by mass. Due to their structural similarity to humic acid, PA are also called humic-like substances (HULIS). Based on the classification method, a corresponding model substance can be selected to investigate the properties of WSOCs. As a biomass burning product tracer, levoglucosan is usually chosen as the model species of neutral compounds. Succinic acid and phthalic acid can be selected as surrogates of dicarboxylic acids because of their abundant contents in atmospheric particles. Humic acid is used to represent the HULIS (Svenningsson et al., 2006; Zamora and Jacobson, 2013).

Previous studies have mainly focused on the hygroscopic properties of individual WSOCs, especially straight chain dicarboxylic acids and their mixtures with inorganic salts such as ammonium sulfate (AS) or sodium chloride (Braban et al., 2003; Brooks et al., 2003; Cruz and Pandis, 2000; Peng et al., 2001; Pope et al., 2010; Prenni et al., 2001). Only a few studies have involved the water uptake behaviors of multicomponent WSOC aerosols (Mochida and Kawamura, 2004; Svenningsson et al., 2006; Zamora and Jacobson, 2013). Marcolli et al. (2004) considered that the interactions between organic components may increase the solubility of single species, and mixed aerosol particles may remain liquid irrespective of ambient humidity. Since the interaction between species has potential impact on the phase and water uptake of aerosols, it is necessary to investigate the hygroscopicity of multicomponent organic aerosols and their influence on the water uptake of inorganic salts. Thus, further study on the hygroscopicity of internally mixed particles containing multicomponent WSOCs with inorganic salts could help to understand the hygroscopic properties and phase state of atmospheric aerosols under different humidity conditions. Furthermore, the measurement data can be used to evaluate the predictive ability of aerosol thermodynamic models (Peng et al., 2001).

In this study, hygroscopic growth was measured using a hygroscopicity tandem differential mobility analyzer (HTDMA) for atmospheric multicomponent WSOC mixtures and their internal mixtures with inorganic salts, including AS or sodium chloride (NaCl). The multicomponent WSOC mixture was composed of a mix of equal masses of four organics: levoglucosan,

succinic acid, phthalic acid and humic acid, selected as the model species of the WSOCs. The mixing ratios of WSOCs and inorganic salts were related to the water uptake behavior of the mixed particles. Furthermore, the measured hygroscopic growth of the mixtures was compared with predicted curves from the Extended-Aerosol Inorganics Model (E-AIM) or Zdanovskii–Stokes–Robinson (ZSR) method.

1. Experiment and model section

1.1. Sample preparation

The properties of substances studied in this work are given in Table 1, and the chemical structural formulas of organic compounds are shown in Fig. 1. 100 mg humic acid was dissolved in 100 ml ultrapure water (EASY Pure®II UF ultrapure water system, 18.2 MΩ cm). The humic acid could not be dissolved completely, and the aqueous suspension was filtered with filter paper (Whatman, medium speed). The elemental analysis showed that the mass fractions of carbon, hydrogen and nitrogen in the sample were 41.32%, 3.29%, 1.21%, respectively. In order to calibrate the concentration of humic acid filtrate, a total organic carbon analyzer (TOC, Analytik jena multi N/C 2100) was used to measure the carbon concentration. The concentration of humic acid in the filtrate (g/mL) was calculated from the concentration of carbon in the filtrate measured by TOC (g/mL) divided by the mass fraction of carbon in the solid humic acid sample.

The filtrate with calibrated concentration was used for the following mixed solution preparation. The other three organics (levoglucosan, succinic acid, phthalic acid) in equal mass were added into the filtrate to prepare the MIXORG (levoglucosan, succinic acid, phthalic acid, humic acid, by equal mass) solution, and the amount of each species was equal to that of humic acid. The obtained solution was diluted to around 0.1% total mass fraction. The bulk solutions containing inorganic salt (AS or NaCl) and MIXORG at different mass ratios were also prepared in a similar way.

1.2. Hygroscopic growth measurements

The HTDMA has been fully described in our previous study (Jing et al., 2015) and will be briefly introduced here. The polydispersed aerosols were generated from a constant output atomizer (MSP, 1500) containing prepared bulk solution. After leaving the atomizer, the particles passed through silica gel diffusion dryers (SDD) and a Perma Pure drying tube (PD-100T-24MSS), where the aerosol flow was dried to below 5% relative humidity (RH).

Table 1 – Properties of species used in this study.

Substance	Chemical formula	MW (g/mol)	ρ (g/cm ³)	Supplier/purity
Ammonium sulfate	(NH ₄) ₂ SO ₄	132.1	1.769	Alfa Aesar, 99.95%
Sodium chloride	NaCl	58.44	2.165	Alfa Aesar, 99.99%
Levoglucosan	C ₆ H ₁₀ O ₅	162.1	1.62	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%
Humic acid	–	–	1.5	Aldrich

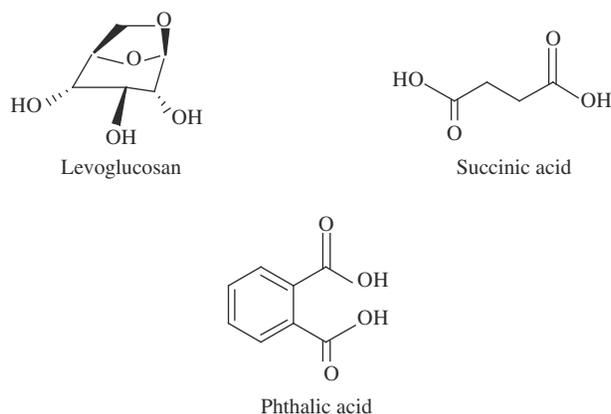


Fig. 1 – Chemical structural formulas of three WSOCs (water soluble organic compounds).

The dry aerosols were charged and then entered the first differential mobility analyzer (DMA1) to select monodispersed particles with a diameter of 100 nm. After size selection, the aerosol flow was pre-humidified by using a Perma Pure tube and fully humidified to a given RH by using another Perma Pure tube. The residence time of particles at a desired RH was 5 sec before entering the second differential mobility analyzer (DMA2). The size distribution of humidified aerosol diameter was measured by DMA2 and a condensation particle counter (CPC). The sheath gas flow was recirculated between DMA2 and the humidification section to ensure that the aerosol flow remained at the same humidity. The humidity of the sheath flow at the outlet of DMA2 was measured using a dew point hygrometer (MICHELL, OPTIDEW VISION, $\pm 0.08\%$ RH, ± 0.1 K). By gradually increasing the RH of the sheath flow, the mobility diameter (D_p) of aerosol particles at specific RH values was measured. The ambient temperature was maintained at 298 ± 1 K.

The hygroscopic growth factor (GF) is defined as:

$$GF = D_w/D_d$$

where D_w is the mobility diameter of a humidified particle at a certain RH and D_d is the mobility diameter of a dry particle measured by DMA2 at RH < 5% in this work. The hygroscopic growth of AS was measured to validate the instrument performance because of its well-known deliquescence point and GFs. The measured GFs and deliquescence point of AS were in agreement with model predictions and reported values in the literature (Kreidenweis et al., 2005; Sjogren et al., 2007).

1.3. Model methods

In this work, it was more accurate to use the water activity (a_w) as the independent variable instead of the RH due to the curvature effect for the submicron particles. According to Köhler theory, the RH can be converted to a_w as follows:

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

where M_w is the molecular weight of water, σ_{sol} is the surface tension of the droplet, R is the universal gas constant, T is the temperature, ρ_w is the density of pure water and D_p is the diameter of the particle. The surface tension of pure water (0.072 J/m²) was used as that of the droplet.

E-AIM is a thermodynamic model designed for calculations of gas/liquid/solid partitioning in aerosol systems containing important atmospheric inorganic and organic species (Wexler and Clegg, 2002). This model can be used to predict the water content, particle volume and density of mixed aerosol particles over a wide range of humidity conditions. Also, E-AIM combined with the UNIFAC (universal quasi-chemical functional group activity coefficients) is applied to estimate the activity coefficient of multicomponent aerosol systems composed of inorganic and organic components in aqueous phase (Hansen et al., 1991). Considering that the standard UNIFAC model may result in large deviations for organics with strong polar functional groups less than four carbon atoms, the UNIFAC model revised by Peng et al. (2001) was applied for WSOCs studied in the present study. According to the volume additive assumptions, the volume of an aerosol particle after absorbing water is the additive volume of both the dry particle and the water contents (Moore and Raymond, 2008; Topping et al., 2005). Based on the water content prediction from E-AIM and spherical particle assumption, the GF at a given RH and 298 K is expressed as:

$$GF = \frac{D_{wet}}{D_{dry}} = \left[1 + \frac{m_w\rho_s}{m_s\rho_w}\right]^{1/3} \quad (2)$$

where D_{wet} is the diameter of particles at a certain RH, D_{dry} is the diameter of the dry particle, m_w and ρ_w is the mass and density of water, respectively, m_s and ρ_s is the mass and density of the solute, respectively.

The ZSR method has been successfully used to calculate the hygroscopic growth of mixed aerosol particles. The hygroscopic growth factor of mixed particle (GF_{mixed}) can be predicted from the GFs and volume fractions of each pure component by the ZSR relation (Malm and Kreidenweis, 1997; Stokes and Robinson, 1966):

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

where GF_k is the growth factor of pure component k , ε_k is the volume fraction of pure component k in a dry particle. In actual calculations, the GFs of inorganic salts are given by the thermodynamic E-AIM, which are highly consistent with the measurements (Jing et al., 2015), while the GFs of organic materials (except for succinic acid with GF = 1) are obtained from data fitting. The volume fraction of each component in a dry particle can be calculated with Eq. (4):

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

where w_i is the mass fraction of component i in the dry particle, ρ_i is the density of pure component i .

To quantify the effect of organics on the hygroscopic growth of inorganic salts, Cruz and Pandis (2000) proposed a parameter to describe it:

$$\xi_w = \frac{GF^3 - 1}{(1 - \varepsilon_o)(GF_{inorg}^3 - 1)} \quad (5)$$

where ξ_w is the ratio of water uptake by mixed particles to that by the inorganic components. GF_{inorg} is the growth factor of the inorganic component, ε_o is the volume fraction of the organic component. Here the organics were considered not to absorb any water. Actually, some water soluble organic compounds show significant water uptake under high RH conditions, thus by combining with water uptake from organics Eq. (5) can be rewritten as:

$$\xi'_w = \frac{GF^3 - 1}{\sum_k \varepsilon_k (GF_k^3 - 1)} \quad (6)$$

where ξ'_w is the ratio of water uptake by mixed particles to that by inorganic and organic components. GF is the hygroscopic growth factor of the mixture, GF_k is the hygroscopic growth factor of pure component k , ε_k is the volume fraction of pure component k in the dry mixture. In fact when $\xi'_w = 1$, Eq. (6) is equivalent to the ZSR relation, Eq. (3). This indicates that there are no interactions between components or that the interactions have no influence on the hygroscopicity of the mixed particle.

2. Results and discussion

2.1. Multicomponent organic mixture

The hygroscopic growth of 100 nm mixed organic particles (MIXORG) containing four kinds of WSOs is shown in Fig. 2.

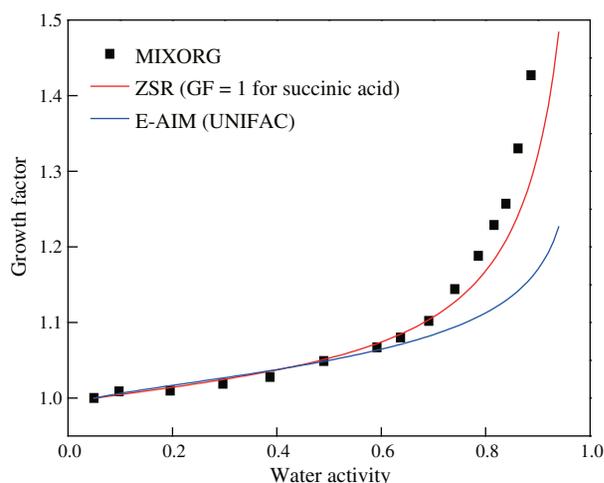


Fig. 2 – Water uptake for MIXORG particles consisting of levoglucosan, succinic acid, phthalic acid and humic acid at equal mass ratio. The red and blue lines represent the hygroscopic growth of the mixture predicted by the ZSR relation and E-AIM, respectively. $GF = 1$ for succinic acid was used in the ZSR relation. ZSR: Zdanovskii–Stokes–Robinson; E-AIM: Extended-Aerosol Inorganics Model; GF: growth factor.

The mixed particles showed a certain amount of hygroscopic growth starting at low RH, and the GFs gradually increased with increasing RH. The smooth hygroscopic curve indicated that no deliquescence transition occurred during humidification. The measured growth factor at 60%, 80%, and 90% RH was 1.07, 1.19, and 1.43, respectively. The growth factors of MIXORG increased slowly from 5% to 70% RH. As the RH was above 70%, the MIXORG particles absorbed more water and the growth factors increased substantially in the high humidity range. The hygroscopic curve predicted by the ZSR relation showed excellent agreement with measured GFs below 70% RH, while at higher humidity the predictions obviously underestimated the water uptake of the organic mixture. The deviations between predictions by E-AIM and measured GFs were more significant at high RH. One possible reason is that the water uptake by other components in mixed particles at high RH may lead to partial dissolution of succinic acid, which could take part in the hygroscopicity and thus enhance the water uptake ability of the mixture. Svenningsson et al. (2006) also found that the ZSR relation underestimated the hygroscopic growth of mixed particles composed of levoglucosan, succinic acid and fulvic acid without taking the dissolution of succinic acid into consideration.

2.2. AS/organic mixture

The multicomponent organic solution (MIXORG) containing equal mass levoglucosan, succinic acid, phthalic acid and humic acids was mixed with AS at varying mass ratios. The hygroscopic growth of AS/MIXORG mixed particles is given in Fig. 3. Those mixed particles exhibited obvious differences in water uptake behaviors with changes in composition. The experimental values for three mixtures were compared with two model predictions. When the mass fraction of organics was 25%, the particles seldom absorbed water, and the GFs approximated to 1 from 5% to 70% RH. When the RH was above 78%, this mixture obviously deliquesced and the hygroscopic growth factor increased rapidly. The hygroscopic behavior was described well by E-AIM over the whole range of RH. The ZSR predictions were also consistent with measured GFs after full deliquescence. With organic composition increasing to 50%, the particle size increased slightly below 70% RH. After that the mixture kept taking up water and totally deliquesced at 75% RH. The deliquescence point of mixed particles shifted to a lower value, 75% RH, compared to 78% RH for the mixture containing 25% MIXORG. The ZSR method could reproduce the measurement results at high RH, while E-AIM slightly underestimated the hygroscopic growth of mixed particles. In the case of organic content up to 75%, the mixed particles showed continuous hygroscopic growth without significant phase transition in the RH range. It was obvious that both ZSR and E-AIM significantly underestimated the water uptake of mixed particles over a wide RH range.

Zardini et al. (2008) measured the water uptake behavior of internally mixed particles consisting of AS and carboxylic acids (citric acid, glutaric acid, adipic acid) in parallel with a HTDMA and an electrodynamic balance (EDB). Their results showed that the water uptake of mixtures could be well described by the ZSR relation as long as the mixed particles, such as AS-citric acid and AS-glutaric acid systems, were

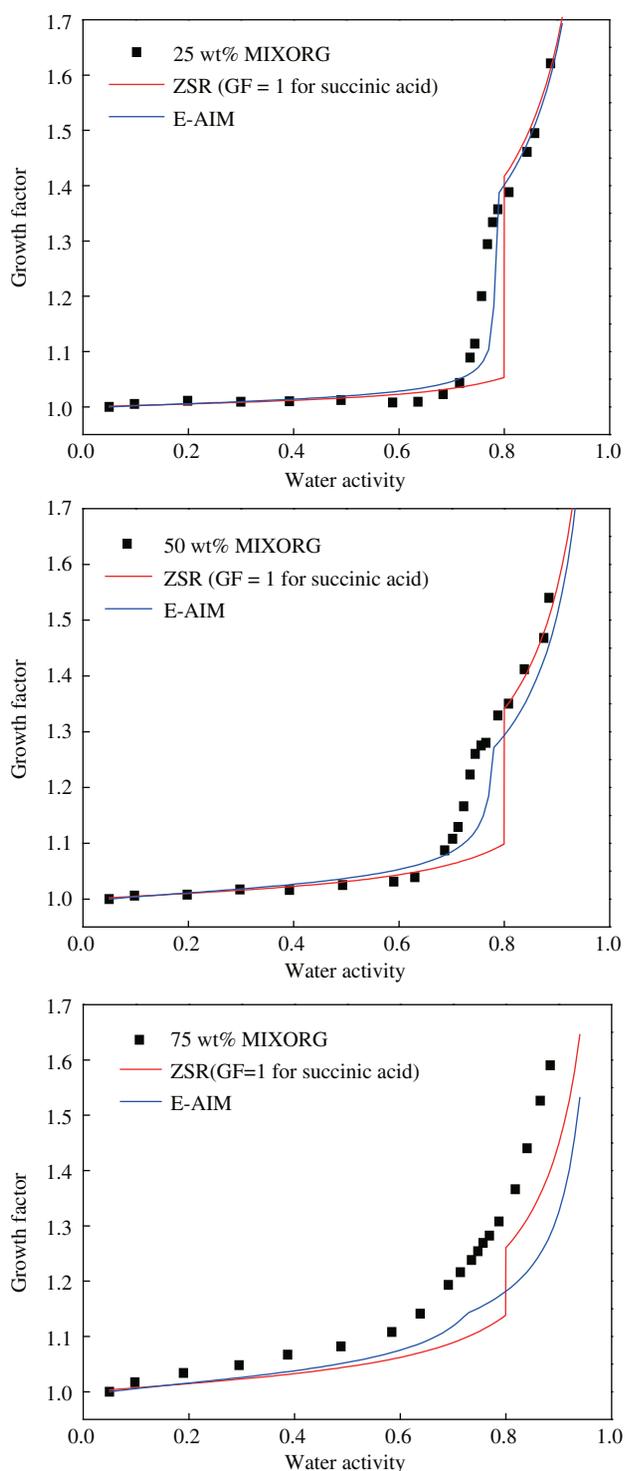


Fig. 3 – Water uptake for mixtures containing MIXORG and ammonium sulfate at 1:3, 1:1, 3:1 MIXORG/AS mass mixing ratios. The red and blue lines represent the hygroscopic growth predicted by the ZSR relation and E-AIM, respectively. GF = 1 for succinic acid was used in the ZSR relation. AS: ammonium sulfate; ZSR: Zdanovskii–Stokes–Robinson; E-AIM: Extended-Aerosol Inorganics Model; GF: growth factor.

completely liquid. Otherwise the measured values could deviate considerably when a solid component was present. For the 1:3 AS/MIXORG mixture, the enhancement of water uptake at low RH may be caused by the partial dissolution of AS. After full deliquescence of AS in the mixed particles, the reason for enhancement of water uptake was complex. Sjogren et al. (2007) investigated the hygroscopic growth of aerosol particles containing adipic acid and AS. They found that the GFs of AS/adipic acid particles with mass ratios of 1:2 and 1:3 were higher than ZSR predictions, which could be attributed to a morphology effect resulting in a negative Kelvin effect. They used SEM images to analyze the morphology of mixed particles and observed cracks, pores and veins between them, which may promote the formation of a concave meniscus, leading to more water condensation. Considering that succinic acid may remain solid even at 90% RH, the morphology effect on the hygroscopic growth of 1:3 AS/MIXORG mixed particles cannot be ruled out. Another possible reason is that succinic acid was partially dissolved in the droplets at high RH and thus contributed to water uptake, which could also explain the discrepancy between measured GFs and model predictions. Svenningsson et al. (2006) found that the hygroscopic growth of organic mixtures composed of levoglucosan, succinic acid and fulvic acid was in good agreement with the ZSR-predicted curve when the limited solubility of succinic acid was incorporated into the predictions. In the case of mixed particles with MIXORG not larger than 50%, the model predictions are in agreement with the measurements. It should be noted that the mass fractions of succinic acid in such mixtures are about 6% and 12%, respectively. Due to the minor amount of succinic acid, the water uptake from succinic acid may not contribute significantly to the hygroscopic growth of mixed particles. Another possible reason is that the partial dissolution of succinic acid is suppressed when the inorganic salt content is dominant in the mixtures. Prenni et al. (2003) also found that the hygroscopic growth of AS/succinic acid mixtures could be well predicted by the ZSR method, assuming GF = 1 for succinic acid when AS content was larger than 50% mass fraction.

2.3. Sodium chloride/organic mixture

Fig. 4 shows the hygroscopic growth of 100 nm aerosol particles containing sodium chloride and MIXORG at three different mass ratios. The difference between the three systems was obvious. When the mass fraction of organics was 25%, the particles almost did not absorb water before 60% RH and the growth factors were nearly 1. The measured hygroscopic growth was in good agreement with E-AIM predictions. However, the deliquescence point predicted by E-AIM was higher than the measurement result (70% RH). The water uptake predicted by the ZSR relation approached the measurements below and above the deliquescence point. As the proportion of organics in the mixture increased to 50%, the particles also took up very little water from 5% to 70% RH. After the complete deliquescence of NaCl, the GFs reached 1.43 and the particle size started to increase rapidly. The E-AIM underestimated the water uptake in the RH range of 60%–75%, and the predicted DRH was higher than the measured value for 70% RH. However, the hygroscopic growth

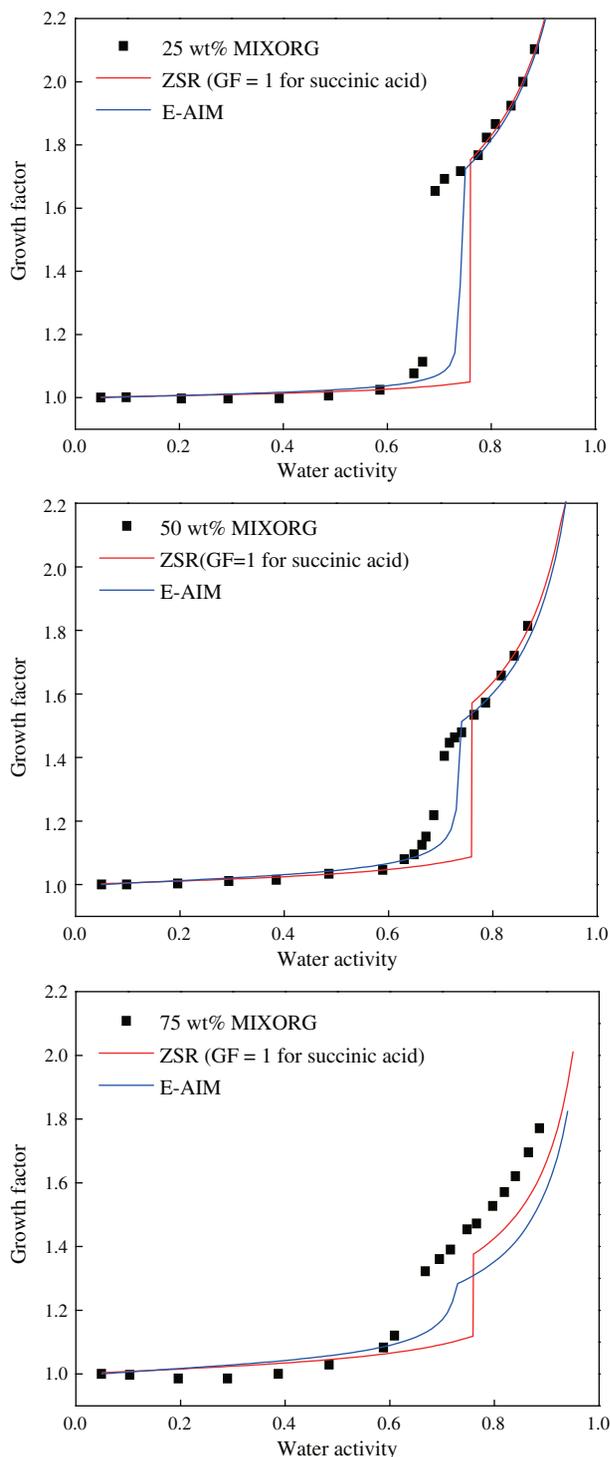


Fig. 4 – Water uptake for mixtures containing MIXORG and sodium chloride at 1:3, 1:1, 3:1 MIXORG/NaCl mass mixing ratios. The red and blue lines represent the hygroscopic growth predicted by the ZSR relation and E-AIM, respectively. GF = 1 for succinic acid was used in the ZSR relation. ZSR: Zdanovskii–Stokes–Robinson; E-AIM: Extended-Aerosol Inorganics Model GF: growth factor.

predicted by ZSR was consistent with measurements below 60% RH and after full deliquescence. When the organic content reached 75%, the mixed particle appeared to completely

deliquesce around 68% RH, much lower than the E-AIM predicted value. The GFs slightly decreased to lower than 1 below 40% RH, which may be explained by microstructural rearrangement (Mikhailov et al., 2004). Both the models underestimated the hygroscopic growth of this mixture above 60% RH. With the organic content at 50% and 75%, the corresponding GFs of particles were 1.57 and 1.53 at 80% RH, respectively. This indicated that with increasing mass fraction of organics, the GFs of NaCl/MIXORG mixed particles would not decline obviously at high RH. The reason for the enhanced water uptake of the 1:3 NaCl/MIXORG mixture may be the same as for the AS/MIXORG mixture.

2.4. Evaluating the effects of the organic mixture on the hygroscopicity of inorganic salt

The experimental result showed that the measured hygroscopic curve for mixed particles showed deviation from theoretical models. This suggested that interactions between the components had an influence on the water uptake behaviors of the aerosol particles. To quantify the influence of interactions between components on the hygroscopicity of mixed aerosol particles, Eq. (6) was used to calculate the ξ_w at different RH after full deliquescence of AS or NaCl, as shown in Fig. 5. ξ_w of aerosol particles containing MIXORG was always over 1 after 80% RH, indicating that the interactions between components could promote the water uptake of mixtures, especially at high RH. For mixed aerosol particles containing MIXORG with AS or NaCl, when the mass fraction of MIXORG was 75%, ξ_w was significantly greater than 1 and had positive correlation with RH. As for the 1:3 MIXORG/AS mixture, ξ_w was below 1 at 90% RH. And ξ_w fluctuated up or down around 1 for the 1:1 mass ratio. The mixtures consisting of MIXORG and NaCl exhibited an inverse tendency. The interactions between MIXORG and inorganic salts are related to the type of salts, also confirmed by Chan and Chan (2003).

Choi and Chan (2002) used an EDB to study the influence of malonic acid, succinic acid, glutaric acid and citric acid on the hygroscopic behaviors of inorganic aerosols (AS or NaCl). They found that the GFs of mixed particles were smaller than those of pure inorganic components. Compared with pure salts, the presence of those organic acids could reduce the water uptake of NaCl, but increase that of AS. Pope et al. (2010) used an EDB to study the hygroscopicity of internally mixed particles containing dicarboxylic acid (malonic acid or glutaric acid) with NaCl. The results showed that the mass growth factors of mixtures depended on the mole fraction of each component.

3. Conclusions and atmospheric implications

The hygroscopic growth of multicomponent WSOCs and their influence on the water uptake behaviors of inorganic salts (AS, NaCl) were determined using the HTDMA technique. It was found that the organic content played an important role in the water uptake of mixed particles. When the organic content was dominant in the mixture (75%), the measured hygroscopic growth was higher than predictions from E-AIM or the ZSR relation.

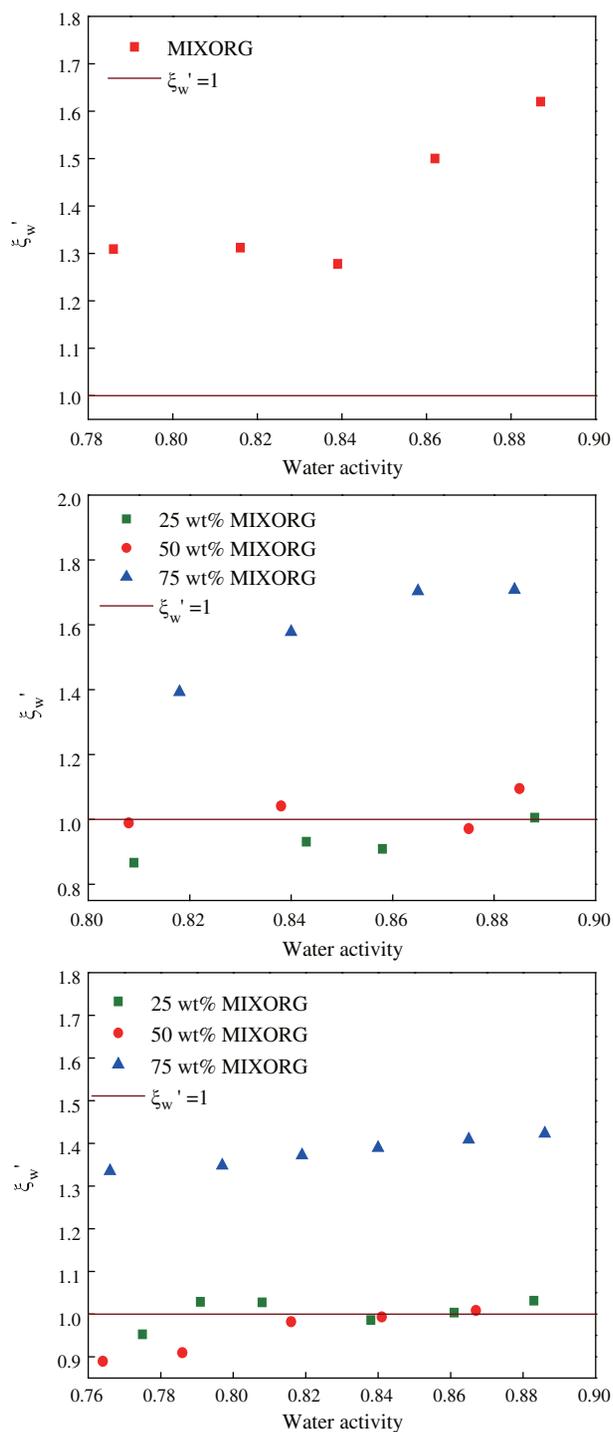


Fig. 5 – ξ_w' for mixtures including MIXORG, MIXORG/AS, and MIXORG/NaCl as a function of water activity. The green boxes, red circles and blue triangles represent the mass fraction of MIXORG in the mixed particles, respectively. AS: ammonium sulfate.

It is difficult to accurately predict the hygroscopicity of multicomponent WSOCs at high humidity by thermodynamic models when a solid component is present over a wide RH range. One possible reason is that the interaction between organics can promote the partial dissolution of the solid

component, thus resulting in more water uptake at high RH. For the particles composed of organics and inorganic salts, the water uptake behavior can be affected by the organic content. When the mass fraction of organics is not higher than 50%, the hygroscopic growth of the mixture is in good agreement with model predictions. In addition, the influence of the interaction between inorganic and organic species on the hygroscopicity of mixed particles is related to the salt type and organic content.

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