



Hygroscopicity of internally mixed multi-component aerosol particles of atmospheric relevance



Qifan Liu^{a,1}, Bo Jing^{a,b,1}, Chao Peng^{a,1}, Shengrui Tong^a, Weigang Wang^a, Maofa Ge^{a,*}

^a 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

^b The Institute of Chemical Physics, Key Laboratory of Cluster Science, Beijing Institute of Technology, Beijing 100081, China

HIGHLIGHTS

- We report the hygroscopicity of multi-component particles related to haze pollution.
- The measurement results are compared with thermodynamic model predictions.
- Coexisting species strongly affect the phase behaviors of NH_4NO_3 in dry particles.
- The phase of NH_4NO_3 in dry particles notably affects the hygroscopicity of mixtures.
- The potential inorganic–organic interactions at high RH conditions are analyzed.

ARTICLE INFO

Article history:

Received 22 May 2015

Received in revised form 30 October 2015

Accepted 2 November 2015

Available online 6 November 2015

Keywords:

Hygroscopicity

H-TDMA

Phthalic acid

Levoglucosan

Multi-component aerosol particles

ABSTRACT

The hygroscopic properties of two water-soluble organic compounds (WSOCs) relevant to urban haze pollution (phthalic acid and levoglucosan) and their internally mixtures with inorganic salts (ammonium sulfate and ammonium nitrate) are investigated using a hygroscopicity tandem differential mobility analyzer (H-TDMA) system. The multi-component particles uptake water gradually in the range 5–90% relative humidity (RH). The experimental results are compared with the thermodynamic model predictions. For most mixtures, Extended Aerosol Inorganic Model (E-AIM) predictions agree well with the measured growth factors. The hygroscopic growth of mixed particles can be well described by the Zdanovskii–Stokes–Robinson (ZSR) relation as long as the mixed particles are completely liquid. ZSR calculations underestimate the water uptake of mixed particles at moderate RH due to the partial dissolution of ammonium sulfate in the organic and ammonium nitrate solution in this RH region. The phase of ammonium nitrate in the initial dry particles changes dramatically with the composition of mixtures. The presence of organics in the mixed particles can inhibit the crystallization of ammonium nitrate during the drying process and results in water uptake at low RH (RH < 60%). These results demonstrate that certain representative WSOCs can substantially influence the hygroscopicity of inorganic salts and overall water uptake of particles.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Hygroscopicity, one of the most important characteristics of aerosol particles, can cause considerable atmospheric issues including air quality, health effects and climate change (Pöschl, 2005). Therefore, researchers pay much attention on the inter-

actions between water vapor and aerosol particles. Atmospheric aerosols consist of a great number of organics as well as inorganic species. The major inorganic components of atmospheric aerosols are relatively well understood and are thought to make a main contribution to the water uptake by aerosols. The hygroscopic behaviors of these inorganic salts, such as ammonium sulfate (AS) and ammonium nitrate (AN), have been characterized by many groups (Gysel et al., 2002; Mikhailov et al., 2004). As for the organics, the detailed composition remains largely uncertain due to the lack of quantitative and qualitative information on the chemical constituent. But it has been recognized that a large fraction of organic aerosol is water-soluble

* Corresponding author.

E-mail address: gemaofa@icc.ac.cn (M. Ge).

¹ These authors contributed equally to this work.

(Zappoli et al., 1999; Choi and Chan, 2002), indicating that organic species may also play a role in the hygroscopic growth of aerosol particles. Furthermore, organics are typically found to be internally mixed with inorganic components (Lee et al., 2002; Murphy et al., 2006), and may therefore have impact on the hygroscopic property of inorganic fraction (Cruz and Pandis, 2000; Zardini et al., 2008).

Many studies suggest that organics have significant influence on the hygroscopic behaviors of inorganic species. For example, Brooks et al. (2002) investigated the hygroscopicity of mixtures composed of AS and organic acids, they found that the presence of water-soluble dicarboxylic acids (such as malonic acid and maleic acid) could result in a lower deliquescence relative humidity (DRH) compared to the pure AS. Shi et al. (2012) showed that the internally mixed AS + benzoic acid particles displayed a decrease in growth factor at 80% RH with increasing organic mass fraction. Most of these studies focus on the water uptake of mixtures consisting of one inorganic salt and one model organic compound, few work have investigated the hygroscopicity of multi-component aerosols (Marcolli et al., 2004; Svenningsson et al., 2006; Zamora and Jacobson, 2013), more research is necessary to better understand this issue. Moreover, these experimental results indicate that the interactions between the inorganic and organic compounds are complex, investigating their influence on the water uptake of inorganic–organic mixed particles is an ongoing research.

Recently, there is a growing concern about haze pollution in China due to its links to adverse health effects, visibility reduction and ecosystem disruption (Liu et al., 2013). Secondary inorganic aerosols, mainly composed of AS and AN, are considered to play a vital role during the haze evolution. Huang et al. (2014) reported that AS and AN were important contributors to the urban PM_{2.5} (fine particulate matter diameter less than 2.5 μm) mass in cities such as Beijing, Shanghai and Guangzhou, they accounted for 20–42% of total PM_{2.5} mass during the haze events. Based on the chemical analyses for PM_{2.5} during a polluted period in Beijing, the mass fractions of sulfate, nitrate and ammonium were measured to be 23–26%, 12–27% and 13–14%, respectively (Guo et al., 2014). Organic matters also contribute greatly to the haze pollution. Phthalic acid (PA), a secondary product derived from photo-oxidation of precursors such as xylene, toluene and other anthropogenic contaminants (Seinfeld and Pankow, 2003), has been shown to exist in the urban particulate matter (Wang et al., 2011a). The estimated secondary organic aerosol mass was found to be well correlated with PA concentration in the fine particles during a smog episode in California (Schauer et al., 2002). Cheng et al. (2013) found PA concentration in the haze episode was much higher than that in the clean periods in Xi'an, implying that anthropogenic emissions of pollutants make an important contribution to the haze formation. Biomass burning emission is another factor that influences the haze pollution. For example, levoglucosan (LG), an organic tracer for straw burning smokes, was reported to be the most abundant species among the measured WSOCs during a severe urban haze event in Nanjing (Wang et al., 2011b). To our knowledge, the water uptake of multi-component particles containing these four representative substances (AS, AN, PA and LG) that related to urban pollution with varying organic mass fractions has not been well-characterized in earlier studies.

In this work, the hygroscopic behaviors of internally mixed particles composed of AS and AN as inorganic component and either PA or LG as organic component are investigated in the 5–90% RH using the H-TDMA technique. E-AIM and ZSR approach are used to predict the water uptake behaviors of aerosol particles. The effect of organic–inorganic interactions on the hygroscopic growth of multi-component particles is also analyzed.

2. Experimental

2.1. H-TDMA instrument

The experimental setup has been fully described before (Lei et al., 2014), which consists of three main parts: (1) an aerosol generator, (2) a relative humidity control section, (3) a particle sizing and humidification system. Here is a brief description. The solutions were prepared by mixing chemical compounds with ultra-pure water (typically 1 g/L) and all solutes appeared to be completely dissolved at visual inspection. Aerosol particles generated by an atomizer, were dried to RH < 5% through silica gel diffusion dryers. The dry particles were subsequently brought to charge and then flowed into the first differential mobility analyzer (DMA1), which selected quasi-monodisperse aerosols of the desired dry diameter (~100 nm). The size-selected particles then entered into the humidification tubes (~5 s residence time), where RH could be regulated in the range 5–90% RH. After equilibration at a set RH, the particle size distribution of humidified aerosols was measured by the second DMA (DMA2) combining with a condensation particle counter (CPC, Model 1500, MSP). All experiments were performed in the laboratory and the room temperature was air-conditioned to be 298 ± 1 K. The physical properties of the chemical used in this study are shown in Table 1.

2.2. Data evaluation and modeling methods

The hygroscopic growth factor (GF) is typically defined as the ratio of the humidified particle diameter (D_p) at a specific RH to the initial particle diameter (D_0) measured by DMA2 at dry conditions (RH ~ 5%). To minimize the effect of droplet curvature, we convert RH to water activity (a_w). The Köhler equation can be used to describe the relationship between a_w and RH at equilibrium:

$$\text{RH}/100\% = a_w \times K_e \quad (1)$$

$$K_e = \exp\left(\frac{4\sigma_{\text{sol}}M_w}{RT\rho_w D_p}\right) \quad (2)$$

where K_e is the Kelvin correction factor, M_w is the molar mass of water, σ_{sol} is the surface tension of the solution (assuming $\sigma_{\text{sol}} = \sigma_{\text{water}}$), ρ_w is the density of pure water, R is the universal gas constant and T is the temperature. Using an expression proposed by Kreidenweis et al. (2005), we can obtain a hygroscopic growth curve for an individual compound:

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

ZSR method and E-AIM model are used to predict the hygroscopic growth of the mixed particles at different RH. According to the ZSR method, GF of a mixture (GF_{mix}) can be calculated using the following equation (Malm and Kreidenweis, 1997):

$$\text{GF}_{\text{mix}} = \left[\sum_i \varepsilon_i (\text{GF}_i)^3\right]^{1/3} \quad (4)$$

where GF_i is the growth factor of the pure component i and ε_i is its respective volume fraction in the mixture. Assuming that the volume remains unchanged after compounds are mixed, ε_i can be

Download English Version:

<https://daneshyari.com/en/article/6337229>

Download Persian Version:

<https://daneshyari.com/article/6337229>

[Daneshyari.com](https://daneshyari.com)