



Investigation of gel formation and volatilization of acetate acid in magnesium acetate droplets by the optical tweezers

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ABSTRACT

Hygroscopicity and volatility of single magnesium acetate (MgAc_2) aerosol particles at various relative humidities (RHs) are studied by a single-beam optical tweezers, and refractive indices (RIs) and morphology are characterized by cavity enhanced Raman spectroscopy. Gel formation and volatilization of acetate acid (HAc) in MgAc_2 droplets are observed. Due to the formation of amorphous gel structure, water transposition in droplets at $\text{RH} < 50\%$ is significantly impeded on a time scale of 140,000 s. Different phase transition at $\text{RH} < 10\%$ is proposed to explain the distinct water loss after the gel formation. To compare volatilization of HAc in different systems, MgAc_2 and sodium acetate (NaAc) droplets are maintained at several different stable RHs during up to 86,000 s. At $\text{RH} \approx 74\%$, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) inclusions are formed in MgAc_2 droplets due to the volatilization of HAc, and whispering gallery modes (WGMs) of MgAc_2 droplets in the Raman spectrum quench after 50,000 s. In sharp contrast, after 86,000 s at $\text{RH} \approx 70\%$, NaAc droplets are in well-mixed liquid states, containing soluble sodium hydroxide (NaOH). At this state, the RI of NaAc droplet is increased, and the quenching of WGMs is not observable.

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1. Introduction

Atmospheric aerosols are ubiquitous and play an important role in climate and atmospheric chemistry [1]. The specific effect of the aerosol on these processes depends on its size, chemical composition, phase and physics or chemistry properties [2]. Aerosols generally contain both organic components and inorganic components such as sulfates, nitrates and ammonium [3]. Organic material accounts for 20% to 50% in total fine aerosol mass at continental mid-latitudes and for as much as 90% in tropical forested areas [1,4]. Although large uncertainty remains concerning the detailed composition, it is now recognized that 20–70% of the total particulate carbon in the atmosphere is water soluble [5], incorporating organic components in thermodynamic models remain challenging. At the same time, the organic fraction can have a profound effect on the light scattering, hygroscopicity, and phase transition properties of multicomponent atmospheric aerosols [6].

Magnesium compounds play an important role in different processes including industrial chemistry and biology [7], and their salts are ubiquitously present in atmospheric aerosols [8]. The acetate ion occurs widely in nature, for instance, being produced by microorganisms and by decomposition of humic acids [9]. Different from many atmospheric hygroscopic aerosols, which are expected to quickly equilibrate with the environment in the water evaporation and condensation

processes, magnesium acetate (MgAc_2 , where Ac is the conjugate base of acetate acid) droplets are found to exhibit a significant delay in water evaporation at high concentrations [10], which is similar with magnesium sulfate aerosol [11]. The changing of MgAc_2 droplets' size in the humidifying process shows significant mass transfer limitations at $\text{RH} < 50\%$. Limitations of mass transport and charge effect may also induce the formation of porous structures and irregular envelope shape [12].

The hygroscopicity of aerosols has received considerable attention [13–16]. It is an important property of aerosols with implications for climate, as it is directly related to the ability of aerosol particles to serve as cloud condensation nuclei (CCN). Through changing the environmental relative humidity (RH), the solution concentration in aqueous aerosol particles will affect the physical and chemical properties of aerosols, e.g., the sizes, radiative properties, and chemical reaction [17]. In the atmosphere, many aerosol particles with soluble inorganic components show properties of deliquescence, efflorescence and hygroscopic growth. Inorganic aerosols and soluble atmospheric organics may also present such properties in humidifying/dehumidifying processes. Although the hygroscopicity of inorganic components is well studied and modeled [18–20], the hygroscopic properties of organics aerosol are not as well known as that of the inorganic parts.

The equilibrium partitioning of organic compounds between the gas and condensed phases in atmospheric aerosols governs particle size distributions and compositions, and can impact heterogeneous reaction rates, optical extinction cross-sections and the efficiencies of aerosol

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particles as CCN [21,22]. Understanding the mechanism of HAC volatilization from micron-sized acetates droplets such as MgAc_2 and sodium acetate (NaAc) in the atmosphere is important to predict cloud droplet growth rates and to determine the effect of aerosol composition on cloud properties [23–27].

There have been many technologies used to study the hygroscopic properties of aerosols. Raman spectroscopy [10,11,28,29] as well as Fourier transform infrared (FTIR) spectroscopy [30,31] have been frequently used and provided the vast majority of data on the physical and chemical properties of typical aerosols. More recently, optical techniques have been used to monitor particles mounted on hydrophobic or hydrophilic substrates in whole relative humidity range [15,32–34]. Single particle studies, while require care in extrapolating to the ensemble level, can bridge the gap between aerosol ensembles and bulk/surface properties [35,36]. The use of optical force to sort and separate particles of different refractive indices (RIs) and sizes has also attracted increasing interest [37,38]. A fine example of the ingenuity within this field is the technique referred to as aerosol optical tweezers (AOTs). Reid and co-workers provide how to apply AOTs coupled with Raman spectroscopy to investigate the levitated droplets and to simulate the atmospheric environment [39]. Studies on single particles by using AOTs provide precise measurements of aerosol RIs, hygroscopic growth, evaporation of semi-volatile components and other important atmospheric properties of the aerosol droplets. In the meantime, this method can also provide the information of the size changing of aerosol droplets in nanoscale with a time-resolution of <1 s [40]. When interacts with light, the spherical micro droplet trapped by aerosol optical tweezers acts as a microscopic optical cavity, in which total internal reflection of discrete wavelengths of beam occurs at the boundary between the outer circumference and the surrounding medium, forming circulating standing waves inside the cavity with a path length of an integral numbers of wavelength. This phenomenon is termed as whispering gallery mode (WGM) [41]. Pan and co-workers showed a universal optical trap combined with Raman spectroscopy (RS) and microscopy imaging for single-particle studies. This integrated OT-RS system provides a new approach to concurrently characterize and monitor physical and chemical properties of single micrometer-sized objects optically trapped in air [42]. They also observed the entire temporal evolution process of fluorescence and Raman spectra of single solid particles optically trapped in air [43].

In this paper, the aerosol optical tweezers technique is employed to study the hygroscopicity of MgAc_2 droplets at various RHs, especially after the gel-state formation. In addition, we maintain MgAc_2 and NaAc droplets at various stable RH conditions for up to 86,000 s to observe how the acetate acid (HAC) volatilizes from different acetate salts particles.

2. Experimental Methods

A detailed introduction to aerosol optical tweezers and the experimental approach has been described elsewhere [44–46] and only a brief outline of the experiments is given below. The trapping beam from a 532 nm laser (Opus 4 W + mpc6000 power supply) first passes through two sets of beam expansion optics. After that the beam is reflected from a dichroic mirror and then from a 50:50 beam splitter onto the back aperture of the microscope objective. Backscattered light from the trapped particle passes through the 50:50 beam splitter before reaching a long pass filter positioned in front of spectrograph. With the adding of long pass filter, only the scattering at long wavelength is allowed to pass and imaged onto the entrance slit of a 0.5 m spectrograph (diffraction grating blazed at 640 nm with 1200 g/mm, Omni- λ 5006) coupling with a CCD (iDus DV420A-BV) for recording a dispersed Raman spectrum with a spectral resolution of 0.04 nm. The bright field images of the droplet are obtained with the same microscope objective of trapping. The additional illumination is achieved by positioning a blue LED with 455 nm wavelength above the sample cell

and the light was focused into the cell using a Plano-convex lens with 10 cm focal lengths. Half portion of the visible blue light transmits through the 50:50 beam splitter and the same dichroic filter of incident beam reflection and is finally identified by a CCD camera (Watec, 1/3 in., model 231S2).

The $0.5 \text{ mol} \cdot \text{L}^{-1}$ MgAc_2 and NaAc solution are prepared from crystal produces of MgAc_2 and NaAc crystal and triply distilled water without further purification. The solutions' RIs are measured by WYA-2S Abel refractometer. An ultrasonic medical nebulizer (Yuyue 402AI model) is used to generate aerosols which have typical sizes between 3 and 6 μm . Aerosols are delivered by the air flow to the sample cell through a custom-made nozzle. The droplet is trapped in an aerosol cell, which is fabricated from stainless steel with a volume of 7 cm^3 . The RH in the cell is controlled by varying the flow rate mixing one steam of dry nitrogen through a bubbler containing triply distilled water and one of dry nitrogen and monitored at an interval of 10 s by humidity temperature meter (Cemtertek Center 310) with accuracies of $\pm 2.5\%$ RH and ± 0.7 °C. The total flow rate up to 0.1 L/min is used to investigate the hygroscopicity of a MgAc_2 droplet, and 0.3 L/min is used to study volatilization of HAC in MgAc_2 and NaAc droplets.

The changing spectra of the droplet are monitored in real time with a time-resolution of 1 s. The spontaneous Raman spectrum provides a signature of the composition of the droplet. The stimulated Raman spectrum, occurring at wavelengths commensurate with WGM, is used to characterize the size of droplet. The wavelengths of the WGM are dependent on the size and refractive index of the droplet and by comparing these wavelengths with predictions from the Mie scattering theory, the droplet size can be determined with 10 nm accuracies.

3. Results and Discussion

3.1. The Gel Formation of Magnesium Acetate Droplets

As shown in Fig. 1, by comparing the wavelengths of WGMs with predictions from the Mie scattering theory [47], the radius of a MgAc_2 droplet held in the optical tweezers as the effect of changing RH can be observed. The droplet goes through a number of rapidly changing RH steps until the readings from the precell RH probe reaches to 4%. The droplet is allowed to equilibrate at every RH step for 3 h. Within the dehumidifying process with $\text{RH} > 50\%$ in Fig. 1a, the changes in radius at every RH step have the tendency to equilibrate with the changes in RH, suggesting that there is no mass transport limitation in the water evaporation process of MgAc_2 droplets at $\text{RH} > 50\%$. When the RH is decreased below 50% at which the gel state forms, there is a significant slowing in the size change, extending beyond the timescale of the RH change. These observations are in agreement with previous studies [10]. The shaded area in Fig. 1a denotes the time during which the droplet is in the gel state, and water transport is consistently impeded within this time period. Generally, in the gel state, the droplet size responds very slowly to the RH changes and never appears to approach the equilibrium state at a certain RH.

As shown in Fig. 1b, which is an expanded view of Fig. 1a, similar magnitudes of RH changes ($\text{RH} < 50\%$) were applied in water evaporation and condensation and the size changes recorded during water condensation steps are consistently less than those recorded during the evaporation steps, indicating that water transport is kinetically hindered. This is in line with the previous measurements for amorphous aerosols, that is, the hysteresis in size is observed on evaporation/condensation cycles [48].

It is interesting that in the dehumidifying process, considerable water is retained within the particle even at 25% RH, with slow but substantial decreasing in size, as shown in Fig. 1b. In general, Mg^{2+} has a strong tendency to retain its hexahydrated structure because of its high hydration energy in aqueous solutions [49–51]. In previous work, the formation of the bidentate contact-ion pairs between Mg^{2+} and CH_3COO^- was found starting at the molar water-to-solute ratio (WSR)

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