



Contents lists available at ScienceDirect

## Journal of Aerosol Science

journal homepage: [www.elsevier.com/locate/jaerosci](http://www.elsevier.com/locate/jaerosci)

# Morphological effects on the hygroscopic properties of sodium chloride–sodium sulfate aerosols



Joshua P. Darr\*, Shannon Q. Davis, Yohei Kohno, Kevin McKenna, Paul Morales

University of Nebraska at Omaha, Department of Chemistry, 6001 Dodge St., DSC 337 Omaha, Nebraska 68182, USA

## ARTICLE INFO

## Article history:

Received 8 June 2014

Received in revised form

8 August 2014

Accepted 8 August 2014

Available online 19 August 2014

## Keywords:

Morphology

Hygroscopicity

Sodium chloride aerosol

Sodium sulfate aerosol

Infrared spectroscopy

Metastable phase

## ABSTRACT

The hygroscopic properties of sodium sulfate,  $\text{Na}_2\text{SO}_4$ ; sodium chloride,  $\text{NaCl}$ ; and their mixed aerosols are monitored using a flow-cell apparatus and Fourier-transform infrared spectroscopy. While  $\text{Na}_2\text{SO}_4$  exhibits the typical water uptake for an inorganic salt, spectra of  $\text{NaCl}$  and mixed  $\text{NaCl}$ – $\text{Na}_2\text{SO}_4$  aerosols reveal water content below the deliquescence relative humidity. This is explained on the basis of two different morphologies for  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$ . While  $\text{Na}_2\text{SO}_4$  can be described by a simple crystalline solid,  $\text{NaCl}$  contains pockets that trap water. The  $\text{NaCl}$ – $\text{Na}_2\text{SO}_4$  mixtures contain a combination of these two structural motifs, weighted by the relative amounts of the  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  components. This makes  $\text{NaCl}$ – $\text{Na}_2\text{SO}_4$  mixtures an interesting candidate for exploring the effects of morphology on atmospherically relevant properties in a systematic fashion. Additionally, the formation of metastable  $\text{Na}_2\text{SO}_4$  (III) is confirmed using Raman spectroscopy, though its effects on the hygroscopicity of  $\text{NaCl}$ – $\text{Na}_2\text{SO}_4$  mixtures are believed to be minimal.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Atmospheric aerosols have important implications for climate, particularly as they affect Earth's radiative balance (Seinfeld & Pandis, 2006). Despite this, many of their physical and chemical properties are not well understood. Some of the largest uncertainty in climate modeling, for instance, is attributed to the effects of aerosols (Randall et al., 2007). One important property of aerosols that can be monitored relatively easily is their hygroscopicity. The hygroscopicity of aerosols, or their propensity to absorb water, is important because as aerosols absorb water, they can undergo a phase change from a solid to a solution (Martin, 2000). This phase change will potentially change both their optical properties and chemical reactivity (Cwiertny et al., 2008; Finlayson-Pitts, 2003), each of which has important ramifications for climate modeling.

Laboratory studies on the hygroscopicity of many single-component inorganic salts have been reported (Martin, 2000). In the atmosphere, however, aerosols are a complicated mixture of multiple components. It is important, therefore, to extend our understanding beyond the idealized single-component case to instances when multiple components are present. We do that in this work by reporting the hygroscopic properties of mixed sodium chloride–sodium sulfate ( $\text{NaCl}$ – $\text{Na}_2\text{SO}_4$ ) aerosols. These compounds are atmospherically relevant because inorganic salts such as  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  represent a large portion of the aerosol mass in the troposphere, and  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  are some of the most abundant ions present in sea salts (Seinfeld & Pandis, 2006). Equally important, they also still represent a simple enough system to allow for comparison between experiment and thermodynamic models. For instance, using the Extended Aerosol Inorganic Model website

\* Corresponding author. Tel.: +1 402 554 2653.

E-mail address: [jdarr@unomaha.edu](mailto:jdarr@unomaha.edu) (J.P. Darr).

(E-AIM), <http://www.aim.env.uea.ac.uk/aim/aim.php>, one can readily perform thermodynamic calculations for the NaCl–Na<sub>2</sub>SO<sub>4</sub> system (Clegg et al., 1998).

An aerosol's morphology is important because it affects its hygroscopic properties, which in turn affect both the aerosol's optical properties and its chemical reactivity (Ellison et al., 1999; Garland et al., 2009). Consequently, the potential to systematically vary morphology with prototype aerosols would prove useful. Theoretical work based on experimental evidence suggests that a limited degree of morphological control over aerosol particles can be attained (Leong, 1987). For a single-component inorganic salt, the morphology is usually characterized as a crystalline solid until a specific relative humidity (RH) is reached. Once this RH is reached, the solid absorbs water from the surrounding environment until it is dissolved and becomes a saturated aqueous solution (Seinfeld & Pandis, 2006). However, depending upon both the aerosol composition and the method of aerosol generation, there are exceptions. For example, when NaCl aerosols were generated with an atomizer, a different morphology was reported. Multiple studies performed on NaCl aerosols with infrared (IR) spectroscopy have reported the observation of water at RHs significantly below the deliquescence relative humidity (DRH) (Cziczo & Abbatt, 2000; Cziczo et al., 1997; Weis & Ewing, 1999). These NaCl aerosols were generated using an atomizer and subsequently dried with a diffusion dryer before being analyzed with an IR spectrometer. Using a thorough analysis, as well as Mie theory calculations, Weis and Ewing (1999) characterized the morphology of NaCl as a solid crystal, or perhaps shell, with pockets containing aqueous NaCl solution. Particles containing enclosed water pockets have been reported using other techniques as well (Braun & Krieger, 2001; Cheng et al., 1988). Furthermore, as multiple components are added to the aerosol, this morphology is likely to become more common (Schlenker & Martin, 2005) and other more complex crystalline morphologies with pockets of water are likely to be observed as well. For example, Colberg et al. (2004) observed several different morphologies where complex crystal structures were observed with liquid pockets.

In addition to morphology, another factor that can influence hygroscopicity is the crystal phase. A number of research groups have reported aerosol particles that crystallize into metastable phases that can potentially affect the particle's hygroscopicity (Colberg et al., 2004; Dong et al., 2009; Hoffman et al., 2004; Ling & Chan, 2007, 2008; Rosenoern et al., 2008; Schlenker et al., 2004; Schlenker & Martin, 2005; Tong et al., 2010). For example, Na<sub>2</sub>SO<sub>4</sub> has several different crystal phases that need to be considered. For instance, it can exist as an anhydrous salt or a hydrated crystal. Furthermore, anhydrous Na<sub>2</sub>SO<sub>4</sub> can exist in five different phases (I–V) in the solid state (Oswald et al., 2008; Rodríguez-Navarro et al., 2000; Steiger & Asmussen, 2008). Phase V is the most stable state at room temperature; however, phase III can also be observed following crystallization. The transition from phase III to phase V is slow, but it can be catalyzed in the presence of water (Xu & Schweiger, 1999). The two phases can be clearly distinguished from one another on the basis of their Raman spectra (Choi & Lockwood, 2005), and phase III has been observed in some aerosols (Dong et al., 2009; Tong et al., 2010).

This paper explores the effects of both morphology and crystal phase on the hygroscopic properties of NaCl–Na<sub>2</sub>SO<sub>4</sub> mixtures. There have been some previous reports of the hygroscopicity of NaCl–Na<sub>2</sub>SO<sub>4</sub> mixtures (Tang, 1997; Tang and Munkelwitz, 1994). Tang and Munkelwitz (1994) studied NaCl–Na<sub>2</sub>SO<sub>4</sub> using an electrodynamic balance—a different method than Weis and Ewing—to investigate the hygroscopic properties of particles 6–8 μm in diameter. For an equimolar mixture, Tang (1997) found only a slight decrease of the DRH below that of pure NaCl, from 75.3% to 74.2%, in good agreement with thermodynamic predictions. Here, we use a flow tube apparatus coupled to an IR spectrometer—similar to Weis and Ewing—to investigate the hygroscopicity of NaCl–Na<sub>2</sub>SO<sub>4</sub> at five different relative concentrations, 0%, 33%, 59%, 75%, and 100% mole fraction Na<sub>2</sub>SO<sub>4</sub>. Unlike Tang and co-workers, our results are not in accord with predictions of thermodynamic models. From them, however, we are able to infer morphologies of the NaCl–Na<sub>2</sub>SO<sub>4</sub> particles generated using this method. Furthermore, we propose it as a system which can be used to probe the effects of morphological changes on selected atmospheric properties. Finally, we examine the influence of the metastable phases of Na<sub>2</sub>SO<sub>4</sub> on the hygroscopicity of NaCl–Na<sub>2</sub>SO<sub>4</sub>.

## 2. Experimental methods

### 2.1. Aerosol generation

The apparatus utilized for conducting these experiments is shown in Fig. 1 and is similar to that described by other groups (Miñambres et al., 2008; Weis & Ewing, 1999). In order to generate the aerosols, ≈ 30 psi (210 kPa) of nitrogen gas was supplied to a constant output atomizer containing a 100 g/L aqueous solution of Na<sub>2</sub>SO<sub>4</sub> and NaCl. According to manufacturer specifications, the atomizer produces an output with a lognormal distribution of aerosol particles less than two microns in diameter. The mean diameter and geometric standard deviation are specified as ≈ 0.35 μm and 1.8, respectively.

The hygroscopicity of the aerosols was monitored by mixing them with nitrogen gas with a well-defined RH. The RH was controlled by dividing the nitrogen flow so that some of it was bubbled through water and the rest was kept dry. The two flows were mixed before they were added to the aerosols. The flow in each line was monitored with a flowmeter and controlled with a needle valve in order to achieve the necessary RH, which was monitored at the outlet of the flow cell using a thermohygrometer. This experimental setup allowed us to achieve RH values ranging from 2% for completely dry nitrogen to 90% for only humidified nitrogen. The thermohygrometer was calibrated by placing it in a sealed container with a saturated salt solution which was allowed to equilibrate overnight. To achieve the higher RH values, it was necessary to heat the water in the bubbler to slightly above room temperature, ≈ 35 °C. This was also reported by others (Miñambres et al., 2008, 2010) to increase the range of RH values achievable without changing the temperature at the outlet of the cell

Download English Version:

<https://daneshyari.com/en/article/4452372>

Download Persian Version:

<https://daneshyari.com/article/4452372>

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