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# Water uptake of internally mixed particles containing ammonium sulfate and dicarboxylic acids

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## Abstract

There is increasing evidence that organic compounds comprise a significant fraction of tropospheric particles at all altitudes. The presence of these compounds can affect the particles' ability to take up water and to form ice in the atmosphere. In this paper we present studies that investigate the hygroscopic behavior of internal mixtures of ammonium sulfate and low molecular weight dicarboxylic acids. We find that the ammonium sulfate dominates water uptake behavior for mixtures that contain 100:1 and 10:1 mass ratios of ammonium sulfate:dicarboxylic acid. However, for 1:1 mixtures, the dicarboxylic acids play an important role in determining water uptake characteristics. Observed water contents can be predicted within experimental uncertainties by assuming that each component contributes independently to the total particle water content, in accord with previous measurements for the pure components.

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**Keywords:** Hygroscopic growth; Organics; HTDMA; Deliquescence

## 1. Introduction

Organic compounds are often present in fine particulate matter in the atmosphere (Chow et al., 1994; Novakov and Penner, 1993; Rogge et al., 1993), including aerosol at high altitudes (Murphy et al., 1998). Field studies indicate that 20–70% of condensed-phase organic carbon is water soluble (Facchini et al., 1998; Saxena and Hildemann, 1996). These compounds can have multiple functional groups (Decesari et al., 2000) and may vary in polarity (Blando et al., 1998). Particles containing organics may exhibit vastly different hygroscopic and ice-nucleating behavior than pure inorganic particles, with corresponding implications for visibility and climate. In a previous study, we investigated water uptake and ice formation in particles containing low molecular weight dicarboxylic acids (Prenni et al., 2001). Dicarboxylic acids are

abundant throughout the atmosphere (Kawamura et al., 1996a,b), have low vapor pressures (Makar, 2001; Silva et al., 1999), and are water-soluble (Saxena and Hildemann, 1996), and so they are expected to be present in the aqueous fraction of the condensed phase (Makar, 2001; Saxena and Hildemann, 1996). Here, we extend that study to examine water uptake of low molecular weight dicarboxylic acids internally mixed with ammonium sulfate.

Thermodynamic properties of mixed organic/inorganic particles have been modeled (Clegg et al., 2001; Ming and Russell, 2001). These authors note that there is a need for an improved knowledge of the physical properties of the organic component in the aerosol. Laboratory studies suggest that the presence of organic compounds may alter the deliquescence point (Andrews and Larson, 1993; Lightstone et al., 2000), the rate of deliquescence (Wagner et al., 1996), and the hygroscopic behavior (Chen and Lee, 1999; Hameri et al., 1992; Hansson et al., 1998; Lightstone et al., 2000; Xiong et al., 1998) of inorganic particles. A study in the Great Smoky Mountains (USA) indicated

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excess water increased with increasing mass fraction of organics in particles, implying that the organic fraction of the aerosol was somewhat hygroscopic (Dick et al., 2000). This study also showed that organic-associated water was considerably less than sulfate-associated water at high relative humidity with respect to water ( $RH_w$ ), but was comparable or greater at low  $RH_w$ . Saxena et al. (1995) showed that organics can alter the water uptake behavior of inorganic aerosol both positively (non-urban) and negatively (urban), depending on location. Finally, a model study suggests that the presence of water-soluble organic compounds can significantly increase cloud condensation nuclei in marine, rural, and urban environments (Mircea et al., 2002).

The humidified tandem differential mobility analyzer has been used previously to measure hygroscopic growth of ambient particles (Berg et al., 1998; Brechtel and Kreidenweis, 2000; Dick et al., 2000; Weingartner et al., 2002), to measure the growth of pure organic compounds (Cruz and Pandis, 2000; Prenni et al., 2001) and to measure water uptake by internal mixtures of ammonium sulfate and certain carboxylic acids at equal mass ratios (Hämeri et al., 2002). In this study, we investigate the water uptake of ammonium sulfate internally mixed at a range of mass ratios with dicarboxylic acids, including adipic acid, succinic acid, oxalic acid, malonic acid, and glutaric acid. These compounds may play an important role in altering the characteristics of the inorganic particles and, hence, altering their cloud nucleating ability.

## 2. Experimental

The humidified tandem differential mobility analyzer (HTDMA) has been used previously in our laboratory to measure the hygroscopic growth of sub-micrometer particles. The experimental procedure has been described fully (Brechtel and Kreidenweis, 2000; Prenni et al., 2001) and will be described only briefly here. Polydisperse, sub-micrometer particles are generated using a TSI 3076 atomizer and bulk solutions with mass ratios of 1:1, 10:1, and 100:1 ammonium sulfate:dicarboxylic acid. The aerosol is then dried using a combination of gentle heating ( $\sim 30^\circ\text{C}$ ), diffusion driers, and dilution with dry air before entering the experimental chamber. For all experiments, this drying procedure produced conditions of  $<5\% RH_w$  at  $30^\circ\text{C}$ .

The experimental chamber is maintained at  $30^\circ\text{C}$ . The desired particle diameter of 100 nm is selected using the first differential mobility analyzer (DMA 1), operating at a 10:1 sheath:sample flow ratio, producing a near-monodisperse aerosol. After size selection, the aerosol is humidified using Perma Pure tubing (model MD-110-48S). A size distribution is then measured for the 'wet'

aerosol using the second DMA (DMA 2) and a particle counter (TSI model 3010). The sheath flows for the Perma Pure tubing and DMA 2 are operated at the same humidity.

In each experiment, the modified size distribution is measured using DMA 2 at  $\leq 5\% RH_w$ . In most cases, the peak of the dry distribution fell near 100 nm. However, for 1:1 mixtures of ammonium sulfate with oxalic acid, succinic acid, glutaric acid, and malonic acid, particle evaporation after DMA 1 caused a decrease in the dry particle diameter. Experiments were repeated using only ammonium sulfate whenever size decreases were noted in order to confirm the absence of instrumental artifacts. The vapor pressure of ammonium sulfate is negligible at  $30^\circ\text{C}$ , and so we assume that only the dicarboxylic acids evaporate. We perform growth calculations based on the measured diameter in DMA 2 at  $\leq 5\% RH_w$ , and the amount of remaining organic acid mass in the condensed phase. For these conditions, the actual dry sizes are 100, 94, 94, 89 and 94 nm, respectively, for 1:1 mixtures of ammonium sulfate with adipic, succinic, oxalic, malonic, and glutaric acids, respectively. These diameters correspond to actual mass fractions of 1, 1.4, 1.5, 2.3, and 1.5 for these mixtures, instead of the 1:1 value present in the atomized aerosol. These mass ratios are listed in Table 2. Other studies have noted volatilization as an experimental issue for mixed particles that are 50% organic by mass. Hämeri et al. (2002) found up to 5% decreases in the diameter of 100 nm mixtures of succinic and malonic acids with ammonium sulfate using a TDMA system. These diameter reductions are nearly equivalent to those found in our study. Peng et al. (2001) mention evaporation as an issue for malonic, succinic, oxalic and glutaric acids during 40 min growth/evaporation cycles in studies using an electrodynamic balance. They note only a 3% mass change, but it is difficult to compare their results to ours because that study used single drops of  $10^3$  times greater mass than within our monodisperse droplet population. Clearly, drop size and mass must affect organic volatilization. Finally, we note that the volatilization issue should not have significantly impacted the mass composition of 1:1 mixed particles prior to DMA 1 because the equilibrium vapor pressure of organic is readily met by the much greater mass in the polydisperse aerosol coming from the atomizer.

The near-monodisperse aerosol is exposed to increasing relative humidity following DMA 1 and particle diameter is monitored. The DMA channel width for DMA 2 at 100 nm is 4.2 nm. Hygroscopic growth must therefore exceed  $\sim 4\%$  of the dry particle diameter to be detected. The humidity at the inlet of DMA 2 is measured for both the aerosol sample flow and the sheath flow using ROTRONIC HydroClip humidity sensors (type S). These sensors are accurate to  $\pm 1.5\% RH_w$  over the humidity range studied.

We calculate predicted water uptake for the mixed ammonium sulfate/dicarboxylic acid solution particles. For these calculations we assume that the organic and inorganic components take up water independently, i.e., the well-known Zdanovskii, Stokes and Robinson (ZSR) assumption (Seinfeld and Pandis, 1998). Further, we assume that the volume change of mixing is zero, and that the particles are spherical. Hygroscopic growth is predicted for ammonium sulfate using Köhler theory, with solution property data for ammonium sulfate as listed in DeMott et al. (1994) and water activity from Clegg et al. (1998). Hygroscopic growth is predicted for the dicarboxylic acids using data from a previous study (Prenni et al., 2001). We use the following expression (Dick et al., 2000) to model the  $RH_w$ -dependent particle growth factor (see next section) for the pure organics from our previous study:

$$G_O = \left[ 1 + (a + b(RH_w - 100) + c(RH_w - 100)^2) \times \frac{RH_w}{100 - RH_w} \right]^{1/3} \quad (1)$$

In the study of the pure dicarboxylic acids, only oxalic acid, malonic acid, and glutaric acid exhibited hygroscopic behavior in the humidity range studied. Fit parameters for 100 nm particles of these compositions are given in Table 1. The following expression, based on the ZSR and volume additivity assumptions, was used to determine the theoretical mixed particle growth factor,

$$G_M = (\varepsilon_O G_O^3 + \varepsilon_{IN} G_{IN}^3)^{1/3}, \quad (2)$$

where  $\varepsilon_O$  and  $\varepsilon_{IN}$  are the organic and inorganic volume fractions, respectively, in the dry particle, and  $G_O$  and  $G_{IN}$  are the hygroscopic growth factors at the same  $RH_w$  for the organic and inorganic components, respectively. Eq. (2) is identical to that used by Cruz and Pandis (2000) and others to model hygroscopic behavior of mixtures. To determine volume fractions, we first convert our mass ratio to volume ratio based on the compound densities. The densities used were  $1.769 \text{ g cm}^{-3}$  for ammonium sulfate,  $1.36 \text{ g cm}^{-3}$  for adipic acid,  $1.572 \text{ g cm}^{-3}$  for succinic acid,  $1.653 \text{ g cm}^{-3}$  for oxalic acid (dihydrate form assumed in our experimental setup, following Prenni et al., 2001),  $1.619 \text{ g cm}^{-3}$

for malonic acid, and  $1.424 \text{ g cm}^{-3}$  for glutaric acid (Weast and Astle, 1981).

### 3. Results

The hygroscopic growth factor indicates the amount of water absorbed by the particles and is calculated:  $G = D_{\text{wet}}/D_{\text{dry}}$ , where  $D_{\text{wet}}$  is the diameter of the particle at the enhanced humidity, and  $D_{\text{dry}}$  is the diameter determined from DMA 2 measurements at  $\leq 5\%$   $RH_w$ . Particles that do not grow with increasing humidity have a constant growth factor of  $G = 1$ , while particles that take up water have  $G > 1$ . Ammonium sulfate was used to test the experimental setup because of its well-known deliquescence point (Onasch et al., 1999) and water uptake behavior, with measured growth factors of 1.47 at 80%  $RH_w$  and 1.69 at 90%  $RH_w$ , in excellent agreement with predicted growth factors. Near the ammonium sulfate deliquescence point, a fraction of the aerosol deliquesces and a fraction remains crystalline. This results because the humidity in the system is not completely uniform; this variability is included in the  $RH_w$  uncertainty shown in the figures. In these cases, the dominant peak is used for determining the hygroscopic growth factor.

The first mixture studied was ammonium sulfate and adipic acid. Note that pure adipic acid does not take up any water at humidities as high as 93%  $RH_w$  (Prenni et al., 2001), so that it is essentially treated as an insoluble component. Data for 100:1 ammonium sulfate:adipic acid are shown in Fig. 1a, along with the predicted water uptake based on the calculations described above. The data agree well with the modeled behavior within the uncertainty of the measurements. This was true of all of the 100:1 mixtures, with equally good agreement between the modeled behavior and the data. However, there is little difference between the predicted behavior for 100:1 ammonium sulfate:dicarboxylic acid mixtures and that for pure ammonium sulfate, and so the presence of the dicarboxylic acids is not expected to greatly affect water uptake at this low concentration.

Fig. 1b shows water uptake data for 10:1 ammonium sulfate:adipic acid particles, as well as the predicted behavior for this mixture. Again, good agreement is obtained with the prediction that assumes that adipic acid attracts no additional water. However, the increased concentration of the organic fraction results in a reduction of the overall particle hygroscopicity. For example, for pure ammonium sulfate,  $G = 1.47$  at 80%  $RH_w$  and 1.69 at 90%  $RH_w$ , while we measure  $G = 1.40$  at 80%  $RH_w$  and 1.62 at 90%  $RH_w$  for the 10:1 ammonium sulfate:adipic acid aerosol. For all of the 10:1 ammonium sulfate:dicarboxylic acids studied, the measured data agree with the predicted behavior within

Table 1  
Fit parameters for Eq. (1) for low molecular weight dicarboxylic acids

Compound	<i>a</i>	<i>b</i>	<i>c</i>
Oxalic acid	0.39411	−1.16473	1.07393
Malonic acid	0.61761	−0.95833	0.86825
Glutaric acid	0.99597	−2.34929	1.58981

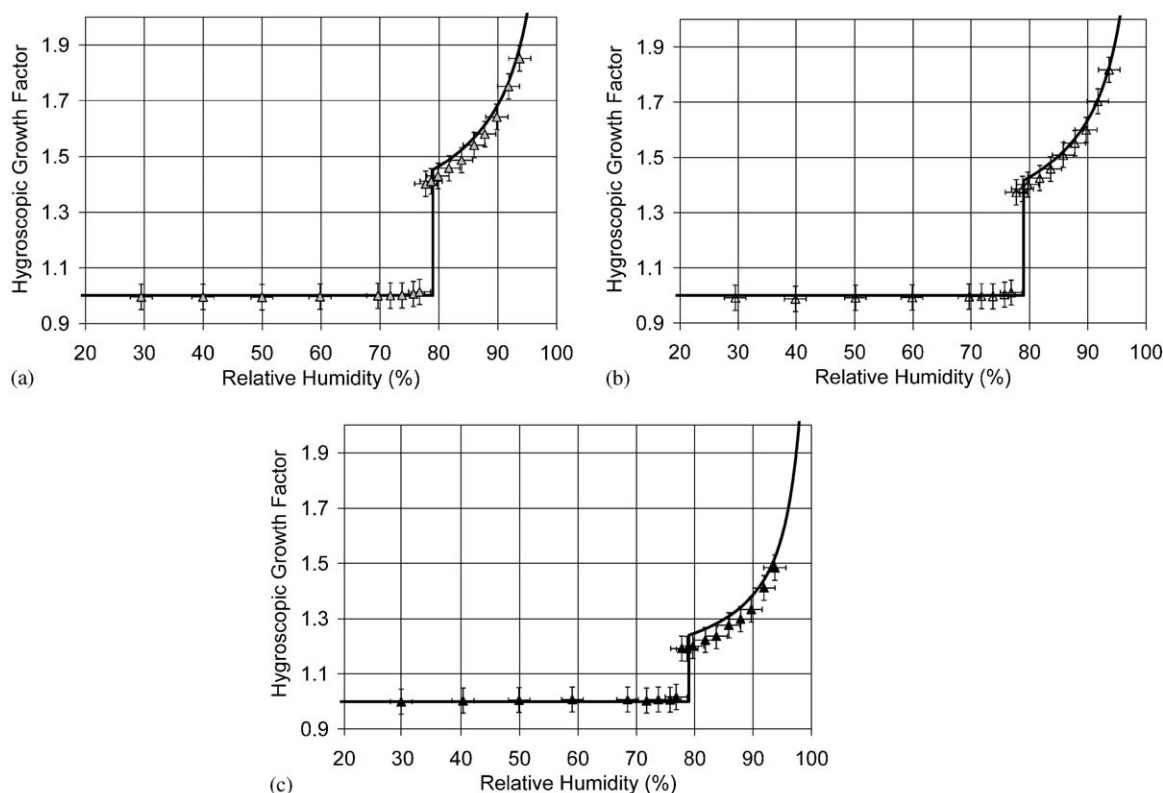


Fig. 1. (a) Water uptake for 100:1 ammonium sulfate:adipic acid at 30°C. Predicted water uptake for this mixture is shown as a solid line. (b) Water uptake for 10:1 ammonium sulfate:adipic acid at 30°C. Predicted water uptake is shown as a solid line. (c) Water uptake for 1:1 ammonium sulfate:adipic acid at 30°C. Predicted water uptake is shown as a solid line.

the uncertainty of the measurements. Results for all mixtures are given in Table 2.

The most dramatic reduction in water uptake occurred for 1:1 ammonium sulfate:adipic acid, as seen in Fig. 1c. Here, measured hygroscopic growth factors at 80% and 90% RH<sub>w</sub> are only 1.20 and 1.35, respectively. For comparison, Hämeri et al. (2002) measure a slightly larger growth factor of ~1.24 at 80% RH<sub>w</sub> for 1:1 ammonium sulfate:adipic acid aerosol. Our measured growth factors also appear to agree quite well with the behavior predicted by Eq. (2), within the uncertainty of the measurements.

As expected, hygroscopic growth measurements of 1:1 (1.4:1 actual mass ratio after evaporation) ammonium sulfate:succinic acid produced similar results as those for 1:1 ammonium sulfate:adipic acid, as shown in Fig. 2. In this figure we also note an additional curve for predicted water uptake that does not account for the noted evaporation of succinic acid in the 1:1 mixtures. We measure  $G = 1.30$  at 80% RH<sub>w</sub> and 1.52 at 90% RH<sub>w</sub> for the 1:1 ammonium sulfate:succinic acid particles. For comparison, Hämeri et al. (2002) measured a slightly larger growth factor of ~1.35 at 80% RH<sub>w</sub>

for 1:1 (not adjusted for noted evaporation) ammonium sulfate:succinic acid aerosol. Choi and Chan (2002), using an electrodynamic balance method for several micron sized particles, obtained a growth factor of 1.43 for succinic acid mixed with ammonium sulfate in a 1:1 mole ratio (1.12:1 ammonium sulfate:succinic acid mass ratio) at 85% RH<sub>w</sub>. We measured  $G = 1.41$  at 86% RH<sub>w</sub>, indicating good agreement with that study as well. Since succinic and adipic acids are treated as non-hygroscopic in our application of Eq. (2) (i.e.,  $G_0 = 1$ ), the mixed particles exhibit less water uptake than pure ammonium sulfate. However, the 1:1 ammonium sulfate:succinic acid particles exhibit greater water uptake than 1:1 ammonium sulfate:adipic acid. A primary reason for this is the partial evaporation of the succinic acid, which, in combination with differing organic densities, leads to a lower organic volume fraction (higher ammonium sulfate volume fraction).

Unusual behavior was observed for 1:1 (1.5:1 actual mass ratio after evaporation) ammonium sulfate:oxalic acid, as shown in Fig. 3. In this figure, the predicted behavior for both metastable solutions and the case of crystallized ammonium sulfate are shown. The aerosol is

Table 2

Deliquescence behavior and hygroscopic growth factors of ammonium sulfate mixed with dicarboxylic acids

Mixture	$\varepsilon_0$	$G$ (80% RH <sub>w</sub> )		$G$ (90% RH <sub>w</sub> )		Deliquesce RH <sub>w</sub> (%)
		Measured	Predicted	Measured	Predicted	
100:1 amm. sulf.:adipic acid	0.013	1.43	1.46	1.66	1.68	77.8
10:1 amm. sulf.:adipic acid	0.126	1.40	1.43	1.62	1.64	77.7
1:1 amm. sulf.:adipic acid	0.565	1.20	1.25	1.35	1.39	77.7
100:1 amm. sulf.:succinic acid	0.011	1.41	1.46	1.66	1.69	77.7
10:1 amm. sulf.:succinic acid	0.111	1.38	1.43	1.61	1.64	77.6
1.4:1 amm. sulf.:succinic acid	0.449	1.30	1.30	1.52	1.47	76.3
100:1 amm. sulf.:oxalic acid	0.009	1.44	1.47	1.66	1.69	77.8
10:1 amm. sulf.:oxalic acid	0.094	1.43	1.45	1.66	1.67	77.0
1.5:1 amm. sulf.:oxalic acid	0.383	1.39	1.36	1.69	1.59	Not observed
100:1 amm. sulf.:malonic acid	0.011	1.42	1.45	1.65	1.68	77.2
10:1 amm. sulf.:malonic acid	0.108	1.42	1.44	1.65	1.68	77.7
2.3:1 amm. sulf.:malonic acid	0.322	1.42	1.43	1.66	1.69	Not observed
100:1 amm. sulf.:glutaric acid	0.012	1.42	1.45	1.64	1.67	79.3
10:1 amm. sulf.:glutaric acid	0.121	1.39	1.42	1.61	1.65	78.3
1.5:1 amm. sulf.:glutaric acid	0.453	1.30	1.33	1.50	1.55	77.3
Amm. sulfate	1.00		1.47		1.69	79.3 <sup>a</sup>
Adipic acid <sup>b</sup>	1.00	1.00		1.00		
Succinic acid <sup>b</sup>	1.00	1.01		1.01		
Oxalic acid <sup>b</sup>	1.00	1.17		1.43		
Malonic acid <sup>b</sup>	1.00	1.37		1.73		
Glutaric acid <sup>b</sup>	1.00	1.15		1.29		

Mass fraction ratios listed include evaporative losses.

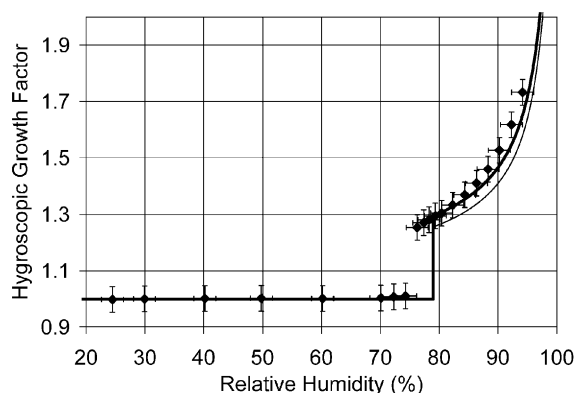
<sup>a</sup>Onasch et al. (1999).<sup>b</sup>Prenni et al. (2001).

Fig. 2. Water uptake for 1:1 ammonium sulfate:succinic acid at 30°C. Predicted water uptake is shown as a thick solid line. This curve accounts for the noted evaporation of succinic acid (see text). The thin solid line does not account for evaporation.

clearly affected by the presence of oxalic acid in that particles show water uptake throughout the humidity ranged studied, as predicted for fully dissolved ammonium sulfate, except perhaps at very low RH<sub>w</sub>. This indicates that the particles never fully crystallized during the drying procedure, despite reaching humidities of <5% RH<sub>w</sub>. This is consistent with hygroscopic growth

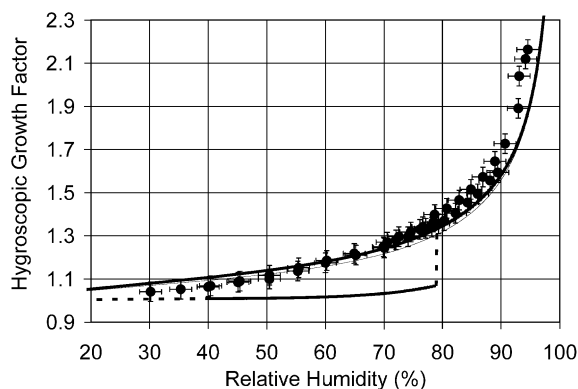


Fig. 3. Water uptake for 1:1 ammonium sulfate:oxalic acid at 30°C. Predicted water uptake is shown as a thick solid line. Water uptake values for metastable ammonium sulfate solutions are used for humidities below the deliquescence point. This curve accounts for the noted evaporation of oxalic acid. The thin solid line does not account for evaporation. The thick dashed line assumes that the ammonium sulfate volume fraction fully crystallized during the drying stage.

measurements of pure oxalic acid (Prenni et al., 2001), which did not show a distinct deliquescence transition, but rather demonstrated continual water uptake. In contrast, Peng et al. (2001), using electrodynamic



balance measurements of larger drops, observed crystallization of oxalic acid at 51.8–56.7% RH<sub>w</sub>. However, residence times are much longer (many minutes versus ~25 s) and drops have volumes that are at least 10<sup>6</sup> times greater, so crystallization events are detected at many orders of magnitude slower than would have to occur during particle drying in the HTDMA system (i.e., we do not detect crystallization except by the absence of deliquescence during rehumidification). We therefore cannot directly compare crystallization results except to note that longer times and larger particles favor crystallization. The relevant result for the atmosphere will depend on the cycle of humidity through which a particle is exposed. Efflorescence of pure ammonium sulfate occurs at ~32% RH<sub>w</sub> (Onasch et al., 1999), and so the ammonium sulfate was expected to crystallize during the drying process in our mixed particles. The presence of oxalic acid apparently inhibits nucleation of ammonium sulfate. This is also in contrast to measured water uptake of ammonium oxalate, for which deliquescence was not observed at RH<sub>w</sub> < 94% (Peng and Chan, 2001). These results suggest that particles of relevant sizes containing large fractions of oxalic acid could remain as solutions in the atmosphere.

Similar behavior was observed for 1:1 (2.3:1 actual mass ratio after evaporation) ammonium sulfate:malonic acid, as shown in Fig. 4. As with the oxalic mixture, the particles show water uptake throughout the humidity ranged studied and good agreement is obtained with the predicted behavior of metastable droplets. Identical behavior was observed in another TDMA study for 1:1 (by mass, prior to evaporation) ammonium sulfate:malonic acid aerosol (Hämeri et al., 2002). Likewise, Choi

and Chan (2002), using a scanning electrodynamic balance technique, saw significant water uptake by 1:1 (by moles) ammonium sulfate:malonic acid particles prior to the ammonium sulfate deliquescent point. This again indicates that the particles never fully crystallized, and likely did not even partially crystallize, during the drying procedure. Like oxalic acid, pure malonic acid does not exhibit a clear deliquescence transition, and continuous water uptake is observed at humidities greater than 40% RH<sub>w</sub>. Once wetted in the atmosphere, particles containing large fractions of malonic acid are likely to remain as aqueous solutions. Measured hygroscopic growth factors at 80% and 90% RH<sub>w</sub> are 1.42 and 1.66, respectively, in reasonably good agreement with other studies. For example, Hämeri et al. (2002) measured a slightly smaller growth factor of ~1.38 at 80% RH<sub>w</sub>. Choi and Chan (2002) reported a growth factor of 1.45 at 85% RH<sub>w</sub>. Our closest comparable RH<sub>w</sub> was 86%, where we measured  $G = 1.52$ .

The hygroscopic behavior of 1:1 (1.5:1 actual mass ratio after evaporation at ≤5% RH<sub>w</sub>) ammonium sulfate:glutaric acid was predicted quite well by Eq. (2) at high humidities, as seen in Fig. 5a. The growth factors in this high RH<sub>w</sub> range were also in good agreement with previous studies at approximately the same mass ratio of ammonium sulfate to glutaric acid. Cruz and Pandis (2000) measured  $G = 1.37$  for 100 nm particles of 1:1 mass ratio at 85% RH<sub>w</sub>, while we measured  $G = 1.37$  at 84% RH<sub>w</sub>. Choi and Chan (2002) measured  $G = 1.38$  at 85% RH<sub>w</sub> for ~10 μm particles of similar composition. Unusual behavior was observed at low humidities for particles generated from the 1:1 ammonium sulfate:glutaric acid solutions in the current study. First, even at low humidities, the ‘dry’ size is less than 94 nm. This reduction in size results from evaporation of the particles after size selection in DMA 1, and before measuring particle size in DMA 2. This was also observed for 1:1 mixtures containing oxalic acid, succinic acid, and malonic acid. However, for the 1:1 glutaric acid mixture, there is a further reduction in particle size as humidity is increased from <5% RH<sub>w</sub> to ~40% RH<sub>w</sub>, as shown in Fig. 5b. Assuming that this difference results only from the exchange of glutaric acid between the gas phase and the condensed phase, this indicates that glutaric acid coverage decreases as humidity increases. This could result if the gas/particle partitioning of glutaric acid is dependent on relative humidity. Evidence of such behavior has been reported for a variety of organic species, and a number of explanations have been put forth (Pankow et al., 1993). For example, reduced competition with water vapor could increase organic sorption onto solids at low relative humidities, leading to a maximum organic coverage on inorganic salts at the lowest humidities.

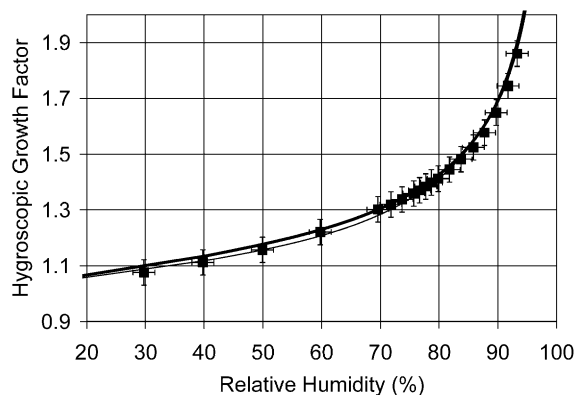


Fig. 4. Water uptake for 1:1 ammonium sulfate:malonic acid at 30°C. Predicted water uptake is shown as a thick solid line. Water uptake values for metastable ammonium sulfate solutions are used for humidities below the deliquescence point. This curve accounts for the noted evaporation of malonic acid (see text). The thin solid line does not account for evaporation.

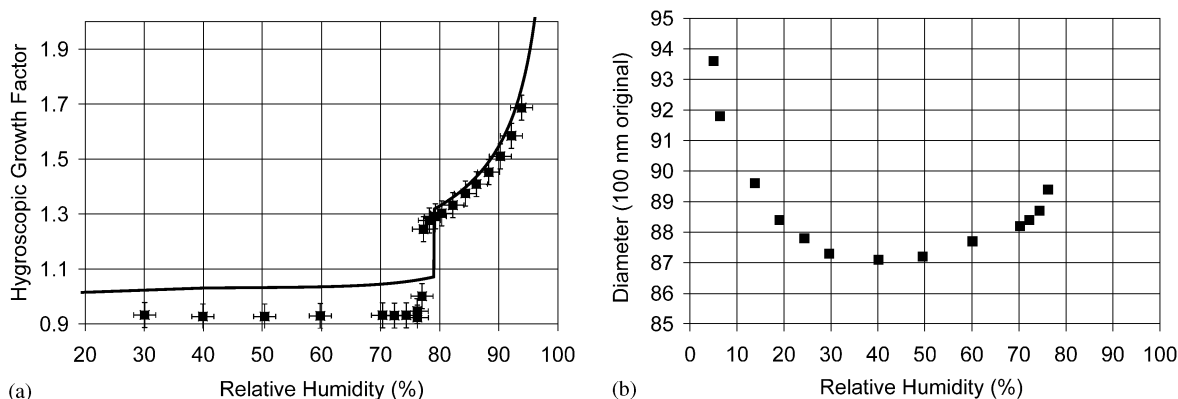


Fig. 5. (a) Water uptake for 1:1 ammonium sulfate:glutaric acid at 30°C. Predicted water uptake is shown as a solid line, using the mass fraction of glutaric acid in particles after noted evaporation at  $\leq 5\%$  RH<sub>w</sub>. (b) Change in particle diameter as a function of relative humidity. The diameter unexpectedly decreases further with increasing humidity to 40% RH<sub>w</sub> in DMA 2.

#### 4. Summary and conclusions

Measurements of water uptake were conducted on internal mixtures of ammonium sulfate and low molecular weight dicarboxylic acids. Mixtures of 100:1, 10:1, and 1:1 ammonium sulfate:dicarboxylic acid were investigated for adipic, succinic, oxalic, malonic, and glutaric acids at 30°C. For the 100:1 mixtures, water uptake was very similar to that of pure ammonium sulfate, with the organic having little effect on the particles' hygroscopicity. For 10:1 mixtures, water uptake was still dominated by ammonium sulfate. However, the increased organic fraction had a greater effect on the particles' overall hygroscopicity. Still, even for the least soluble of the organics, adipic acid, growth factors decreased by less than 5% at 90% RH<sub>w</sub>. Under most conditions, it is unlikely that atmospheric particles will contain more than 10% dicarboxylic acid, by mass, and so these compounds are unlikely to play a major role in the hygroscopic properties of atmospheric particles.

For the particles most concentrated in organics, the 1:1 mixtures, the dicarboxylic acids had a dramatic effect on aerosol water uptake. For the less hygroscopic adipic and succinic acids, water uptake was reduced considerably in the mixtures, as demonstrated in Figs. 1c and 2. In these particles, the water content of the mixture could be adequately represented by assuming that only the inorganic fraction of the particle was hygroscopic, as suggested by the ZSR theory and by results for the pure organics. For the more soluble organics, very different behavior was observed. First, particles containing oxalic acid and malonic acid exhibited water uptake at humidities as low as 30% RH<sub>w</sub>. This indicates that the particles never effloresced during the drying procedure, despite reaching humidities

of  $< 5\%$  RH<sub>w</sub>. This suggests that, once wetted, particles containing large fractions of these organics will remain as solutions in the atmosphere, and at higher humidities, these mixtures will exhibit significant water uptake. Glutaric acid, which is also very soluble, showed slightly less hygroscopic behavior compared to predicted values in a 1.5:1 ammonium sulfate:glutaric acid mixture at high humidities. This observation may be an artifact of the experiment, as significant evaporation of glutaric acid was observed during the measurement. Cruz and Pandis (2000) and Choi and Chan (2002) have suggested that the change in water uptake, defined as

$$\xi_w = \frac{G^3 - 1}{(1 - \varepsilon_O)(G_{IN}^3 - 1)} \quad (3)$$

can be used to describe the effect of the organic component on increasing ( $\xi > 1$ ) or decreasing ( $\xi < 1$ ) water uptake of the inorganic portion of particles. Both previous studies characterized  $\xi_w$  at 85% RH<sub>w</sub>. Cruz and Pandis (2000) calculated  $\xi_w = 1.2$ –1.4 for 1:1 (by mass) ammonium sulfate:glutaric acid particles. Choi and Chan (2002) report  $\xi_w = 1.36$  for 1:1 (by moles) ammonium sulfate:glutaric acid particles, and  $\xi_w = 1.66$  and 1.99 for 1:1 mixtures of ammonium sulfate with succinic and malonic acid, respectively. For RH<sub>w</sub> testing conditions within 1% of 85% RH<sub>w</sub> in the present study, we would calculate  $\xi_w = 1.2$ , 1.2 and 1.4 for similar mass ratio mixtures of ammonium sulfate with glutaric, succinic and malonic acid, respectively. Thus, our results in Eq. (3) agree quantitatively with previous results for glutaric acid mixtures, but only qualitatively for succinic and malonic acid mixtures. Rather than attempting to understand this result, we must note that Eq. (3) does not distinguish whether an increase in water uptake occurs due to potential inorganic/organic interactions or due to water uptake by the organic itself. A version of



Eq. (3) that accounts for the expected water uptake of the organic volume fraction would also have to include an added  $\epsilon_0^*(G_0^3 - 1)$  term in the denominator. In such a case, our modified  $\xi_w$  values would be 1.0, 1.2 and 1.0 in the three cases noted above, and 1.0 for the average of all 1:1 mixtures at all  $RH_w$  above 80%. This simply restates our conclusion that the net water uptake by the mixed particles is generally as expected if both the inorganic and organic volume fractions take up water independently, in accord with Eq. (2). Other interactions between the ammonium sulfate and dicarboxylic acid components are not readily apparent, within experimental uncertainty.

In addition to altering the amount of water uptake, organic compounds have been shown to affect the deliquescence point of the inorganic component (Andrews and Larson, 1993; Lightstone et al., 2000), and theory suggests that the deliquescence  $RH_w$  of a mixture of salts is always lower than that of the individual components (Seinfeld and Pandis, 1998). The observed deliquescence points for the mixtures studied are shown in Table 2. In all but one instance, the observed deliquescence point was slightly lower than what is expected for pure ammonium sulfate. However, in all but one case where deliquescence occurred, the observed deliquescence humidity did not differ from the deliquescence point of pure ammonium sulfate by more than the uncertainty of the measurement. This is consistent with laboratory measurements of deliquescence of ammonium sulfate internally mixed with glutaric acid, which showed no change in the deliquescence relative humidity of the salt (Cruz and Pandis, 2000).

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