

10-23-2003

# Hygroscopic Growth of Ammonium Sulfate/ Dicarboxylic Acids

Matthew E. Wise

*University of Colorado, Boulder, mawise@cu-portland.edu*

Jason D. Surratt

*University of Colorado, Boulder*

Daniel B. Curtis

*University of Colorado, Boulder*

John E. Shilling

*University of Colorado, Boulder*

Margaret A. Tolbert

*University of Colorado, Boulder*

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## Recommended Citation

Wise, Matthew E.; Surratt, Jason D.; Curtis, Daniel B.; Shilling, John E.; and Tolbert, Margaret A., "Hygroscopic Growth of Ammonium Sulfate/Dicarboxylic Acids" (2003). *Faculty Research*. 71.

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## Hygroscopic growth of ammonium sulfate/dicarboxylic acids

Matthew E. Wise, Jason D. Surratt, Daniel B. Curtis, John E. Shilling,  
and Margaret A. Tolbert

Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, USA

Received 13 May 2003; revised 29 July 2003; accepted 5 August 2003; published 23 October 2003.

[1] Recent studies have shown that tropospheric sulfate aerosols commonly contain 50% by mass organic species. The influence of these organics on the chemical and physical properties of sulfate aerosols is not fully established. We have measured the water activity of pure dicarboxylic acids and eutonic mixtures of ammonium sulfate/dicarboxylic acids at 25°C and have calculated van't Hoff factors for each individual system. We have also used the vapor pressure data to determine the hygroscopic growth curves for pure dicarboxylic acids and eutonic mixtures and provide power law fits to the data. For the systems studied we find that the presence of soluble dicarboxylic acids at the eutonic proportion depresses hygroscopic growth when compared to pure ammonium sulfate. In addition, we find that the presence of low-solubility dicarboxylic acids at the eutonic proportion has no effect on the hygroscopic growth when compared to pure ammonium sulfate. To model the hygroscopic growth curves of the eutonic solutions, we employed the Zdanovskii, Stokes, and Robinson method. It was found that this approximation was accurate to within 17% for all the systems studied. *INDEX TERMS*: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS*: hygroscopic growth, ammonium sulfate, dicarboxylic acids

**Citation:** Wise, M. E., J. D. Surratt, D. B. Curtis, J. E. Shilling, and M. A. Tolbert, Hygroscopic growth of ammonium sulfate/dicarboxylic acids, *J. Geophys. Res.*, 108(D20), 4638, doi:10.1029/2003JD003775, 2003.

### 1. Introduction

[2] Sulfate aerosols are ubiquitous in the upper troposphere (UT) and are known to affect the Earth's atmosphere in several ways. These aerosols can impact the Earth's radiation balance directly by scattering and absorbing radiation [Charlson *et al.*, 1992] and indirectly by serving as cloud condensation nuclei [DeMott and Rogers, 1990]. Sulfate aerosols can also serve as surfaces for heterogeneous chemistry in the UT. The impact of aerosols on atmospheric chemistry and climate depends, in part, on the particle phase and size, which is in turn depends on atmospheric relative humidity (RH) and particle composition.

[3] Aerosol particles with different chemical compositions will behave differently as RH changes. At very low RH values some aerosols remain in the liquid phase and absorb water continuously as relative humidity increases. Conversely, some aerosols are in the solid phase at low RH values and their size will remain unchanged until the RH increases to the deliquescence RH (DRH). Once the DRH is reached, the particle dissolves and becomes a saturated solution droplet. If the RH increases past the DRH, the solution aerosol undergoes hygroscopic growth to maintain equilibrium with the water vapor surrounding it.

[4] Field measurements have shown that background tropospheric aerosols are largely composed of inorganic species such as ammonium sulfate. However, there is also evidence that organic material may comprise 50% or more of the particle mass [Murphy *et al.*, 1998]. Rogge *et al.* [1993] identified more than 80 different organic compounds in tropospheric aerosols including water soluble, low molecular weight dicarboxylic acids such as oxalic, malonic, and succinic acids. It has been shown that the presence of organic material in ammonium sulfate aerosols can lower their DRH [Wexler and Seinfeld, 1991; Clegg *et al.*, 2001; Brooks *et al.*, 2002] and can alter their hygroscopic growth [Saxena *et al.*, 1995].

[5] Previous laboratory studies [see Martin, 2000] as well as thermodynamic models [Clegg *et al.*, 1998] have firmly established the DRH and the hygroscopic growth curve of pure ammonium sulfate. Recent laboratory studies have also determined the DRH and hygroscopic growth curves of a variety of low molecular weight dicarboxylic acids and multifunctional acids [Peng *et al.*, 2001; Prenni *et al.*, 2001] using both particle and bulk solution techniques. Further laboratory studies and thermodynamic models have determined the DRHs and hygroscopic growth curves of mixed inorganic and organic particles [Ansari and Pandis, 2000; Cruz and Pandis, 2000; Brooks *et al.*, 2002; Choi and Chan, 2002a, 2002b; Hameri *et al.*, 2002; Ming and Russell, 2002; Brooks *et al.*, 2003]. However, these studies have been limited to a small number of dicarboxylic acids

**Table 1.** Precursor Solution Composition and Deliquescence Relative Humidities (DRH)<sup>a</sup>

	Precursor Solution				Previous Studies	
	Manufacturer, Purity %	Organic, mol/mol	Ammonium Sulfate, mol/mol	Vapor Pressure at Deliquescence, torr <sup>b</sup>	DRH, % <sup>b</sup>	DRH, %
<i>Pure Species in Water</i>						
Ammonium sulfate	Fischer (99.7)		0.095	18.8	80.0	81.7, <sup>c</sup> 79.0, <sup>d</sup> 79, <sup>c</sup> 80, <sup>f</sup> 81 <sup>g</sup>
Malonic acid	Aldrich (99)	0.22		16.7	71.9	74.3, <sup>c</sup> 65.2, <sup>h</sup> 70, <sup>i</sup> 74–91 <sup>j</sup>
Glutaric acid	Aldrich (99)	0.17		20.8	88.9	87.5, <sup>c</sup> 83.5–85, <sup>k</sup> 85, <sup>d</sup> 85.2 (83), <sup>l</sup> 88.0–88.5, <sup>h</sup> 92, <sup>i</sup> 89–99 <sup>j</sup>
Maleic acid	Aldrich (99)	0.10		20.7	88.9	87.5, <sup>c</sup> 86 (71), <sup>l</sup> 89 (20), <sup>m</sup> 85–100 <sup>j</sup>
l-malic acid	Aldrich (97)	0.26		13.5	57.6	58.9 <sup>c</sup>
Oxalic acid	Aldrich (99+)	0.025		22.6	97.1	93.0, <sup>c</sup> 97.3, <sup>h</sup> 97–99 <sup>j</sup>
Succinic acid	Aldrich (99+)	0.014		22.8	97.6	91.0, <sup>c</sup> 98.8, <sup>h</sup> 99, <sup>i</sup> 98–100 <sup>j</sup>
<i>Eutonic Mixtures in Water</i>						
Malonic acid/ammonium sulfate		0.16	0.10	15.8	67.8	70.9, <sup>c</sup> (58), <sup>n</sup> 73.7 (57.8) <sup>o</sup>
Glutaric acid/ammonium sulfate		0.08	0.07	18.0	76.7	77.5, <sup>c</sup> 72, <sup>n</sup> 76.6 (68.7), <sup>o</sup> 79 <sup>p</sup>
Maleic acid/ammonium sulfate		0.11	0.09	16.0	68.5	71.5, <sup>c</sup> 75 (19) <sup>q</sup>
l-malic acid/ammonium sulfate		0.25	0.13	12.6	53.7	56.4 <sup>c</sup>
Oxalic acid/ammonium sulfate		0.006	0.095	18.4	78.6	77.3 <sup>c</sup>
Succinic acid/ammonium sulfate		0.004	0.094	18.5	79.1	82.9, <sup>c</sup> 79 (77.5), <sup>o</sup> 79, <sup>r</sup> 80 <sup>n</sup>

<sup>a</sup>Parentheses represent the onset of deliquescence.

<sup>b</sup>Bulk solution measurements, 24.7°–24.9°C.

<sup>c</sup>Brooks *et al.* [2002], bulk solution measurements, 24°C.

<sup>d</sup>Cruz *et al.* [2000], TDMA measurements, 22°–26°C.

<sup>e</sup>Cziczko *et al.* [1997], absorption cell measurements, room temperature.

<sup>f</sup>Onasch *et al.* [1999], flow tube measurements, 22°C.

<sup>g</sup>Cziczko *et al.* [1999], flow tube measurements, 10°C.

<sup>h</sup>Peng *et al.* [2001], bulk solution measurements, 25°C.

<sup>i</sup>Ming *et al.* [2002], 100 nm particles, model predictions.

<sup>j</sup>Saxena *et al.* [1997], UNIFAC predictions, 25°C.

<sup>k</sup>Peng *et al.* [2001], EDB measurements, 25°C.

<sup>l</sup>Choi *et al.* [2002a], EDB measurements, 20°–23°C.

<sup>m</sup>Brooks *et al.* [2003], flow tube measurements, 0°C.

<sup>n</sup>Ming *et al.* [2002], 1:1 mass ratio, 100 nm particles, model predictions.

<sup>o</sup>Choi *et al.* [2002b], 1:1 mole ratio, EDB measurements, 20°–23°C.

<sup>p</sup>Cruz *et al.* [2000], 1:1 mass ratio, TDMA measurements, 22°–26°C.

<sup>q</sup>Brooks *et al.* [2003], 1:1 mass ratio, flow tube measurements, 0°C.

<sup>r</sup>Hameri *et al.* [2002], 1:1 mass ratio, TDMA measurements, room temperature.

and have not been conducted for eutonic composition solutions, which may have the largest effect on the hygroscopic growth.

[6] We have measured the water activities of both pure dicarboxylic acids and eutonic mixtures of ammonium sulfate/dicarboxylic acids at 25°C. The organic compounds studied are the C-2 to C-6 dicarboxylic acids, as well as maleic and l-malic acid. We report van't Hoff factors for each individual system so that if particle water content is known, an estimation of water activity can be made. We use the water activities to determine the hygroscopic growth curves and provide power law fits so that at any given water activity, the growth of the particle can be calculated. We compare our results to those obtained in previous studies as well as those obtained by thermodynamic equilibrium models where available. Finally, we use the additivity analysis of Zdanovskii, Stokes, and Robinson (ZSR) to determine if the eutonic mixtures can be treated as two separate components.

## 2. Experiment

[7] Ammonium sulfate and pure organic precursor saturated solutions were prepared by the addition of each component to distilled water until a small excess of undissolved solid remained. Each precursor solution was

maintained at 25°C by placing it in a temperature-controlled water bath with a thermometer calibrated to  $\pm 0.2$  K. The solutions were mixed for approximately 24 hours to ensure that the species in solution were in equilibrium with the undissolved solids. To create eutonic composition precursor solutions, ammonium sulfate and each organic were simultaneously mixed in distilled water and stirred until crystals of both components would not dissolve. Because the solid ammonium sulfate crystals are cubic and translucent, while most of the organics in this study are powdery white solids, we were able to visibly distinguish the point at which the solution was saturated with respect to both components. The resultant solution was handled as before. The compositions of each solution were taken from Brooks *et al.* [2002] and are listed in Table 1. Brooks *et al.* [2002] estimate errors in the eutonic compositions to be approximately  $\pm 1 \times 10^{-2}$  molar ratio for the water soluble organics and  $\pm 1 \times 10^{-3}$  molar ratio for the less water soluble organics. As shown by Brooks *et al.* [2002], the maximum solubility of each component in eutonic solutions is not dependent on the order in which the components are added.

[8] Bulk RH measurements were conducted on the supernatant of each precursor solution using a sealed test tube placed in a 25°C temperature controlled water bath. Approximately 5–10 mL of solution was placed in the test tube

and attached to a mechanically pumped glass line. The vapor pressure of the sample was measured using a 100 Torr Baratron capacitance manometer that is accurate to  $\pm 0.15\%$  of the pressure reading. The vapor pressure of pure water was calculated at the bath temperature from data by *Perry* [1941]. Pure water samples were tested as outlined above to verify that the measured water vapor pressure agreed with calculated value (i.e., the thermometer was calibrated). It was found that, within error, both values of water vapor pressure agreed. The sample relative humidity was then determined by ratioing the measured sample vapor pressure to the saturation vapor pressure of water. Because the accuracy of the capacitance manometer is very high, the uncertainty in the sample temperature was used to calculate the uncertainty in the relative humidity measurements, which we report to be between 0.50 and 1.35% RH.

[9] Simulation of water uptake by the saturated solutions was accomplished by adding varying aliquots of water to the supernatant of each saturated precursor solution. After adding water to the saturated solutions, the RH was determined as outlined above. In this way, hygroscopic growth curves were constructed. To check this method of simulating water uptake by saturated solutions, we added a weighed portion of each organic and ammonium sulfate separately to various amounts of water, mixed, and measured the RH. It was found that this method of preparing the solutions yielded the same RH values (within error) as by adding varying amounts of water to saturated solutions.

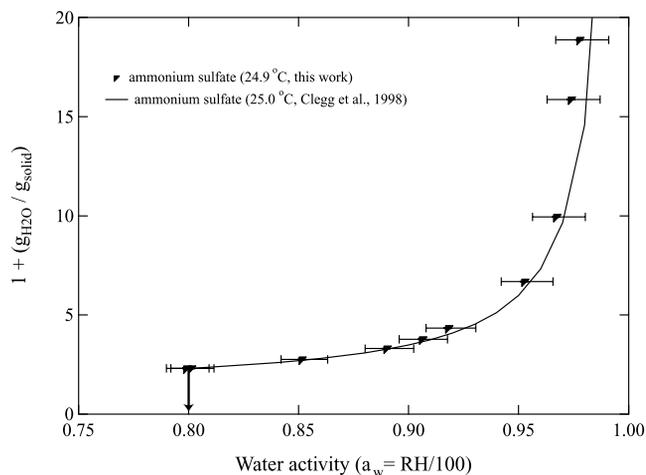
### 3. Results and Discussion

[10] To validate our experimental method for studying hygroscopic growth, the water uptake curve was first determined for ammonium sulfate. Figure 1 shows the inverse of the mass fraction solid soluble ( $1/mfs$ ) versus water activity for ammonium sulfate at and after the DRH in this study as well as predicted values from the thermodynamic model of *Clegg et al.* [1998] at 25°C. The inverse of the mass fraction solid soluble is calculated using equation (1):

$$1/mfs = 1 + (g_{\text{water}}/g_{\text{solid}}) \quad (1)$$

where  $g_{\text{water}}$  is the grams of water in solution and  $g_{\text{solid}}$  is the grams of solid in solution. We measure a DRH of 80.0% at 24.9°C (denoted by a downward arrow in the figure) for the ammonium sulfate precursor solution, which is in excellent agreement with the DRH reported in aerosol studies [*Cziczo et al.*, 1997; *Cziczo and Abbatt*, 1999; *Onasch et al.*, 1999] and in bulk studies [*Brooks et al.*, 2002]. Within the experimental error, the water uptake curve we measure by adding various aliquots of water to the saturated ammonium sulfate solution agrees well with the predicted values from the *Clegg et al.* [1998] model.

[11] Table 1 includes the solution vapor pressure and the corresponding DRH that we determined for each pure component and eutonic composition precursor solution along with previous bulk and particle measurements. We are in fairly good agreement with the majority of the literature DRH values except for the groups that also report the onset of deliquescence (indicated by parentheses in the table) prior to full deliquescence. A disadvantage of bulk measurements is that water absorption prior to full deli-



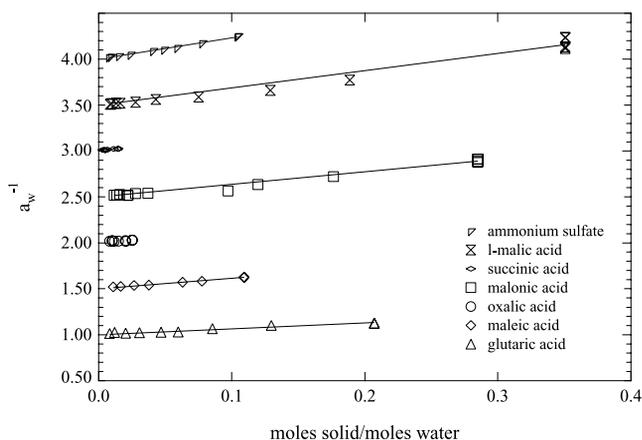
**Figure 1.** Inverse of the mass fraction solid soluble ( $1/mfs$ ) versus water activity for ammonium sulfate at and after the DRH in this study as well as predicted values from the thermodynamic model of *Clegg et al.* [1998] at 25°C. We measure a DRH of 80.0% at 24.9°C (denoted by a downward arrow) for ammonium sulfate.

quescence cannot be measured. This phenomenon is important because it extends the range of RH values at which liquid phase reactions might be able to occur on the aerosol. *Choi et al.* [2002a] showed that maleic acid aerosol starts to absorb water at 71% RH, well before the full DRH of 86%. *Brooks et al.* [2003] observed the same phenomena in their maleic acid measurements as the aerosol started to absorb water at 20% RH and became fully deliquesced at 89% RH. We are in good agreement with these groups at full deliquescence as we report a full DRH value of 88.7% for malic acid. These results further validate our method for studying the hygroscopic growth of organic and mixed ammonium sulfate/organic particles.

[12] The water activity of an ideal solution of containing a nonvolatile, nonelectrolyte is always lower than that of a pure solvent and decreases as more of the nonelectrolyte dissolves. In an ideal solution, this relationship is expressed as Raoult's Law where the water activity is equivalent to the mole fraction of solvent in solution. If our solutions were comprised solely of nonelectrolytes and were ideal, we could make an estimation of particle water activity with the knowledge of water content. However, our solutions do contain electrolytes and are far from ideal because of substantial quantities of solute dissolved in them. Therefore, to estimate water activity in our solutions, deviations from ideality must be measured. The van't Hoff factor has been used as a measure of solution nonideality [*Pruppacher and Klett*, 1980] and is defined through the relation:

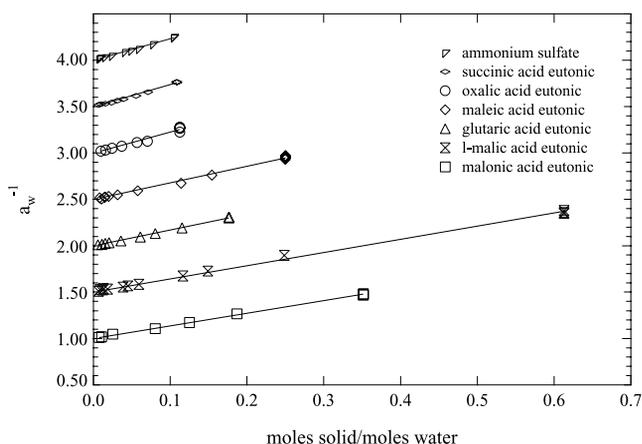
$$a_w^{-1} = 1 + i(n_s/n_w) \quad (2)$$

where  $i$  is the van't Hoff factor,  $n_s$  is the moles of solute in solution, and  $n_w$  is the moles of water in solution. Figures 2a and 2b show our water uptake data plotted as  $a_w^{-1}$  versus  $n_s/n_w$  for pure species in water and for each eutonic solution respectively. A straight line, with the  $y$  intercept forced through 1, satisfactorily fits each soluble dicarboxylic acid data set and each eutonic solution data set. Therefore the



**Figure 2a.** Our water uptake data plotted as  $a_w^{-1}$  versus  $n_s/n_w$  for the pure components. A straight line (with the  $y$  intercept forced through 1) satisfactorily fits each soluble dicarboxylic acid solution data set. Therefore the slope of the line yields the van't Hoff factor, which can be used to estimate the water activity of the solutions if water content is known (data set offset by  $a_w^{-1} = 0.5$  each from the previous data set for clarity).

slope of each data set yields  $i$ , which can be used to estimate the water activity of the solutions if water content is known. The uncertainty in the slope of the straight line fits to the data (one standard deviation) is one measure of the error in the van't Hoff factors, which we find to be  $\leq 5\%$  in all cases. We have also calculated van't Hoff factors for each system without forcing the  $y$  intercept through 1. The percent difference between the van't Hoff factors for the “forced” and “unforced” fits is  $\leq 10\%$  for the pure species in water and  $\leq 6\%$  for the eutonic solutions. The calculated van't Hoff factors and percent deviation from ideality for the soluble dicarboxylic acids and each eutonic system are listed in Table 2 for the fits forced through unity.



**Figure 2b.** Our water uptake data plotted as  $a_w^{-1}$  versus  $n_s/n_w$  for the eutonic solutions. A straight line (with the  $y$  intercept forced through 1) satisfactorily fits each eutonic solution data set. Therefore the slope of the line yields the van't Hoff factor, which can be used to estimate the water activity of the solutions if water content is known (data set offset by  $a_w^{-1} = 0.5$  each from the previous data set for clarity).

[13] A van't Hoff factor of 1 indicates that the solution behaves as an ideal solution, whereas as a progressively larger (or smaller) factor indicates a progressively larger deviation from ideality. The calculated  $i$  for ammonium sulfate in this work (2.31) is in good agreement with the “effective” van't Hoff factor used in Kohler theory calculations for ammonium sulfate, of between 2 and 2.5, [Gerber *et al.*, 1977; Rogers and Yau, 1989] to account for solution nonidealities. For the pure species in water, ammonium sulfate shows the largest deviation from ideality. For the soluble dicarboxylic acids, the more acid dissolved in water, the greater the deviation from ideality. It is surprising that, although the  $pK_a$  values for each of the soluble dicarboxylic acids in water are similar, the van't Hoff factor for glutaric acid is less than 1 while the van't Hoff factors for the other dicarboxylic acids are greater than one. This is most likely due to specific interactions that occur in the glutaric acid solution. Because oxalic and succinic acid have such low solubility in water, a wide range of  $n_s/n_w$  values could not be studied. Therefore we have not included van't Hoff factors for these systems in Table 2.

[14] For the eutonic solutions, the oxalic and succinic systems show the largest deviation from ideality, likely due to the fact that ammonium sulfate comprises the majority of the solid in solution. The deviation from ideality in the remaining eutonic solutions show no systematic dependence on the amount of solid in solution or the fraction of ammonium sulfate in solution. However, there is a good dependence on the  $pK_a$  of the first proton of the diacid. The higher the  $pK_a$ , the larger the deviation from ideality.

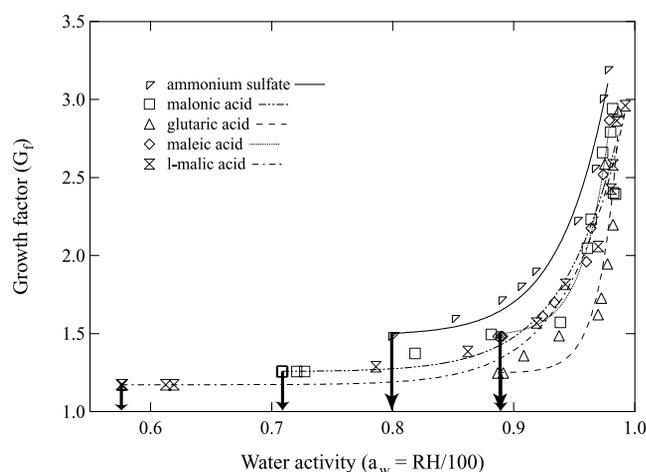
[15] The hygroscopic growth factor,  $G_f$ , is widely used to represent the hygroscopic growth of aerosols where  $G_f = R_{p,2}/R_{p,1}$  with  $R_{p,1}$  representing the dry particle radius and  $R_{p,2}$  representing the wet particle radius at a specific RH. To quantify the water uptake by each solution in this study we used our mfs data to calculate  $G_f$ . Using the formalism of Peng *et al.* [2001],  $G_f$  is calculated using equation (3):

$$G_f = [(mfs_1\rho_1)/(mfs_2\rho_2)]^{1/3} \quad (3)$$

where  $mfs_1$  is the mass fraction solid in the dry particle ( $= 1$ ),  $mfs_2$  is the mass fraction solid in the wet particle,  $\rho_1$  is the dry particle density, and  $\rho_2$  is the wet particle density. The

**Table 2.** Van't Hoff Factors ( $i$ ) at 25°C for Dicarboxylic Acids and Eutonic Mixtures of Dicarboxylic Acids and Water

	$i$	% Deviation From Ideality ( $i = 1$ )
<i>Pure Species in Water</i>		
Ammonium sulfate	2.31	131
Malonic acid	1.37	37
Glutaric acid	0.64	36
Maleic acid	1.14	14
l-malic acid	1.87	87
<i>Eutonic Mixtures in Water</i>		
Malonic acid/ammonium sulfate	1.36	36
Glutaric acid/ammonium sulfate	1.70	70
Maleic acid/ammonium sulfate	1.78	78
l-malic acid/ammonium sulfate	1.42	42
Oxalic acid/ammonium sulfate	2.25	125
Succinic acid/ammonium sulfate	2.36	136



**Figure 3a.** Calculated hygroscopic growth factors as a function of water activity for all the pure systems in this study with the exception of the low-solubility dicarboxylic acids (oxalic and succinic), which did not exhibit deliquescence until an RH greater than 97%. Each line represents a power law expression fit to each data set with the general form of  $G_f = y_0 + B(a_w)^C$ .

particle density (assuming additivity of the volumes) is estimated from equation (4):

$$1/\rho = \sum mf_i/\rho_{i0} \quad (4)$$

where  $mf_i$  and  $\rho_{i0}$  are the mass fraction of water or solute in solution and the corresponding density of the water or solute, respectively.

[16] Figure 3a shows the calculated hygroscopic growth factors as a function of water activity for all the pure systems in this study with the exception of the low-solubility dicarboxylic acids (oxalic and succinic) which did not exhibit deliquescence until an RH greater than 97%. Included are power law fits to each data set of the general form:

$$G_f = y_0 + B(a_w)^C \quad (5)$$

where  $y_0$ ,  $B$ , and  $C$  are empirical fitting parameters. This empirical equation satisfactorily fits each data set and the empirical fitting parameters for each system are listed in Table 3. This method of plotting the data shows that the solutions do not exhibit significant water uptake until an RH of 90% is attained. The growth factors for the soluble dicarboxylic acid/ammonium sulfate eutonic solutions are shown in Figure 3b and are much closer to the growth of the ammonium sulfate solution than their pure dicarboxylic acid counterparts. This finding is in qualitative agreement with *Cruz and Pandis* [2000] as they found a decrease in particle growth with an increase in mass fraction of glutaric acid in their glutaric acid/ammonium sulfate mixtures. In addition, the hygroscopic growth factors of the low-solubility dicarboxylic acid/ammonium sulfate solutions (Figure 3c) are nearly the same as the ammonium sulfate solution.

[17] Using equation (5),  $G_f$  values for each system can be calculated at any water activity. Table 3 includes the  $G_f$  values calculated for 85% RH and 90% RH for all the dicarboxylic acids and eutonic solutions studied here. Also listed in Table 3 are  $G_f$  values determined by other groups. Our  $G_f$  values are in fairly good agreement with those in the literature at both 85% RH and 90% RH. If the DRH of a

**Table 3.** Growth Factors ( $G_f$ ) at 25°C for Dicarboxylic Acids and Eutonic Mixtures of Dicarboxylic Acids and Water

	Fit Coefficients <sup>a</sup>			$G_f$ (85%)			$G_f$ (90%)		
	$y_0$	$B$	$C$	This Work	Other Studies	ZSR Model <sup>b</sup>	This Work	Other Studies	ZSR Model <sup>b</sup>
<i>Pure Species in Water</i>									
Ammonium sulfate	1.49	2.81	24.6	1.54	1.51, <sup>e</sup> 1.49, <sup>h</sup> 1.6 <sup>l</sup>		1.70		
Malonic acid	1.26	2.04	21.1	1.32	1.40 <sup>j</sup>		1.48	1.73 <sup>g</sup> , 1.53 <sup>k</sup>	
Glutaric acid	1.25	3.73	63.3	1.00 <sup>c</sup>	1.13, <sup>f</sup> 1.10, <sup>h</sup> 1.09 <sup>j</sup>		1.25	1.29 <sup>g</sup> , 1.30 <sup>k</sup>	
Maleic acid	1.48	3.59	46.0	1.00 <sup>c</sup>	1.14 <sup>f</sup>		1.51		
l-malic acid	1.17	2.08	21.3	1.24	1.23, <sup>f</sup> 1.31 <sup>j</sup>		1.39	1.39 <sup>k</sup>	
Oxalic acid				1.00 <sup>c</sup>	1.03 <sup>j</sup>		1.00 <sup>c</sup>	1.43 <sup>g</sup> , 1.08 <sup>k</sup>	
Succinic acid				1.00 <sup>c</sup>	1.06, <sup>f</sup> 1 <sup>j</sup>		1.00 <sup>c</sup>	1.01 <sup>g</sup> , 1 <sup>k</sup>	
<i>Eutonic Mixtures in Water</i>									
Malonic acid/ammonium sulfate	1.21	2.38	17.5	1.34	1.45, <sup>e</sup> 1.55 <sup>l</sup>	1.42	1.58		1.58
Glutaric acid/ammonium sulfate	1.30	2.38	26.5	1.34	1.38, <sup>e</sup> 1.37 <sup>l</sup>		1.45		1.47
Maleic acid/ammonium sulfate	1.26	2.38	21.7	1.33			1.50		1.60
l-malic acid/ammonium sulfate	1.11	2.63	18.4	1.24		1.35	1.49		1.50
Oxalic acid/ammonium sulfate	1.47	2.22	21.3	1.54			1.71		
Succinic acid/ammonium sulfate	1.48	2.87	26.4	1.52	1.43, <sup>e</sup> > 1.5 <sup>l</sup>		1.65		

<sup>a</sup>Fit coefficients to the power law expression,  $G_f = y_0 + B(a_w)^C$ .

<sup>b</sup> $G_f$  calculated using equation (6).

<sup>c</sup>DRH is greater than 95% RH, therefore  $G_f = 1.00$ .

<sup>d</sup>*Choi et al.* [2002a],  $G_f$  calculated from RH = 10–85, 20°–23°C.

<sup>e</sup>*Choi et al.* [2002b], 1:1 mole ratio,  $G_f$  calculated from RH = 10–85, 20°–23°C.

<sup>f</sup>*Ansari et al.* [2000],  $G_f$  calculated from UNIFAC at RH ≤ 10–85%.

<sup>g</sup>*Prenni et al.* [2001],  $G_f$  calculated from RH ≤ 5–90, 30°C.

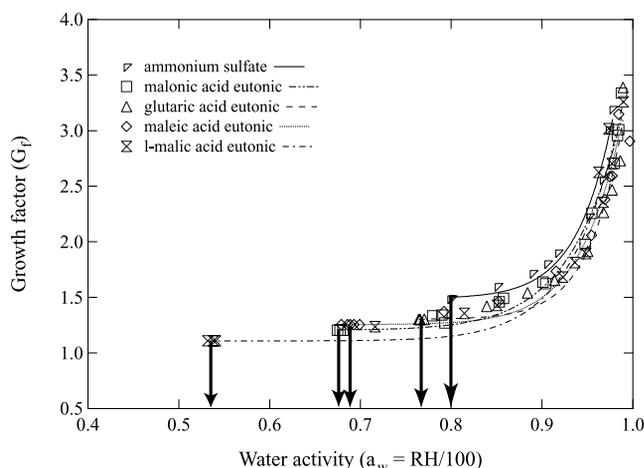
<sup>h</sup>*Cruz et al.* [2000],  $G_f$  calculated from RH ≤ 10–85, 100 nm dry diameter particles, 22°–26°C.

<sup>i</sup>*Cruz et al.* [2000], 1:1 mass ratio,  $G_f$  calculated from RH ≤ 10–85, 100 nm dry diameter particles, 22°–26°C.

<sup>j</sup>*Peng et al.* [2001],  $G_f$  calculated from RH = 5–85, 25°C (used dl-malic acid).

<sup>k</sup>*Peng et al.* [2001],  $G_f$  calculated from RH = 10–90, 25°C (used dl-malic acid).

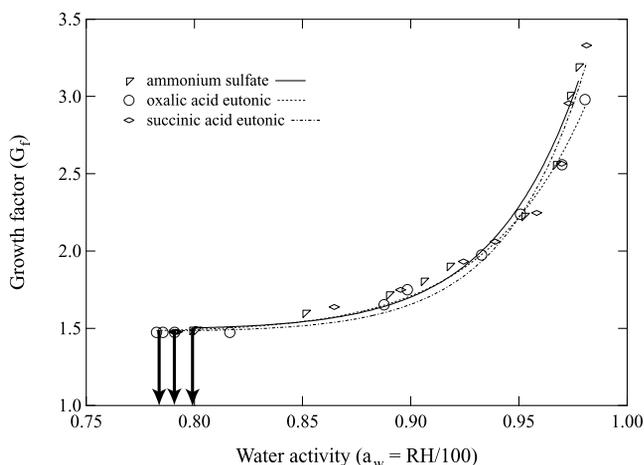
<sup>l</sup>*Hameri et al.* [2002], 1:1 mass ratio,  $G_f$  calculated from RH = 10–85, room temperature.



**Figure 3b.** Calculated hygroscopic growth factors as a function of water activity for the soluble dicarboxylic acid/ammonium sulfate eutonic solutions. Each line represents a power law expression fit to each data set with the general form of  $G_f = y_0 + B(a_w)^C$ .

system in our study was greater than either 85 or 90% RH, we assume that the  $G_f = 1.00$  (no particle growth prior to the DRH). Some groups do report a  $G_f > 1.00$  for particles at RH less than the full DRH of the system. This is due to slight water absorption by the particle prior to full deliquescence or because the particles were not fully effloresced prior to the deliquescence experiment. *Prezzi et al.* [2001], observed no efflorescence transition for oxalic acid which is why the  $G_f$  at 90% RH reported in their study is 1.43 and ours is 1.00.

[18] From these calculations it is evident that for the systems studied, pure dicarboxylic acids take up significantly less water than ammonium sulfate. It is also evident that the presence of soluble dicarboxylic acids at the eutonic proportion affects hygroscopic growth such that the  $G_f$  of these eutonic solutions are at or between that of its pure



**Figure 3c.** Calculated hygroscopic growth factors as a function of water activity for the low-solubility dicarboxylic acid/ammonium sulfate eutonic solutions. Each line represents a power law expression fit to each data set with the general form of  $G_f = y_0 + B(a_w)^C$ .

counterparts. We saw a negligible change in  $G_f$  for the succinic and oxalic acid eutonic systems when compared to pure ammonium sulfate. This is likely due to the fact that the majority of these systems were comprised of ammonium sulfate.

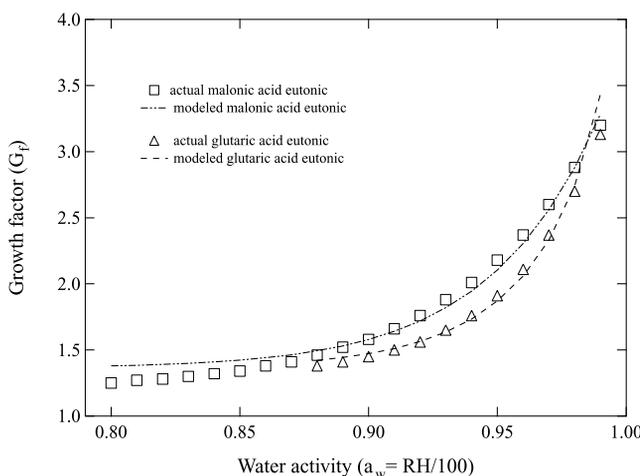
[19] The biggest discrepancy between growth factors calculated in this study and previous studies is for the ammonium sulfate/malonic acid mixed system. This discrepancy is likely due to the fact that *Choi and Chan* [2002b] and *Hameri et al.* [2002] use a 1:1 ammonium sulfate to malonic acid mass ratio in their hygroscopic growth experiments. We use an approximately 0.8:1 ammonium sulfate to malonic acid mass ratio (eutonic proportion) in our hygroscopic growth experiments. Because organic acids take up less water than ammonium sulfate, our hygroscopic growth factors should be lower than the previous studies.

[20] Using the formalism of *Cruz and Pandis* [2000], one approach to modeling mixed particle hygroscopic growth is to assume that the water content of a mixed particle is the sum of the water content of the pure components comprising that particle at a specific relative humidity. The Zdanovskii, Stokes, and Robinson (ZSR) method uses this approach to estimate mixture growth factors using measured growth factors for the pure components. The ZSR equation can be written as:

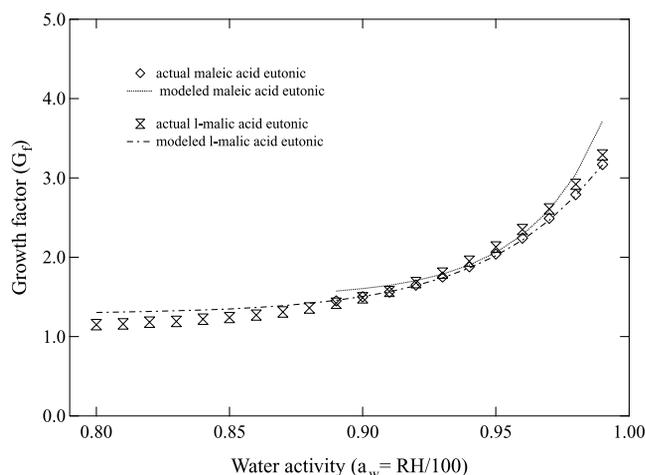
$$G_f(\text{RH}) = [\epsilon_o G_{\text{org}}^3(\text{RH}) + (1 - \epsilon_o) G_{\text{inorg}}^3(\text{RH})]^{1/3} \quad (6)$$

where  $\epsilon_o$  is the organic volume fraction in the dry particle and  $G_{\text{org}}(\text{RH})$  and  $G_{\text{inorg}}(\text{RH})$  are the pure organic and pure inorganic growth factors, respectively.

[21] Figures 4a and 4b show the actual and modeled soluble dicarboxylic acid eutonic growth curves. The actual eutonic growth curves are the power law fits to the data (Equation 5) and the modeled growth curves were calculated using equation (6). The data for the modeled eutonic growth curves are only presented at water activities for which both



**Figure 4a.** Actual and modeled malonic acid and glutaric acid eutonic growth curves. The actual eutonic growth curves are the power law expression fits to the data (shown as open symbols), and the modeled growth curves were calculated using equation (6) (shown as lines).



**Figure 4b.** Actual and modeled maleic acid and l-malic acid eutonic growth curves. The actual eutonic growth curves are the power law expression fits to the data (shown as open symbols), and the modeled growth curves were calculated using equation (6) (shown as lines).

the organic and inorganic components have deliquesced. The modeled growth curves are in good agreement with the actual growth curves over the majority of water activities. In all cases the growth factors estimated by equation (6) are within 17% and in most cases within 10% of the measured values. Table 3 includes the modeled  $G_f$  for 85% and 90% RH using equation (6).

#### 4. Conclusions and Atmospheric Implications

[22] We have determined the water activity of both pure dicarboxylic acids and eutonic mixtures of ammonium sulfate/dicarboxylic acids at 25°C. We report van't Hoff factors so that an empirical approximation of water activity can be made if the water content of each solution is known. It was found that the ammonium sulfate solution showed the greatest deviation from ideality. For the soluble dicarboxylic acids, nonideality was dependant on the organic solubility and for the eutonic solutions, no dependence on solid solubility was found. From these results, it is obvious that deviations in solution ideality due to specific solutes must be taken into account in order to accurately model the water uptake of particles in the atmosphere.

[23] We have also provided power law fits to the hygroscopic growth curves so that at any given water activity, the growth of the particle can be calculated. We find lower growth factors for the binary dicarboxylic acid/water mixtures than for ammonium sulfate. The growth factors of the soluble dicarboxylic acid eutonic solutions with ammonium sulfate were also depressed when compared with the pure inorganic component. Our results show that the ZSR relationship is a good approximation (within 17%) of the hygroscopic growth of a mixed dicarboxylic acid/ammonium sulfate particle.

[24] While measuring the DRH using bulk solutions eliminates the problem of difficulty in fully drying particles, one limitation of bulk studies is that we are unable to map out the efflorescence branch of the water uptake curve and measure the crystallization RH of the solution. This is due

to the inability to make metastable bulk solutions. Therefore we cannot measure the contribution of the organic component to the hygroscopic growth for metastable solutions at low RH. The effect of an organic component on the water uptake of mixed solutions at low RH may be important because *Posfai et al.* [1998] found that organics were responsible for water uptake of ammonium sulfate at low RH. Therefore more particle measurements are needed to quantify the effect organics have on the hygroscopic growth of mixed aerosols at low RH in the metastable region of the hygroscopic growth curve.

[25] While we found that the low-solubility acids had little impact on the hygroscopic growth of ammonium sulfate, they could still be important in the atmosphere. For example, a particle containing a low-solubility organic may have the organic present as a solid "core". This "core" could impact the crystallization RH and ice nucleation RH in the particle. Thus it is of interest to conduct particle measurements to quantify the heterogeneous effect of low-solubility organics in atmospheric particles.

[26] **Acknowledgments.** This research was supported by the Biological and Environmental Research Program (BER), U.S. Department of Energy, Grant No. DE-FG03-01ER63096. M.E.W. would also like to thank the NASA-ESS Fellowship Program for funding. J.D.S. would like to thank the University of Colorado REU program for funding.

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- D. B. Curtis, J. E. Shilling, J. D. Surratt, M. A. Tolbert, and M. E. Wise, Department of Chemistry and Biochemistry and CIRES, University of Colorado, Rm. 318, Boulder, CO 80309-0216, USA. (matthew.wise@colorado.edu)