

Hygroscopic growth of common organic aerosol solutes, including humic substances, as derived from water activity measurements

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[1] Studies have shown that organic matter often constitutes up to 50% by mass of tropospheric aerosols. These organics may considerably affect the water uptake properties of these aerosols, impacting Earth's climate and atmosphere. However, considerable uncertainties still exist about hygroscopic properties of organic carbon (OC) in particles. In this study, we have assembled an apparatus to measure equilibrium water vapor pressure over bulk solutions. We used these results to calculate the hygroscopic growth curve and deliquescence relative humidity (DRH) of representative compounds in three OC categories: saccharides, mono/dicarboxylic acids, and HULIS (Humic-Like Substances). To our knowledge, this is the first study to examine the hygroscopic growth of HULIS by means of a bulk method on representative compounds such as fulvic and humic acids. We also explored the temperature effect on hygroscopic growth within the 0°C–30°C temperature range and found no effect. The DRH and hygroscopic growth obtained were in excellent agreement with published tandem differential mobility analyzer (TDMA), electrodynamic balance, and bulk data for sodium chloride, ammonium sulfate, d-glucose, levoglucosan, succinic acid, and glutaric acid. However, we found a hygroscopic growth factor of 1.0 at a relative humidity of 90% for phthalic, oxalic, humic, and two fulvic acids; these results disagree with various TDMA studies. The TDMA is used widely to study water uptake of organic particles but can be affected by particle microstructural arrangements before the DRH and by the inability to fully dry particles. Thus, in the future it will be important to confirm TDMA data for nondeliquescent organic particles with alternate methods.

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1. Introduction

[2] The hygroscopic growth of atmospheric aerosols plays an important role in the Earth's climate and atmospheric chemistry. The uptake of water by particles affects both their light-scattering properties (direct effect on climate) and their activation into cloud drops and precipitation (indirect effect on climate). Both effects account for the largest cause of uncertainty in the estimates of climate change [*Intergovernmental Panel on Climate Change (IPCC)*, 2007]. In addition, hygroscopic growth of aerosols influences the rate of atmospheric dry and wet deposition, visibility, and human health [*Ferron et al.*, 1988; *Finlay et al.*, 1997; *Broday and Georgopoulos*, 2001; *Schroeter et al.*, 2001; *Chan et al.*, 2002].

[3] The chemical composition of a particle governs its hygroscopic growth behavior. Submicron dry aerosol mass in the troposphere is sometimes 50% or more organic by weight, with 45–75% of this mass composed of water-soluble organic carbon (WSOC) [*Graham et al.*, 2002; *Mayol-Bracero et al.*, 2002; *Cavalli et al.*, 2004; *Decesari et al.*, 2005]. Therefore, the hygroscopic growth behavior of atmospheric aerosols may be strongly influenced by their organic mass content [*Saxena et al.*, 1995; *Saxena and Hildemann*, 1996]. Furthermore, atmospheric particles are composed of organic and inorganic components [*Middlebrook et al.*, 1998; *Murphy et al.*, 1998]. Although the inorganic portion of atmospheric aerosols has been well studied and characterized over the years [*Tang*, 1976; *Tang and Munkelwitz*, 1994; *Weis and Ewing*, 1999], considerable uncertainties still exist about the water uptake properties and phase transitions of organic carbon (OC) in particles [*Cruz and Pandis*, 2000; *Brooks et al.*, 2004; *Parsons et al.*, 2004; *Intergovernmental Panel on Climate Change (IPCC)*, 2007; *Jimenez et al.*, 2009].

[4] Chemical analysis of OC from aerosol filter samples shows that it contains compounds in four categories: (I)

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neutral species, such as sugars; (II) mono/dicarboxylic acids; (III) water-soluble surfactants, including humic-like organic polymers; and (IV) hydrophobic compounds, such as lipids [Fuzzi *et al.*, 2001; Mayol-Bracero *et al.*, 2002; Decesari *et al.*, 2005; Svenningsson *et al.*, 2006]. The first three categories comprise the WSOC fraction. Most studies have focused on the hygroscopic behavior of compounds in the first two categories, though they account for only a small fraction of the total OC mass [Kanakidou *et al.*, 2005, and references therein]. The fact that categories III and IV often comprise over 90% of the OC mass indicates that these species may exert an important influence on the hygroscopic behavior of atmospheric aerosols. Using a proton NMR technique first proposed by Fuzzi *et al.* [2001], up to 40% of WSOC has been identified as polycarboxylic acids resembling the molecular structures of humic materials [Decesari *et al.*, 2001]. The similarity of the polyacidic fraction to humic materials, observed in several studies [Mukai and Ambe, 1986; Havers *et al.*, 1998; Facchini *et al.*, 1999; Gelencsér *et al.*, 2000; Krivácsy *et al.*, 2000; Duarte *et al.*, 2005; Alfarra *et al.*, 2006], has earned this fraction the name Humic-Like Substances (HULIS).

[5] Currently, the instruments most commonly used to study the hygroscopic behavior of aerosols are the electrodynamic balance (EDB) and the tandem differential mobility analyzer (TDMA) [Chan and Chan, 2005]. The TDMA is usually the method of choice to study hygroscopic growth of organic particles both in the field and in the laboratory [McMurry and Stolzenburg, 1989; Swietlicki *et al.*, 1999; Cruz and Pandis, 2000; Dick *et al.*, 2000; Gysel *et al.*, 2004; Svenningsson *et al.*, 2006; Zhang *et al.*, 2008]. However, the hygroscopic properties of inorganic aerosols have been studied primarily by measuring vapor pressure over equilibrated solutions of binary electrolyte solutions [Seinfeld and Pandis, 1998; Jacobson, 1999]. In the past, measured vapor pressures of inorganic multicomponent solutions have been used to parameterize and model the hygroscopic growth of aerosols in the atmosphere [Zhang *et al.*, 1993a, 1993b; Tabazadeh *et al.*, 1994; Jacobson *et al.*, 1996; Lin and Tabazadeh, 2002].

[6] In contrast, relatively few organic aerosol components have been studied by using bulk methods. Bulk water activity measurements have been used to establish deliquescence relative humidity (DRH) and phase transitions [Brooks *et al.*, 2002; Braban *et al.*, 2003; Marcolli *et al.*, 2004], and to calculate hygroscopic growth factors (HGFs) [Wise *et al.*, 2003; Chan *et al.*, 2005] of certain atmospherically relevant organics. These studies include mainly compounds representing OC categories I and II. Bulk studies are lacking on compounds that represent OC category III (water-soluble surfactants) such as humic substances and their mixtures with inorganic salts or hydrophobic matter (OC category IV). The very few published studies on hygroscopic growth of fulvic and humic acids have all been conducted with a TDMA.

[7] Because of their complexity, particle measurement techniques such as the TDMA can be affected by equipment and procedural artifacts in the data. For example, Chan and Chan [2005] found that mass transfer effects due to low residence time of particles for humidification can significantly alter TDMA measure-

ments. An advantage of bulk vapor pressure measurements over particle measurements is the simplicity of the equipment setup and the measurement procedure. Using a simple bulk method eliminates the problems that commonly arise in direct particle measurement and presents a way to corroborate the hygroscopic growth of atmospheric particles.

[8] In this work, we measured equilibrium water vapor pressure over bulk solutions of organics found in atmospheric aerosols and then used those results in a formulation to calculate the HGF. We studied representative organic compounds from the first three categories described above: saccharides, mono/dicarboxylic acids, and water-soluble surfactants. Our aims were to (1) study experimentally the temperature dependence of the hygroscopic growth factor for these substances over the 0°C–30°C range for the first time, (2) investigate through representative compounds the hygroscopic growth of the HULIS fraction of aerosols with a bulk method for the first time, and (3) compare our results to previously published results from TDMA studies.

2. Hygroscopic Growth Calculation

[9] The hygroscopic growth factor (G_f) is commonly used to represent the hygroscopic growth of aerosols. The G_f is defined as $D_{\text{wet}}/D_{\text{dry}}$, where D_{dry} refers to the dry particle diameter (typically at RH < 10%) and D_{wet} refers to the wet particle diameter at a specific RH. Using water activity data obtained from vapor pressure experiments, the G_f is directly computed using

$$G_f = \frac{D_{\text{wet}}}{D_{\text{dry}}} = \left\{ \frac{\rho_{\text{dry}}}{\rho_{\text{wet}}} \left(\frac{C + M_{\text{dry}} m_{\text{wet}}^0}{M_{\text{dry}} m_{\text{wet}}^0} \right) \right\}^{\frac{1}{3}}, \quad (1)$$

where ρ_{dry} and ρ_{wet} refer to the dry and wet particle density in grams per cubic meter; M_{dry} is the molar mass of the solute in g/moles; C is a conversion factor and equals 10^3 g solute/kg water; and m_{wet}^0 is the molality of the wet particle in moles per kilogram of water, which depends on its water activity (a_w). As a result of the Kelvin effect, equation (1) is applicable for particles above 50 nm in diameter for most solutes and above 200 nm in diameter for humic substances [Seinfeld and Pandis, 1998].

[10] An equivalent approach (equation (2)) was used by Ansari and Pandis [2000] to calculate the hygroscopic growth factor from mass concentrations:

$$G_f = \left\{ \frac{\rho_{\text{dry}} m_{\text{wet}}}{\rho_{\text{wet}} m_{\text{dry}}} \right\}^{\frac{1}{3}} = \left\{ \frac{\rho_{\text{dry}}}{\rho_{\text{wet}}} \left(\frac{C + M_{\text{dry}} m_{\text{wet}}^0}{M_{\text{dry}} m_{\text{wet}}^0} \right) \right\}^{\frac{1}{3}}. \quad (2)$$

For a single-component aqueous solution, the mass of a wet particle consists of the mass of water plus the mass of the dry solute present in the system, $m_{\text{wet}} = m_{\text{water}} + m_{\text{dry}}$. The mass of the dry particle is obtained from the density of a dry spherical sphere, $m_{\text{dry}} = [\pi \rho_{\text{dry}} D_{\text{dry}}^3]/6$. The mass of water in the particle can be obtained by defining molality in terms of known variables and rearranging: $m_{\text{water}} = [10^3 \rho_{\text{dry}} D_{\text{dry}}^3]/[6 M_{\text{dry}} m_{\text{wet}}^0]$. The constant C is a conversion factor to obtain m_{water} in units of grams when

m_{wet}^o has units of moles of solute per kg of water. Finally, ρ_{wet} is calculated from a weighted average of the solute and water densities using

$$\rho_{\text{wet}} = x_s \rho_s + x_w \rho_w, \quad (3)$$

where x_s is the mole fraction of solute, x_w is the mole fraction of water, ρ_s is the solute density, and ρ_w is the density of water. It is worth noting that equation (3) results in an approximation of the wet particle density (ρ_{wet}), given that density is not a linear function of mole fraction for many systems. A ρ_{wet} calculation is performed for each measurement using bulk water and solute density values at the solution temperature.

[11] The water activity of an aerosol solution is defined as the ratio of the equilibrium water vapor pressure over the solution to the equilibrium vapor pressure of pure water at the same temperature [Seinfeld and Pandis, 1998]. For any given aerosol solution composition, there is a unique a_w that limits the growth of the particle attributable to water uptake. The relation between m_{wet}^o and a_w is accurately described by this polynomial function:

$$m_{\text{wet}}^o(a_w) = b_0 + b_1 a_w + b_2 a_w^2 + b_3 a_w^3 + \dots \quad (4)$$

where the coefficients b_i ($i = 0, 1, 2, \dots$) are extracted from a least squares fitting of the solution molality as a function of water activity (a_w) for each constant temperature curve. The water activity is calculated from the water vapor pressure measurement as follows:

$$a_w = \frac{p_v(T)}{p_{v,s}(T)}, \quad (5)$$

where $p_v(T)$ is the water vapor pressure over the solution at the measurement temperature and $p_{v,s}(T)$ is the saturation water vapor pressure at the same temperature. Next, each b_i set is plotted as a function of temperature to determine an expression for the temperature dependence of b_i , (i.e., $b_i(T)$). Introducing these expressions into equation (4), we obtain

$$m_{\text{wet}}^o(a_w, T) = b_0(T) + b_1(T) a_w + b_2(T) a_w^2 + b_3(T) a_w^3 + \dots \quad (6)$$

By using this relation, we can calculate the aerosol concentration for a given temperature and water activity. For this application, water activity (a_w) is considered equivalent to RH but expressed in decimal form (i.e., $a_w = \text{RH}/100\%$), and both terms are used interchangeably throughout this paper. The hygroscopic growth factor as a function of RH and temperature can be obtained from introducing equation (6) into equation (1).

3. Experimental Method

3.1. Water Vapor Pressure Measurements

[12] Bulk vapor pressure was measured by using a static technique, similar to that employed by Zhang *et al.* [1993a,

1993b], to measure water vapor pressure over the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4/\text{HCl}/\text{H}_2\text{O}$ systems. The apparatus used consists of a removable glass sample vessel, mechanically pumped glass lines wrapped with heating tape, a temperature-controlled bath, and a 100 torr Baratron capacitance manometer. Solutions were prepared by weighing each solid component and water onto a beaker, then stirring until the solution became homogeneous. Table 1 lists all components used in the solutions, along with the manufacturer and purity. All chemicals were used without further purification. Water used in the preparation of solutions was filtered through a Millipore Synergy 185 system, with a resulting resistivity of 18.2 m Ω . Approximately 12 g of solution were transferred to the sample vessel, which contained a Teflon-coated magnetic stirring bar to ensure a homogenous composition for the solution. After the sample vessel was connected to the apparatus, several freeze-purge-thaw cycles were performed to evacuate the gas headspace above the solution. These cycles consisted of submerging the vessel in liquid nitrogen until the solution was completely frozen, then mechanically pumping the vessel headspace. The solution was then allowed to thaw, stirred for at least two minutes, and then the freezing/pumping steps were repeated until the pressure inside the vessel read 0.0 torr with the final freezing. This procedure ensured that all the air above the solution was removed, allowing the measurement of the water vapor pressure over the solution.

[13] The sample vessel was then submerged in a constant-temperature bath at the desired temperature. The heating tape wrapped around the connecting lines was set 2°C to 3°C above the desired bath temperature to avoid water condensation on their inner surfaces. The temperature was monitored by a thermocouple attached to the outside of the vessel, with an accuracy of $\pm 0.3^\circ\text{C}$. The system was considered to be at equilibrium when the temperature had been maintained within $\pm 0.1^\circ\text{C}$ of the target for at least 30 min. After the vapor pressure reading was recorded from the barometer, the solution was frozen, and any remaining pressure reading was subtracted from the measurement to prevent its distortion by a potential air leak. Air leaks were infrequent and never exceeded 0.1 torr. To avoid directional bias, each data point reported in the vapor pressure versus temperature curves is the average of duplicate measurements taken in both the increasing and decreasing temperature directions.

[14] The DRH was obtained by measuring the water vapor pressure over saturated solutions with visibly undissolved solid and dividing it by the saturation water vapor pressure at the measurement temperature.

3.2. Humic Substances

[15] The experimental procedure to measure bulk water vapor pressure had to be modified slightly for humic substances. For these measurements, 3 g of solution were used because of the limited quantities available of International Humic Substance Society (IHSS) standards such as Suwannee River and Nordic reference fulvic acids (IHSS, Purchase limits for Suwannee River and Nordic reference fulvic acids, 2010, <https://ihss.humicsubstances.org/limits.html>). Experiments were conducted with 3, 6, and 12 g of solution to

Table 1. Solution Properties and Deliquescence Relative Humidity (DRH)^a

Solute	Supplier, Purity	DRH (%)	
		Our Work (25°C)	Other Studies (TDMA, EDB, Model, Bulk)
Sodium chloride	Sigma-Aldrich, 99%	76.6 ± 1.8	75 ± 1^b , 75 ± 1.2^c , 75.3 ± 0.1 ^d
Ammonium sulfate	Sigma-Aldrich, 99%	80.6 ± 1.8	80.0 ± 1.35 ^e , 79 ± 1^b , 80.4 ± 0.3^f , 80 ± 1.2^c , 81.7 ± 3 ^g 90 ± 2 ^h , 89.1 ± 0.7 ⁱ 80 ± 2 ^h
D-Glucose	Sigma-Aldrich, 99%	88.1 ± 1.8	97.6 ± 1.35 ^c , 98.8 ± 0.3 ^j , <u>98–100^k</u> , 91.0 ± 3 ^g , 99.1 ± 0.3 ^l no DHR observed^m
Levogluconan	Sigma, 99%	82.8 ± 1.8	88.9 ± 1.35 ^c , 83.5–85 ^j , 88.0–88.5 ⁱ , <u>89–99ⁿ</u> , 85 ± 5^b , 87.5 ± 3 ^g , 89 ± 2 ^o , 88.2 ± 0.3 ^l
Succinic acid	Acros Organics, 99%	99.5 ± 1.8	97.1 ± 1.35 ^c , 97.3 ± 0.3 ⁱ , <u>97–100ⁿ</u> , 93.0 ± 3 ^g , 97–99.6 ^p , 97.8 ± 0.3 ^l no DHR observed^m
Phthalic acid	Sigma-Aldrich, 99+%	>99.5	no DHR observed^m
Glutaric acid	Aldrich, 99%	90.1 ± 1.8	no DHR observed^q
Oxalic acid	Aldrich, 99%	97.9 ± 1.8	70 ± 2^m
Suwannee River fulvic acid	IHSS	>99.9	
Nordic Reference fulvic acid	IHSS	>99.9	
Humic acid	Fluka	>99.9	

^aTo our knowledge, all available TDMA, EDB and bulk studies that reported the DRH of the solutes above were presented for comparison. Note that TDMA studies are shown in bold text, EDB in italic text, model predictions in underlined text and bulk studies in normal text.

^b*Cruz and Pandis* [2000]; TDMA measurements at 22°C–26°C, (50 mm dry particles: NaCl, (NH₄)₂SO₂; 100 nm dry particles: glutaric acid).

^c*Gysel et al.* [2002]; TDMA measurements at 20°C.

^d*Tang and Mulkwitz* [1993]; EDB measurements at 25°C.

^e*Wise et al.* [2003]; bulk measurements at 24.7°C–24.9°C.

^f*Dinar et al.* [2007]; TDMA measurements at 21°C–23°C.

^g*Brooks et al.* [2002]; bulk solution measurements at 24°C.

^h*Mochida and Kawamura* [2004]; bulk solution measurements at 20°C.

ⁱ*Peng et al.* [2001b]; bulk measurements at 25°C.

^j*Peng et al.* [2001b]; EDB measurements at 25°C.

^k*Ansari and Pandis* [2000]; G_r calculated from UNIFAC at RH = 10%–85%.

^l*Marcolli et al.* [2004]; water activity measurements at 25°C.

^m*Brooks et al.* [2004]; TDMA measurements at 30°C.

ⁿ*Saxena et al.* [1995]; UNIFAC predictions at 25°C.

^o*Treuel et al.* [2009]; EDB and surface aerosol microscope measurements.

^p*Braban et al.* [2003]; bulk measurements at 5.65°C–20.65°C.

^q*Gysel et al.* [2004]; TDMA measurements at 25°C.

confirm that solution quantity had no significant impact in the results.

3.3. Measurement Uncertainties

[16] The vapor pressure apparatus was calibrated against values for pure water obtained from the Aerosol Inorganic Model (AIM) [*Clegg et al.*, 1998] for the 0°C–30°C temperature range. The vapor pressure curve obtained for pure water with our apparatus was 0.2 ± 0.06 torr higher on average than the curve predicted by the AIM. All water vapor pressure measurements were calibrated by subtracting the difference between our values and the AIM values for pure water, for each temperature. In addition, a complete vapor pressure measurement sequence was performed with an empty vessel, including the full range of temperatures 0°C–30°C. The resulting vapor pressure measured was 0.2 ± 0.05 torr on average, showing that the positive bias observed in our pure water measurements was due to leaked air. These experiments confirmed that we were properly subtracting the contribution from air leaks during the calibration process.

[17] The precision of the water vapor pressure measurements was determined by calculating the standard deviation of the data set generated by at least eight replicates of the same set of experimental conditions. Four different sets of

conditions were tested to account for low and high temperature, low and high solute concentration, and solute groups from categories I and II. The uncertainty range in the water vapor pressure measurements was found to be 0.3–1.5% for all solutes but the fulvic acids. The higher uncertainty occurred at the lower temperatures. For the fulvic acids, reproducibility was assessed by measuring water vapor pressure versus temperature curves of duplicate solutions of Nordic reference fulvic acid (NRFA) at both high and low concentrations. The effect of solution aging

Table 2. Uncertainty in the RH Reported as a Function of Temperature

Temperature (°C)	Salts, Category I and II Solutes		Fulvic Acids	
	Low Molality (n = 8)	High Molality (n = 8)	Low Weight Percent (n = 5)	High Weight Percent (n = 7)
0	2.3	2.7	6.1	3.4
5	2.2	2.5	3.7	2.2
10	2.0	2.3	2.7	2.1
15	1.9	2.1	2.0	1.3
20	1.8	2.0	1.6	0.9
25	1.7	1.8	1.4	0.7
30	1.6	1.7	1.1	0.6

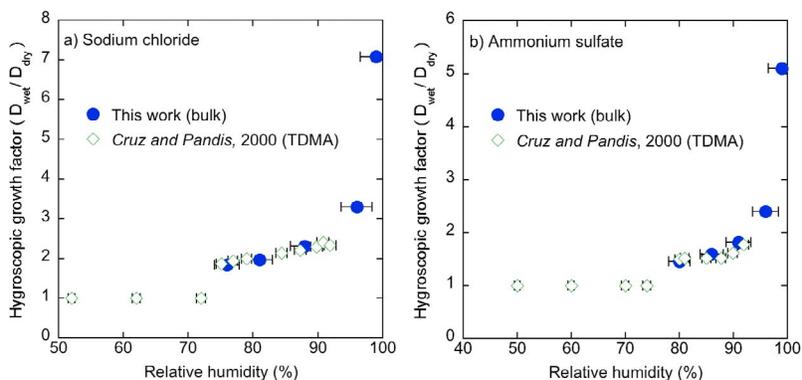


Figure 1. Hygroscopic growth of (a) sodium chloride and (b) ammonium sulfate particles as a function of RH calculated from our water vapor pressure data by using equation (1) (circles) and compared to values measured by *Cruz and Pandis* [2000] with the TDMA (diamonds).

on hygroscopic growth was also investigated to evaluate the possibility of testing multiple dilutions of the same solution. Water vapor pressure versus temperature curves were obtained for the same duplicate samples of NRFA at weeks 0, 1, 2 and 5 after the solution was made. Solutions were stored in a dark room maintained at 4°C to minimize aging. The uncertainty range in the measurements, derived from the standard deviation of this data set, was found to be 0.4–2.4% with the highest uncertainties resulting from the colder solution temperatures. The curves did not vary significantly throughout the 5 weeks. For Suwannee River fulvic acid, a second data curve was obtained by diluting its original solution from 37.8 wt % to 30.0 wt % and retesting it.

[18] For all solutes, the relative humidity (RH) was determined by taking the ratio of the measured vapor pressure over the solution to the saturation vapor pressure of

pure water at the same temperature. The DRH was obtained in the same manner but for visually saturated solutions. On the basis of the accuracy of the thermocouple and the uncertainty obtained for the vapor pressure measurements, the uncertainty of the RH is reported to be between 1.6 and 2.7% RH for category I and II solutes and between 0.6 and 6.1% RH for category III solutes. Table 2 lists maximum uncertainties for different temperatures and solutes.

4. Results and Discussion

[19] To validate our experimental method, water saturation vapor pressure (WSVP) was measured over aqueous solutions of sodium chloride and ammonium sulfate at 25.0°C and used to obtain their hygroscopic growth curves. Our WSVP data matched the values predicted by *Clegg et al.* [1998] within uncertainty limits. The DRHs of these inor-

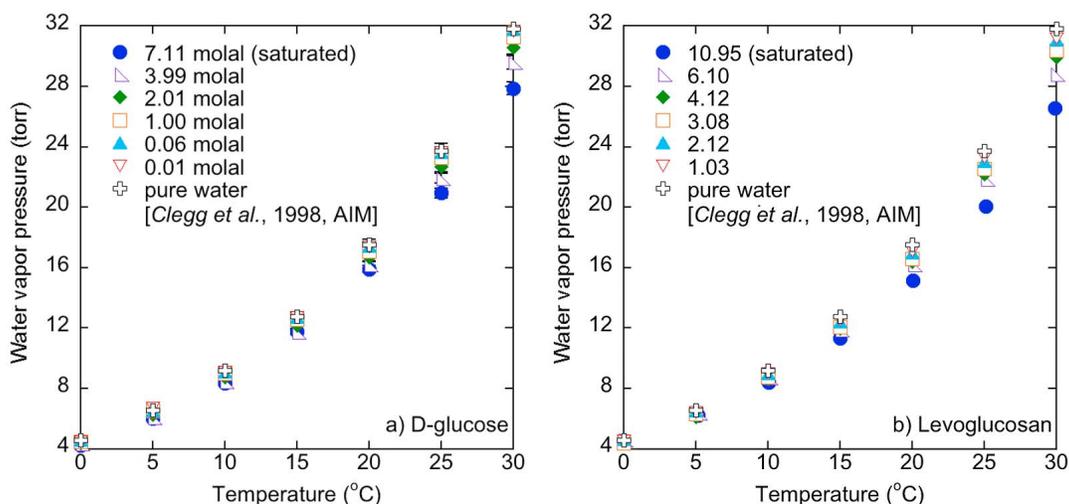


Figure 2. Measured water vapor pressure over aqueous solutions of (a) d-glucose and (b) levoglucosan as a function of temperature for different added solute concentrations compared to predicted values from the thermodynamic model of *Clegg et al.* [1998] for pure water (crosses). Note: Although the molalities are given for guidance on how much solute was added and to differentiate curves for solutions of different concentrations, they are not accurate, since solubility varies with temperature.

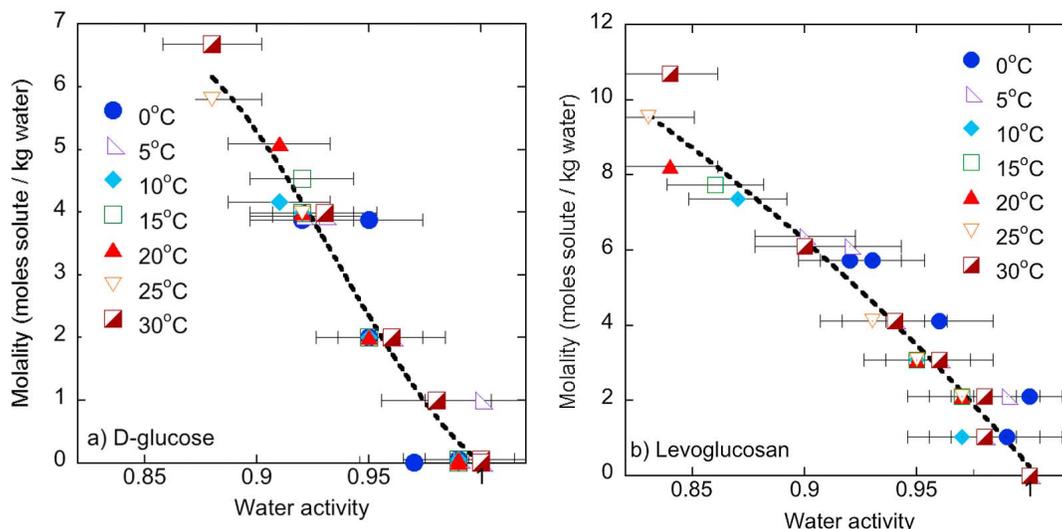


Figure 3. Actual solution molality as a function of water activity in the 0–30°C range for (a) d-glucose and (b) levoglucosan. The intermittent line in both figures represents a third-degree polynomial fit of the molality (m_{wet}^o) versus water activity (a_w) data for all temperatures. Water activity coefficients extracted from both fits to the data are displayed in Table 4.

ganic salts were also measured and are listed in Table 1. The results are in good agreement with values from the published literature, also listed in Table 1. Hygroscopic growth data as a function of RH was obtained from the WSVP versus temperature data by using equation (5) to calculate the water activity ($a_w = \text{RH}/100\%$) and equation (1) to calculate the corresponding G_f . Figures 1a and 1b show that the hygroscopic growth data obtained for sodium chloride and ammonium sulfate matched those reported by Cruz and Pandis [2000] with a TDMA.

4.1. Category I Solutes

[20] Water saturation vapor pressure versus temperature curves were obtained for two saccharides that are often found in atmospheric aerosols over biomass-burning regions: d-glucose and levoglucosan. These curves were obtained for various solution concentrations spanning the compound solubility in water. Figures 2a and 2b show that these curves follow the expected trend for compounds representative of category I: increasing solute concentration lowered the WSVP over both solutions. Note that the solution molality in the plot refers to the molality as calculated with the amount of solute and water added, irrespective of the quantity of solute dissolved, which is temperature dependent. The actual solution molality, accounting for the effect of temperature on solubility, was plotted as a function of water activity for both sugars in Figures 3a and 3b. Added molality and data on solubility as a function of temperature were used to calculate the actual, or dissolved, molality of these solutions. Solubility as a function of temperature data was obtained from Stephen and Stephen [1963] for d-glucose. Because solubility data for levoglucosan were not available in the literature, solubility experiments in the 0°C–30°C temperature range were performed. Water was added to a visibly saturated solution at the target temperature, one drop at a time, until visual

inspection confirmed that the solid present was dissolved. The saturation concentration was determined to be in the range between the concentration before and after the final drop of water. The solubility values obtained for 0°C, 10°C, 20°C, and 30°C are presented in Table 3, along with their associated uncertainties.

[21] Within experimental error, no temperature effect on water activity was observed for d-glucose and levoglucosan for temperature range 5°C–30°C. For both solutes, some of the data points taken at 0°C slightly deviate from the average of all the data, indicating a minor temperature effect at the coldest temperature tested. This observation is consistent with the hypothesis that the temperature dependence of the water activity coefficients is small under lower tropospheric conditions [Jacobson, 2005]. The molality versus water activity data for d-glucose and levoglucosan was fit with a third-degree polynomial to extract the water activity coefficients (b_i) in equation (4); the b_i values are presented in Table 4. The resulting R-squared values, 0.947 and 0.949 respectively, indicate a good fit of the data. Both fits were inserted into equation (1) to calculate the hygroscopic growth curve as a function of RH for d-glucose and levoglucosan, respectively. Figures 4a and 4b show that the hygroscopic growth curves obtained for both saccharides are in excellent agreement with bulk, TDMA, and EDB data from the literature, further validating our experimental method. In the TDMA and EDB studies cited in Figures 4a and 4b, levoglucosan and d-glucose particles present

Table 3. Solubility of Levoglucosan as a Function of Temperature

Temperature (°C)	Solubility (molal)
0	5.73 ± 0.03
10	7.37 ± 0.05
20	8.23 ± 0.10
30	10.70 ± 0.10

Table 4. Water Activity Coefficients (b_i) Extracted From the m_{wet}^o Versus a_w Plot

Solute	b_i Coefficients in Expression $m_{wet}^o = b_0 + b_1 a_w + b_2 a_w^2 + b_3 a_w^3 + \dots$				R^2	Applicable Range for a_w	Applicable Temperature Range (°C)
	b_0	b_1	b_2	b_3			
D-glucose	-2.19219664976e+3	7.16444359866e+3	-7.72545661067e+3	2.75321994937e+3	0.947	0.881–1.00	0–30
Levoglucozan	5.52346654688e+1	-1.2254952103e+2	1.49148376112e+2	-8.1594730380e+1	0.949	0.828–1.00	0–30

reversible water sorption and desorption curves. As noted by those researchers [Peng *et al.*, 2001a; Mochida and Kawamura, 2004; Chan *et al.*, 2005], these curves indicate the presence of metastable supersaturated mixtures in the particles of both solutes. The difference between our data and the particle study data before the DRH is due to the fact that crystallization occurs before achieving these supersaturated mixtures in large bulk solutions.

4.2. Category II Solutes

[22] The hygroscopic behavior of succinic acid, phthalic acid, glutaric acid, and oxalic acid was studied as representative of category II compounds. DRH was measured for all solutes. The results are listed and compared to literature values in Table 1. Within uncertainty limits, our values matched those published in the literature for succinic, glutaric, and oxalic acid. Published DRH values were not found for phthalic acid. HGFs were derived from some of the DRH measurements, since the growth below the deliquescence point should be zero, yielding $G_f = 1$. The associated HGFs at RH = 85%, 90%, and 95% are compared with published bulk and particle measurements in Table 5. The HGF values will be discussed individually below.

[23] Two dicarboxylic acids of different solubilities were chosen for more in-depth study. Figures 5a and 5b show WSVP versus temperature curves for various solution concentrations of succinic and phthalic acids and saturation vapor pressure values for pure water generated by Clegg *et al.* [1998]. For both solutes, increasing the solute con-

centration, even to saturation, did not lower the WSVP over the solution below that of pure water. For succinic acid, full deliquescence was observed at a RH = 99.5% for a temperature of 25°C. This value agrees with the DRH obtained by Wise *et al.* [2003] using a similar bulk method and with the literature DRH values in Table 1, within our uncertainty range. In addition, published TDMA, EDB, and bulk studies agree with our HGF findings for succinic acid, which were derived from both its DRH and WSVP curves (see Table 5). Similarly, our DRH and HGF results for glutaric acid match the published TDMA and bulk data but differ slightly from EDB and UNIFAC values.

[24] However, our measurements for the two other solutes tested in this category disagree with some results in the published literature. Deliquescence was not observed for phthalic acid by RH = 99.5%. The measured WSVP curves and DRH observations indicate no hygroscopic growth for phthalic acid within the 0°C–30°C temperature range. Our results are in disagreement with Brooks *et al.* [2004], the only other published study to date to report the hygroscopic behavior of phthalic acid. They measured a hygroscopic growth factor of 1.15 and 1.19 for phthalic acid particles at RH of 85% and 90%, respectively, using the TDMA. Another instance where our measurements disagree with TDMA measurements is the growth of oxalic acid. Our DRH value and associated hygroscopic growth results for oxalic acid are in agreement with two bulk studies [Peng *et al.*, 2001b, Wise *et al.*, 2003], one EDB study [Peng *et al.*, 2001b] (except for a slight difference at RH = 90%),

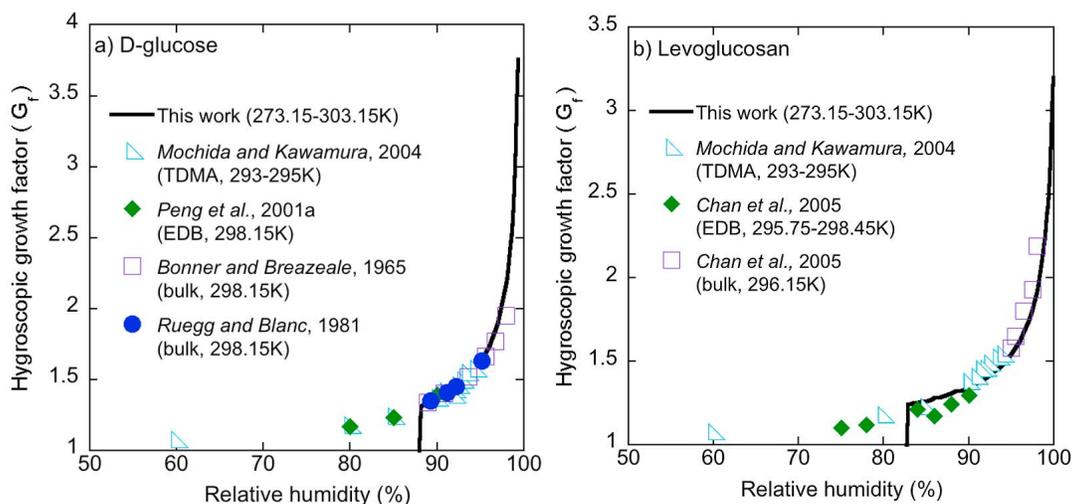


Figure 4. Hygroscopic growth of (a) d-glucose and (b) levoglucosan particles as a function of RH for diverse temperature ranges: derived from our bulk measurements (solid line), and measured by the TDMA (triangles), EDB (diamonds), and other bulk methods (squares, circles). Our hygroscopic growth curve was obtained by inserting the molality versus water function obtained for each solute into equation (1).

Table 5. Hygroscopic Growth Factor (G_f) Data Comparison

Species	G_f (85%)		G_f (90%)		G_f (95%)	
	Our Work	Other Studies ^a (TDMA, EDB ^b , Model, Bulk)	Our Work	Other Studies (TDMA, EDB, Model, Bulk)	Our Work	Other Studies (TDMA, EDB, Model, Bulk)
Succinic acid	1.0 ^c	1.00 ^d , 1.06 ^e , 1 ^f , 1.0^g	1.0 ^c	1.00 ^d , 1.01 ^h , 1 ^f , 1.0^g	1.0 ^c	-
Phthalic acid	1.0 ^c	1.15 ± 0.05ⁱ	1.0 ^c	1.19 ± 0.05ⁱ	1.0 ^c	-
Oxalic acid	1.0 ^c	1.00 ^d , 1.03 ^f	1.0 ^c	1.00 ^d , 1.08 ^f , 1.43^g	1.0 ^c	-
Glutaric acid	1.0 ^c	1.00 ^d , 1.09 ^f , 1.13 ^e , 1.1 ± 0.1^j	1.25	1.25 ^d , 1.30 ^f , 1 ^k , 1.29^g	-	-
Suwannee		1.05ⁱ, 1.08 ± 0.05ⁱ		1.09ⁱ, 1.09 ± 0.05ⁱ		
River fulvic acid	1.0 ^c	1.19 ± 0.03 ^m , 1.07 ± 0.02ⁿ	1.0 ^c	1.13 ± 0.008^o , 1.25 ± 0.03 ^m	1.0 ^c	1.18 ± 0.008^o
Nordic Ref. fulvic acid	1.0 ^c	1.09 ± 0.003^p , 1.33 ± 0.03 ^m	1.0 ^c	1.14 ± 0.003^p , 1.45 ± 0.03 ^m	1.0 ^c	1.18 ± 0.003^p
Humic acid, Fluka	1.0 ^c	1.49 ± 0.06ⁱ	1.0 ^c	1.66 ± 0.07ⁱ	1.0 ^c	2.00 ± 0.08ⁱ

^aTo our knowledge, all available TDMA, EDB and bulk studies that reported the G_f of the solutes above were presented for comparison. Note that TDMA studies are shown in bold text, EDB in italic text, model predictions in underlined text and bulk studies in normal text.

^bFor EDB studies, the hygroscopic growth are typically reported as mass ratio ($m_{\text{wet}}/m_{\text{dry}}$) instead of the typical definition of G_f ($D_{\text{wet}}/D_{\text{dry}}$).

^cAll species have deliquescence above RH > 95%, therefore $G_f = 1.0$ (except glutaric acid, which has a DRH > 85%).

^dWise *et al.* [2003]; bulk measurements at 24.7°C–24.9°C.

^eAnsari and Pandis [2000]; G_f calculated from UNIFAC at RH = 10–85%.

^fPeng *et al.* [2001b]; EDB measurements at 25°C.

^gPrenni *et al.* [2001]; G_f obtained with TDMA from RH = 5–90, 30°C.

^hSaxena *et al.* [1995]; UNIFAC predictions, 25°C.

ⁱBrooks *et al.* [2004]; TDMA measurements at 30°C.

^jCrüz and Pandis [2000]; TDMA measurements at 22°C–26°C (50mm dry particles: NaCl, (NH₄)₂SO₄; 100 nm dry particles: glutaric acid).

^kPeng *et al.* [2001b]; bulk measurements at 25°C; $G_f = 1$ for RH under determined DRH.

^lSvenningsson *et al.* [2006]; TDMA measurements at 25°C–29°C.

^mChan and Chan [2003]; EDB measurements at 22.5°C–23.8°C.

ⁿHatch *et al.* [2009]; TDMA measurements at 20°C.

^oDinar *et al.* [2007]; TDMA measurements at 21°C–23°C; G_f at 95% was extrapolated.

^pGysel *et al.* [2004]; TDMA measurements at 25°C.

and UNIFAC predictions [Saxena *et al.*, 1995]. While our measured vapor pressure indicated no hygroscopic growth for oxalic acid at RH = 90%, Prenni *et al.* [2001] measured a 43% growth at the same RH with a TDMA. In that study, the authors state that because of the prediction of a DRH of 99% from the thermodynamic model, they did not expect to see growth in the RH range studied (5–90%). They propose that the growth observed was due to the lack of efflorescence when the particles were dried to <5% RH, so that the “dry” particles were actually concentrated solutions.

4.3. Category III Solutes

[25] Humic materials form through the decomposition of organic matter in soil and aquatic environments and are composed of polycarboxylic acids that contain aromatic and phenolic functional groups [Diallo *et al.*, 2003]. Humic acids form first and eventually break down into smaller fulvic acids. Well-characterized reference samples of both humic and fulvic acids are available from the IHSS and are routinely used in atmospheric aerosol studies as representative compounds for the HULIS fraction. Humic acid obtained from Fluka and two fulvic acids obtained from the

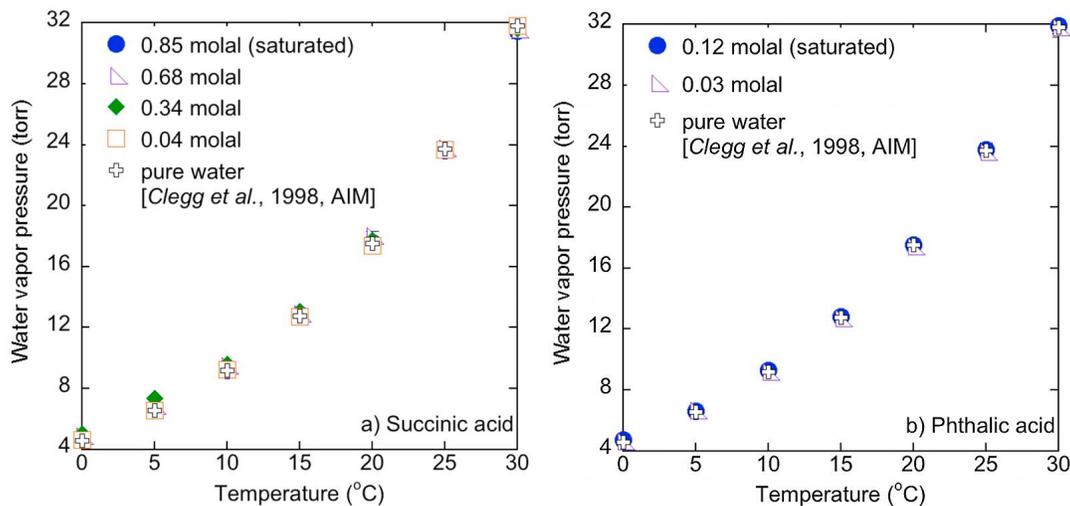


Figure 5. Measured water vapor pressure over aqueous solutions of (a) succinic acid and (b) phthalic acid as a function of temperature for different added solute concentrations compared to predicted values from the thermodynamic model of Clegg *et al.* [1998] for pure water (crosses).

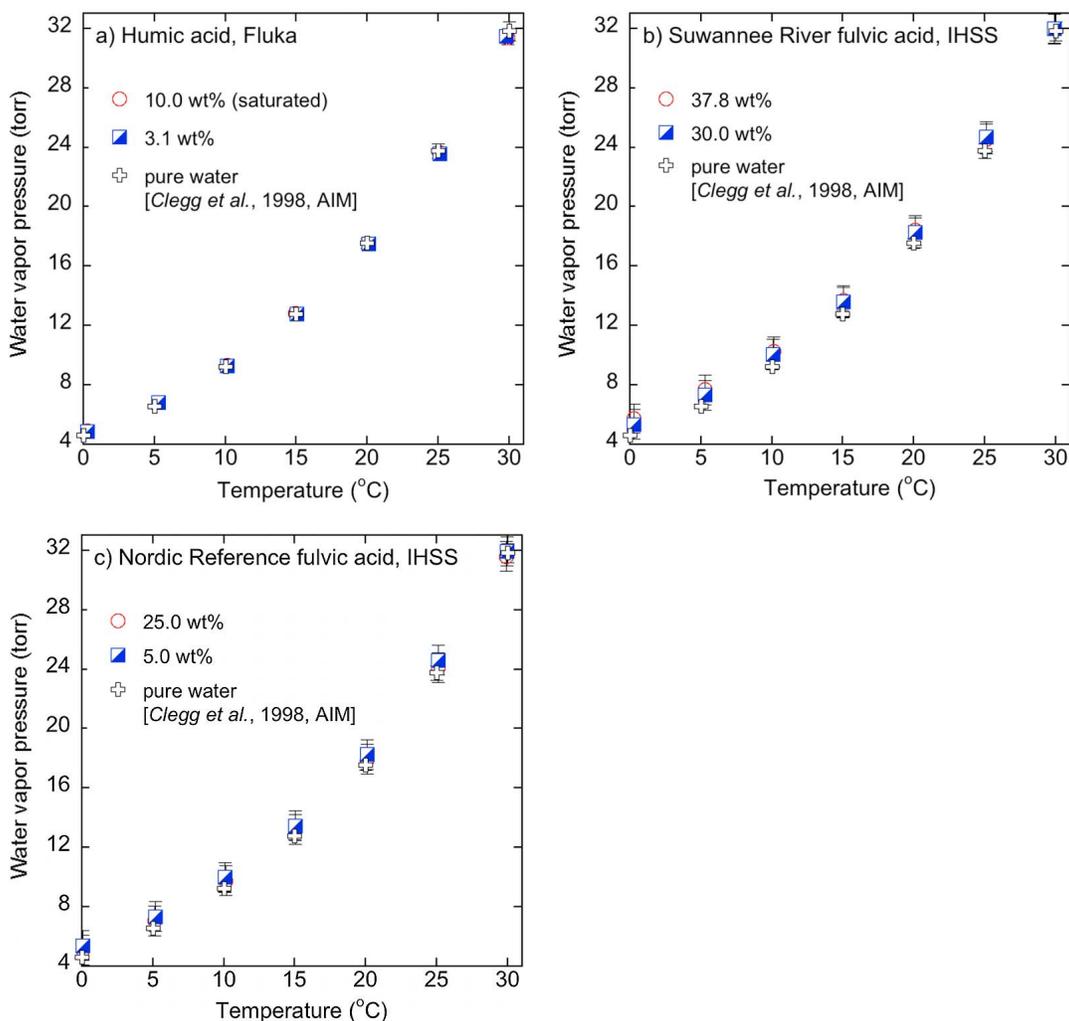


Figure 6. Measured water vapor pressure over aqueous solutions of (a) humic acid from Fluka, (b) Suwannee River fulvic acid from IHSS, and (c) Nordic reference fulvic acid from IHSS as a function of temperature for different added solute weight percentages compared to predicted values from the thermodynamic model of *Clegg et al.* [1998] for pure water (crosses).

IHSS were studied as representatives of water-soluble surfactants (category III compounds). The fulvic acid samples analyzed were Suwannee River Fulvic Acid Standard I and Nordic Aquatic Fulvic Acid Reference. Water vapor pressure versus temperature was plotted for various concentrations of these humic substances in Figures 6a, 6b, and 6c. Since the exact molecular structures and molecular weights for these compounds are unknown, their solution concentrations are reported on a weight percent basis. The highest concentration tested for each of the solutes was visually judged to be saturated, since the solutions appeared murky and nontranslucent. Aqueous solutions of 3.1 and 10.0 wt % Fluka humic acid did not exhibit vapor pressure curves different than that of pure water. Deliquescence for Fluka humic acid was not observed by RH = 99.5%. In contrast, *Brooks et al.* [2004] obtained hygroscopic growth factors for Fluka humic acid of 1.49 and 1.66 for RH = 85% and 90%, respectively. Similarly, the vapor pressure curves of aqueous solutions of Suwannee River fulvic acid (30.0 and 37.8 wt %), and of Nordic reference fulvic acid (5.0 and 25.0 wt %) did

not differ from that of pure water. However, various TDMA studies (see Table 5) have measured HGFs between 1.05 and 2.00 in the 85–95% RH range for Suwannee River and Nordic reference fulvic acids. In addition, one EDB study [*Chan and Chan, 2003*] reported HGFs between 1.19 and 1.45 in the 85–90% RH range for the same acids. In summary, the water vapor pressure curves and nondeliquescent behavior we obtained for all three humic substances indicate no water uptake for particles of equivalent composition. In contrast, various TDMA studies and one EDB study, all listed in Table 5, have measured a range of 5–100% hygroscopic growth on the same humic substance particles.

4.4. Disagreement with TDMA Measurements

[26] There are two possible explanations for the discrepancy between our results and those obtained with the TDMA for nondeliquescent organic compounds. The first possibility is that the particles did not effloresce when exposed to RH < 5%, resulting in concentrated solutions instead of dry particles. This irregularity could happen if

liquid phase diffusion is very slow for the concentrated solutions of certain solutes, so that the water does not have enough time to completely leave the particle. When concentrated droplets flow through the TDMA, instead of the assumed dry particles, measurements of the hygroscopic growth curve are inaccurate. This premise might explain why *Prenni et al.* [2001] obtained a 43% hygroscopic growth at RH = 90% with a TDMA for oxalic acid when other bulk and EDB studies, including ours, found no or minimal growth. In *Prenni et al.* [2001], the authors suggest the same premise for the unexpected growth curve and the lack of deliquescence transition they observed in the 5–90% RH range. It might also explain the discrepancies between our hygroscopic growth data for phthalic acid and the data from the TDMA study by *Brooks et al.* [2004]. In that study, the hygroscopic curve shown for phthalic acid presents smooth growth with no deliquescence transition, similar to that of oxalic acid in *Prenni et al.* [2001].

[27] The second possibility is that a small amount of water adsorption onto a dry particle can change the molecular structure, resulting in a nonspherical particle. The TDMA measures mobility diameter (D_{mob}), which is only equivalent to the mass equivalent diameter (D_{wet}) used in the calculation of the HGF for spherical particles. *Gysel et al.* [2004] confirmed (by scanning electron microscopy) that dry NRFA particles generated from nebulizing an aqueous solution and selected to have ~100 nm diameter using a DMA were near spherical. However, to our knowledge, there has been no confirmation that fulvic acid particles remain spherical as the ambient RH is increased. If in fact these particles do become nonspherical at high RH, it is plausible that a TDMA may read a false hygroscopic growth. A similar effect has been shown to occur with dry sodium chloride particle measurements by TDMA [*Mikhailov et al.*, 2004]. Dry NaCl particles are cubic [*Pruppacher and Klett*, 1997], and therefore their mobility diameter must be shape corrected to get an accurate mass equivalent diameter (D_{wet}). In their study, *Mikhailov et al.* [2004] observed that the partial dissolution of the crystal surface by adsorbed water as the RH was increased caused near-cubic NaCl particles to become near spherical at a RH below its DRH. While this process had no effect on the mass equivalent diameter, it decreased the mobility equivalent diameter ($D_{\text{mob,cube}} > D_{\text{mob,sphere}}$) measured, resulting in a lower reported hygroscopic growth factor. In other words, the TDMA measured a false hygroscopic growth in NaCl particles because of microstructural arrangements resulting from interactions with water vapor at an RH under the DRH. These microstructural arrangements have been reported in earlier studies. *Krämer et al.* [2000] found that the mobility equivalent diameter of dry NaCl particles in the 20–100 nm size range decreased by up to 50% upon interaction with water vapor at RHs under the DRH. *Gysel et al.* [2002] also applied a correction factor of 0.96 to the mobility diameter to calculate the correct HGF for NaCl particles in their TDMA experiments because of the cubic shape of these particles when dry.

[28] In the case of the humic substances, evidence in the literature supports small or no hygroscopic growth. Aqueous solutions of humic and fulvic acids exhibit properties similar to those shown for anionic surfactants [*Ragle et al.*, 1997; *Yates and von Wandruszka*, 1999]. Surfactants are usually organic compounds with a hydrophilic head and hydro-

phobic tail that lower the surface tension of a liquid. Micelle aggregates start forming in an aqueous surfactant solution as soon as the (typically low) critical micelle concentration is reached and increase in concentration as more surfactant is added [*Myers*, 1999]. A micelle is a spherical aggregate in which surfactant molecules are solubilized by orienting their hydrophobic tails toward the center and the hydrophilic heads toward the water. Micelle formation has the effect of lowering the water uptake by a particle by reducing the free ions in solution that would have lowered the vapor pressure by attracting water molecules [*Seinfeld and Pandis*, 1998]. Since the critical micelle concentration is often lowered by a mixture of surfactants, as in the case with humic substances, it is often attained with very low humic or fulvic acids concentrations [*Myers*, 1999]. All solutions prepared had the turbidity associated with micelles in solution, which is due to the micelle ability to scatter or absorb light far more efficiently than a clear solution. Thus, visual inspection and the fact that two of the solutions were over 25 wt % surfactant would lead us to assume that there was a high concentration of micelles in solution, lowering water uptake significantly.

5. Conclusions

[29] We have calculated the hygroscopic growth of inorganic salts, saccharides, dicarboxylic acids, and humic substances from water vapor pressure measurements over their respective aqueous solutions. Results obtained from this bulk method are reported and compared with previous published studies in which EBD or TDMA were used to directly measure the particle HGF and with the few other bulk studies available. We also report the deliquescence RH for all solutions. The DRH measured were in good agreement with published values for sodium chloride, ammonium sulfate, d-glucose, levoglucosan, succinic acid, glutaric acid, and oxalic acid. Deliquescence did not occur by 99.5% RH for phthalic acid, Suwannee River or Nordic reference fulvic acids, or humic acid. The hygroscopic growth data are in excellent agreement with published TDMA, EDB, and bulk G_f data for salts, d-glucose, levoglucosan, succinic acid and glutaric acid. However, our G_f data for phthalic, oxalic, humic, and fulvic acids disagree with published TDMA data and with at least one EDB study for the fulvic acids. In essence, the data show excellent agreement with previous EDB and TDMA measurements for cases where aerosols are known to deliquesce but poor agreement for various organic systems where the deliquescence process does not occur.

[30] As discussed previously, one possible explanation is that microstructural arrangements resulting from interactions with water vapor at a RH under the DRH, documented in NaCl particles, could result in higher hygroscopic growth readings with a TDMA. While dry 100 nm NRFA particles have been confirmed by electron microscopy to be near spherical, there is no confirmation in the literature that these particles remain so when exposed to increasing RHs. A second factor might be that the particles tested were not fully dried before entering the first of the tandem differential mobility analyzers, causing them to present an inaccurate hygroscopic growth curve. Either or both of these effects might explain the growth measured by the TDMA but not confirmed by our bulk method. Furthermore, in the case of

humic and fulvic acid, knowledge about surfactant behavior supports little to no hygroscopic growth.

[31] The very few published studies on hygroscopic growth of fulvic and humic acids were all conducted with particle measurement techniques. To our knowledge, ours is the first study to examine the hygroscopic growth of these particles by means of a bulk method. Studying the water uptake of particles with our bulk method has the limitation that the efflorescence branch of the hygroscopic growth curve cannot be examined because metastable large bulk solutions cannot be made. However, it is a simple method that eliminates the problems of fully drying particles, the effect of low residence times, and the uncertainties in particle solution concentrations that arise in direct particle measurement. Our bulk method presents an additional way to examine hygroscopic growth of atmospheric particles that can corroborate the data from particle measurements. A small error in the water uptake of organic particles could have a significant impact on important calculations for the atmosphere such as light scattering and cloud condensation nuclei when this error is aggregated over all the organic aerosol mass in the troposphere. Thus, it is of interest to conduct additional experiments with this bulk method to examine hygroscopic growth of other relevant atmospheric aerosol components, such as secondary organic aerosols and their mixture with salts and hydrophobic matter.

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