Deliquescence and Crystallization of Ammonium Sulfate Particles Internally Mixed with Water-Soluble Organic Compounds

Matthew T. Parsons, Daniel A. Knopf, and Allan K. Bertram*

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Z1

Received: August 17, 2004; In Final Form: October 15, 2004

The deliquescence and crystallization of ammonium sulfate particles internally mixed with water-soluble organic material have been studied, restricted to an organic mass fraction of less than 0.6. The organic species used were malonic acid, glycerol, levoglucosan (1,6-anhydro-β-D-glucopyranose), and Suwannee River fulvic acid. Our deliquescence results for systems with malonic acid and fulvic acid are in agreement with existing literature values. Glycerol deliquescence results are slightly lower than previous measurements. The levoglucosan results are the first of this kind. Total deliquescence relative humidities for the different systems are the same within the uncertainty of the measurements when the organic mole fraction is less than approximately 0.35. At an organic mole fraction of 0.6, the maximum deviation of total deliquescence relative humidities between the systems is approximately 10% relative humidity. We show that thermodynamic calculations based on a simplified version of a model recently proposed by Clegg et al. (*J. Aerosol Sci.* **2001**, *32*, 713)[1] are in agreement with measured values of deliquescence relative humidity up to an organic mole fraction of approximately 0.4 for most of the systems studied. The crystallization relative humidity (CRH) of mixed systems of ammonium sulfate with malonic acid, glycerol, or levoglucosan decreases significantly from the CRH of pure ammonium sulfate when the organic mole fraction is greater than about 0.25. This is in contrast to our previous study with glutaric acid where CRH remained close to CRH of pure ammonium sulfate up to a glutaric acid mole fraction of 0.4. CRH values are shown to vary depending on the type of organic present. In terms of atmospheric implications, we estimate that organics, on average, are only a minor perturbation on the deliquescence relative humidity of the pure inorganic particles, whereas the organics, on average, may decrease the CRH of pure inorganic particles significantly and this effect depends on the type of organic material.

1. Introduction

Aerosols can have a significant impact on climate, visibility, atmospheric chemistry, and health.[2,3] Before the role of particles in these processes can be quantified, however, the phase and hygroscopic properties of atmospheric particles must be understood and accurately represented. This is because the phase and water content govern the total mass of airborne particles, the amount of light they scatter and absorb, and their reactivity. For example, Thornton et al.[4] have shown that N_2O_5 reactivity on aerosol particles depends on the particle phase and water content. Martin et al.[5] have also shown that radiative forcing due to the direct aerosol effect varies by about 24% depending on the physical state of ammonium + sulfate + nitrate particles.

Studies have shown that aerosols can contain various ratios of inorganic to organic material, and this ratio depends on factors such as location.[6] Also, composition measurements of single particles have shown that organic material is internally mixed with inorganic species in the troposphere.[7,8] An average composition of urban fine particles, based on measurements at several sites, is 28% sulfate, 31% organic carbon, 8% ammonium, 9% elemental carbon, and 6% nitrate by weight.[6] Other field measurements suggest that the organic material typically accounts for 10−50% of the fine particle mass.[2] Despite the abundance of organic material present in aerosol particles, information about phase transitions and hygroscopic properties of organic and mixed organic−inorganic particles is not at a level comparable to inorganic particles.[9]

Hundreds of different organic species with a range of chemical and physical properties have been identified in atmospheric aerosols (see for example, ref 10). However, Fuzzi et al.[11] have suggested that the water-soluble organic material in aerosol particles can be represented with mixtures of the following classes of organic species: dialkyl ketones, polyols, polyphenols, alkanedioic acids, hydroxyalkanoic acids, aromatic acids, and polycarboxylic acids.

Two atmospherically relevant phase transitions are deliquescence and crystallization. Several groups have studied the deliquescence and crystallization of pure organic systems.[12−19] This work has shown that the deliquescence and crystallization properties of organic particles change significantly with the type of organic compound. More recently, Marcolli et al.[20] have shown that increasing the number of organic components in mixed solutions decreases the deliquescence relative humidity. Their study suggested that aerosol particles with numerous organic components are more likely to remain in the liquid state.

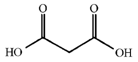
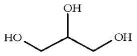
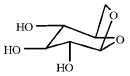
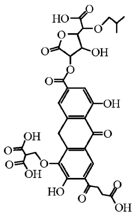
Several research groups have also studied the deliquescence and crystallization of mixed organic−inorganic particles.[21−35] Our preliminary studies suggested that the deliquescence and crystallization properties of inorganic particles only decreased slightly when the mole fraction of organic was less than 0.4.[21] This conclusion was similar to some previous conclusions

---

* To whom correspondence should be addressed. Phone: (604) 822-2113. Fax: (604) 822-2847. E-mail: bertram@chem.ubc.ca.

10.1021/jp0462862 CCC: $27.50 © 2004 American Chemical Society
Published on Web 12/07/2004

TABLE 1: Structures of Organic Species Used in This Study

Organic Compound [Class]	Structure
Malonic Acid [alkanedioic acid]	
Glycerol [polyol]	
Levoglucosan [polyol]	
Fulvic Acid [polycarboxylic acid] (proposed average structural model[66])	

concerning the effects of organics on inorganic phase transitions.[5,24] However, these conclusions are based on only a few organic species. As mentioned above, hundreds of different species with a range of chemical and physical properties have been identified in the atmosphere. Studies with other combinations of inorganics and organics are needed.

In the following we expand on our initial studies by investigating the deliquescence and crystallization of ammonium sulfate particles internally mixed with organic species having a range of chemical and physical properties. These systematic studies are restricted to compositions between 0 and 0.6 organic mass fraction and focus on the effect of organics on the deliquescence and crystallization of ammonium sulfate particles. Our previous measurements showed that glutaric acid only decreased the crystallization relative humidity and deliquescence relative humidity of pure inorganic particles by less than 10% over this entire composition range. Here we determine if other condensed-phase organics found in the atmosphere behave in a similar manner over this range.

The organics studied were malonic acid, glycerol, levoglucosan, and fulvic acid (see Table 1 for the chemical structures). These organics were selected to include several of the classes suggested by Fuzzi et al.[11] Sources of malonic acid, glycerol, and levoglucosan include biomass burning, tobacco smoke, and meat cooking.[10,36−40] Fulvic acid has not been measured in atmospheric aerosols, but it has been suggested as a reasonable model for polycarboxylic acids found in atmospheric aerosols.[11] In addition to measuring deliquescence and crystallization, we compared our measurements with thermodynamic and empirical calculations. These studies should provide further insight into the phase of atmospheric particles.

2. Experimental Section

The technique used in this study has been described in detail elsewhere.[12,21] Here we give an overview of the technique with an emphasis on the experimental conditions and procedures specific to these measurements.

The apparatus consisted of an optical microscope coupled to a flow cell. The particles of interest were deposited on the bottom surface of the flow cell and monitored with the microscope (using unpolarized light). The bottom surface of the flow cell, which supported the particles, consisted of a hydrophobic poly(tetrafluoroethylene) (PTFE) film annealed to a plain glass cover slide. Relative humidity with respect to water (RH) over the particles was controlled by a continuous flow of a mixture of dry and humidified N_2.

All observations were made at a temperature of 293.2 ± 0.1 K with a carrier gas flow rate of about 400 standard $cm^3\ min^{-1}$. Images of the particles in the flow cell were captured at a regular interval (approximately every 15 s) by a digital video camera attached to the microscope. From the images we could determine if the particles were liquid or contained solid material. The temperature of the particles and the dew point or ice frost point of the carrier gas were also recorded and associated with each image. These data were converted into RH using the Goff and Gratch equations.[41] During both deliquescence and crystallization experiments, the RH of the carrier gas over the sample particles was changed at a rate of approximately 0.4% min^{-1}. The uncertainty in measuring the relative humidity of the carrier gas is $\pm 0.3\%$, and the uncertainty in the reported deliquescence and crystallization results, based on the reproducibility of the data, is $\pm 2.1\%$ RH (95% confidence level).[12]

Ammonium sulfate (Fisher, 99.8%), malonic acid (Aldrich, 99%), glycerol (Fisher, 99.9%), levoglucosan (1,6-anhydro-β-D-glucopyranose, Fisher, 99+ %), and fulvic acid (International Humic Substances Society, Suwannee River reference) were all used as supplied. Fulvic acids are soluble in water at all pH values, which distinguishes these acids from humic acids. Bulk mixtures of various compositions were prepared gravimetrically and dissolved in purified 18.2 MΩ water (Millipore Simplicity 185). All solutions were passed through a 0.02 μm filter (Whatman Anodisc 25) twice prior to use. Solutions were then passed through a glass nebulizer producing a stream of submicron particles. These particles were directed onto the bottom surface of the flow cell, resulting in coagulation and the production of supermicron particles. Typically, between 5000 and 10000 particles were deposited on the bottom surface with a maximum diameter of about 15 μm. The diameter of particles monitored in our experiments ranged from 5 to 15 μm, with an average diameter of about 8 μm.

Prior to the deliquescence experiments, the particles were first subjected briefly to approximately 0% RH to crystallize the particles. The relative humidity was then increased to 60−70% RH and the deliquescence experiment started. At this relative humidity the particles were partially solid. The total time required for a single deliquescence experiment was less than 30 min.

In the crystallization experiments, the particles were exposed to decreasing RH starting at 25−40% RH after being placed into the apparatus. The observed particles did not contain any solid material at the start of the experiments. Crystallization experiments lasted at most 1 h from particle deposition to completion.

Evaporation of the organic material during any experiment was not significant due to the large number of particles, and hence the mass of material in the flow cell. This was confirmed by calculations of evaporation rates of the organics as well as separate experiments where we monitored particle size for extended periods of time at a constant relative humidity of approximately 35%. In these experiments, the particle size decreased by less than 2% over 2 h.

3. Results and Discussion

Shown in Figure 1A−D and 1E−H are images recorded during a typical deliquescence and crystallization experiment,

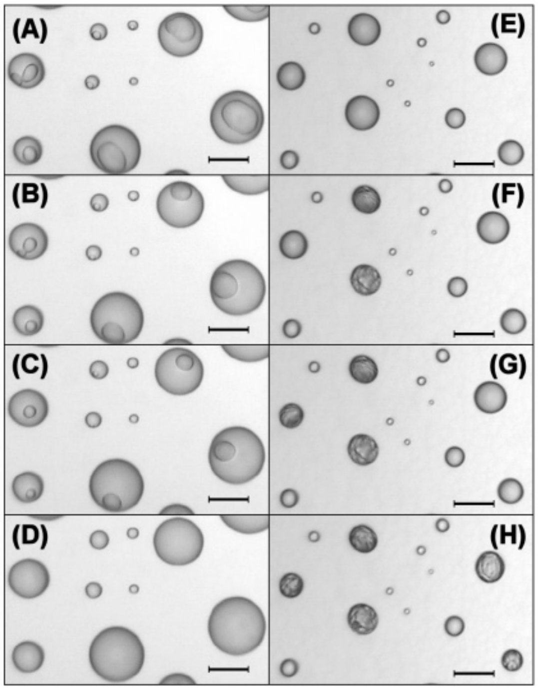


Figure 1. Images of ammonium sulfate + malonic acid particles ($x_{\mathrm{Mal}} = 0.240$) during deliquescence at RH equal to (A) 76.3%, (B) 77.2%, (C) 77.7%, and (D) 78.2%, and during crystallization at RH equal to (E) 30.4%, (F) 29.3%, (G) 29.2%, and (H) 28.1%. Bars indicate a distance of 10 μm.

respectively. Parts A−D of Figure 1 correspond to images of mixed malonic acid + ammonium sulfate particles (malonic acid mole fraction = 0.240) recorded while the RH was increased from 76.3 to 78.2%. In a system with two components plus water, a solid can exist in equilibrium with an aqueous solution over a range of RH as can be seen in Figure 1A−C. The results we report refer to when the particles fully deliquesced. In other words, our results correspond to when the given solids completely dissolved in the particles. In the following we refer to this as the total deliquescence relative humidity (DRH*) as done previously.[1] DRH* occurred between image C and D in Figure 1. Knowledge of the conditions at which particles fully deliquesce is important for predicting if particles are partially or completely solid in the atmosphere. This in turn is important for predicting the chemistry and physics of atmospheric aerosol particles. For example, to predict when ice nucleates on or in atmospheric particles, one first needs to know if the particles are pure liquids or contain solid material. The presence of solids can shift the mode of ice nucleation from homogeneous to heterogeneous and lower the supersaturation required for ice formation.

Parts E−H of Figure 1 correspond to images of mixed malonic acid + ammonium sulfate particles (with the same malonic acid mole fraction as discussed above) as the RH was decreased from 30.4 to 28.1%. Due to the stochastic nature of nucleation, all the particles did not crystallize at the same RH. The crystallization results we report below refer to the RH when half the particles have crystallized (50% CRH) and also the range over which crystallization was observed. We were unable to determine from the images of the particles if they were completely or partially solid after crystallization had occurred. In a future study we will use FTIR-microscopy to investigate if the particles are completely or partially solid after crystallization.

3.1. Total Deliquescence of Mixed Ammonium Sulfate + Organic Particles. Shown in Figure 2 are our DRH* results for mixed ammonium sulfate (AS) and malonic acid (Mal) particles together with previous measurements of this system. In these experiments, AS and Mal can precipitate at low RH, and the lowest DRH* for this system occurs at the eutonic composition.[42] At the eutonic composition, the solution is saturated with respect to both ammonium sulfate and malonic acid. The eutonic composition for the AS + Mal system was previously determined to be 0.645 malonic acid mole fraction.[25] When the malonic acid mole fraction is less than the eutonic composition, as is the case in our experiments, total deliquescence corresponds to the RH at which AS is saturated in the liquid ternary solution. It is possible that other salts, in addition to AS (such as letovicite or ammonium malonate), can precipitate in this system at low relative humidities, because malonic acid is a weak acid. Here we assume that these other salts are of minor importance as the K_a for malonic acid is small (pK_a = 2.85[43]). This assumption appears to be consistent with measurements by Braban and Abbatt.[22]

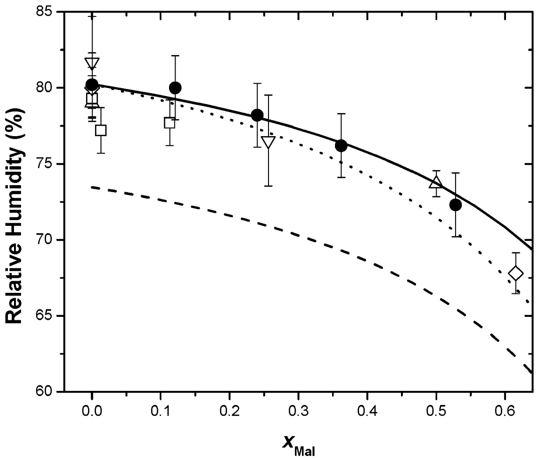


Figure 2. Measured and predicted DRH* for the AS + Mal system as a function of Mal mole fraction, x_{Mal} = moles of Mal/(moles of Mal + moles of AS): (●) this study; (▽) Brooks et al.;[25] (△) Choi and Chan;[28] (□) Prenni et al.;[34] (◇) Wise et al.;[35] (---) calculation 1; (···) calculation 2; (—) calculation 3. Calculations are described within the text.

Also shown in Figure 2 are results from other groups that have studied total deliquescence of the AS + Mal system. Our results are in agreement with these previous studies, which were performed with bulk solutions,[25,35] supermicron particles,[28] and submicron particles.[34] These previous studies were carried out at temperatures ranging from 293 to 303 K. The results show that DRH* decreases continuously with an increase in organic mole fraction over the range of compositions studied; however, this decrease is small (within the uncertainty of the measurements) when the organic mole fraction is less than approximately 0.35. In other words, the results are not statistically different.

DRH* of AS in the presence of glycerol (Gly) is reported in Figure 3. Gly is miscible in water and does not crystallize at room temperature. Hence, there is no eutonic composition for this system, and our results correspond to the total deliquescence of AS in the liquid ternary solution. Similar to the AS + Mal results, DRH* decreases continuously with an increase in organic mole fraction, and this decrease is small (within the uncertainty of the measurements) when the mole fraction of Gly is less than approximately 0.35. Also shown in Figure 3 are results from Choi and Chan[28] who studied DRH* of supermicron particles with an electrodynamic balance. The results from Choi and Chan[28] are approximately 4% RH higher than our measurements. The reason for this small difference is unclear.

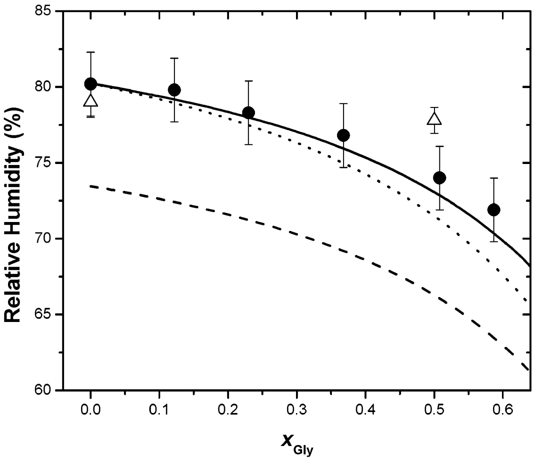


Figure 3. Measured and predicted DRH* for the AS + Gly system as a function of Gly mole fraction, x_{Gly} = moles of Gly/(moles of Gly + moles of AS): (●) this study; (△) Choi and Chan;[28] (---) calculation 1; (···) calculation 2; (—) calculation 3. Calculations are described within the text.

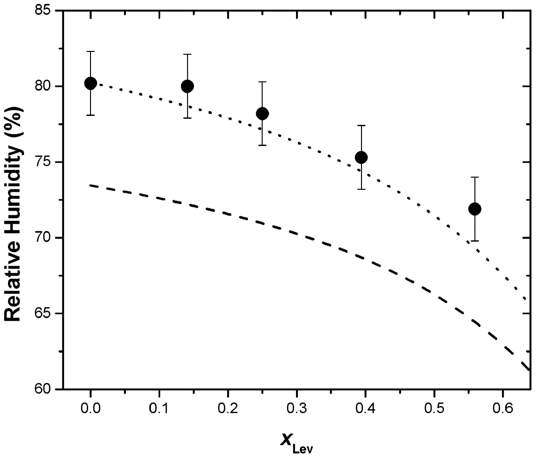


Figure 4. Measured and predicted DRH* for the AS + Lev system as a function of Lev mole fraction, x_{Lev} = moles of Lev/(moles of Lev + moles of AS): (●) this study; (---) calculation 1; (···) calculation 2. Calculations are described within the text.

Figure 4 shows our DRH* results for mixed AS + levoglucosan (Lev) particles. For comparison, the deliquescence relative humidity of pure levoglucosan particles is approximately 81.5%. This value was determined using the same procedure that we used to determine DRH* of mixed inorganic−organic particles. The eutonic composition for the AS + Lev system has not been measured, but on the basis of our data we suggest that it is greater than or equal to a Lev mole fraction of 0.6 ± 0.1, as this composition corresponds to the lowest DRH* measured in our experiments. Similar to AS + Mal and AS + Gly, DRH* decreases continuously with an increase in organic mole fraction. To our knowledge no other group has measured DRH* for this system.

Fulvic acids are a class of compounds with a range of functional groups depending on the source and isolation method. DRH* measurements of AS internally mixed with fulvic acid (Ful) are plotted as a function of Ful mass fraction (primary horizontal axis) and Ful mole fraction (secondary horizontal axis) in Figure 5. The Ful mole fraction scale is approximate and was calculated using an estimated molecular mass of 645 g mol^{-1}.[44]

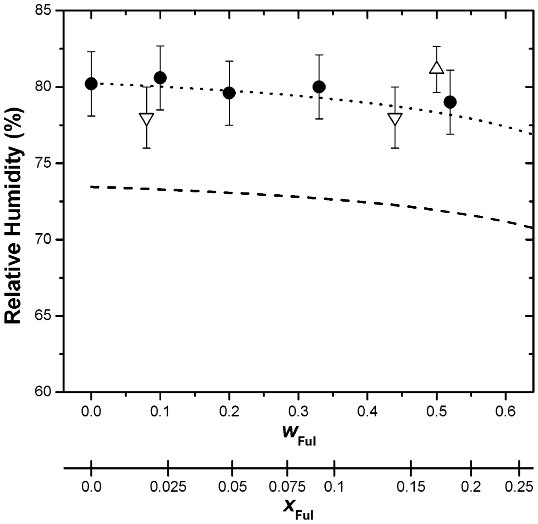


Figure 5. Measured and predicted DRH* for the AS + Ful system as a function of Ful mass fraction, w_{Ful} = mass of Ful/(mass of Ful + mass of AS): (●) this study; (▽) Brooks et al.;[23] (△) Chan and Chan;[26] (---) calculation 1; (···) calculation 2. Calculations are described within the text. The secondary scale of Ful mole fraction, x_{Ful} = moles of Ful/(moles of Ful + moles of AS), is approximate and based on an estimated molecular mass of 645 g mol^{-1} for this particular fulvic acid sample.[44]

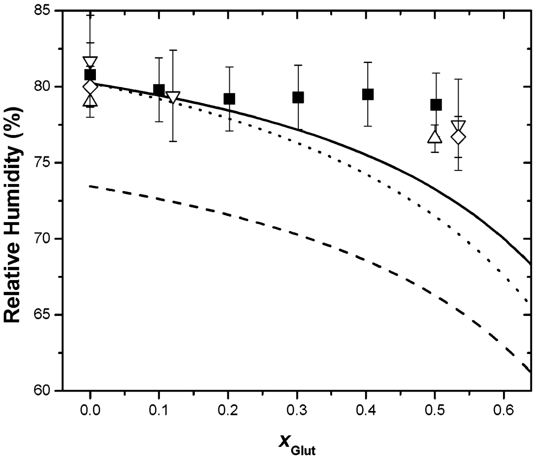


Figure 6. Comparison of thermodynamic calculations with previously measured values of DRH* for AS + Glut as a function of Glut mole fraction, x_{Glut} = moles of Glut/(moles of Glut + moles of AS): (---) calculation 1; (···) calculation 2; (—) calculation 3; (■) Pant et al.;[21] (▽) Brooks et al.;[25] (△) Choi and Chan;[28] (◇) Wise et al.[35]

Brooks et al.[23] and Chan and Chan[26] also measured water uptake of mixed AS + Ful particles using submicron and supermicron particles, respectively. These results are also included in Figure 5 and are in agreement with our observations of DRH*. As shown, DRH* for these particles does not change significantly up to 0.5 Ful mass fraction. This is not surprising as 0.5 Ful mass fraction corresponds to less than 0.2 Ful mole fraction. Mole fraction is the better variable for comparing DRH* values, as DRH* is linear with mole fraction, assuming ideality.[5] When the organic mole fraction is considered, DRH* for AS + Ful changes by about the same amount as for AS + Mal, Lev, or Gly.

In Figure 8, we compare our measurements of DRH* for all the systems we investigated (solid symbols). In addition, we have added our previous measurements of DRH* for AS + glutaric acid (Glut) particles.[21] This figure shows that DRH* values for the different systems are not statistically different from pure ammonium sulfate when the organic mole fraction is less than approximately 0.35. At an organic mole fraction of

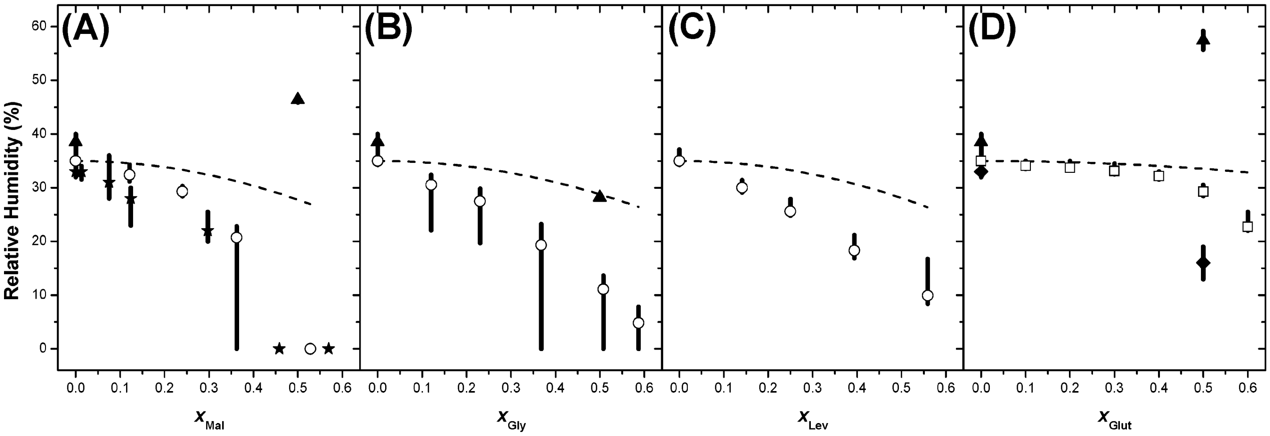


Figure 7. Crystallization of (A) AS + Mal, (B) AS + Gly, and (C) AS + Lev from the current study and (D) AS + Glut from our previous work[21] as a function of organic mole fraction, $x_{Organic}$ = moles of organic/(moles of organic + moles of AS). Data points represent 50% CRH and vertical bars indicate the range over which crystallization was observed. Key: (●) this study; (☐) Pant et al.;[21] (◆) Braban;[50] (★) Braban and Abbatt;[22] (▲) Choi and Chan.[28] Dashed lines represent a ΔRH offset of 45.2% RH from our measured DRH* data sets, as discussed in the text. Values of 0% RH signifies some or all particles were not observed to crystallize under dry conditions.

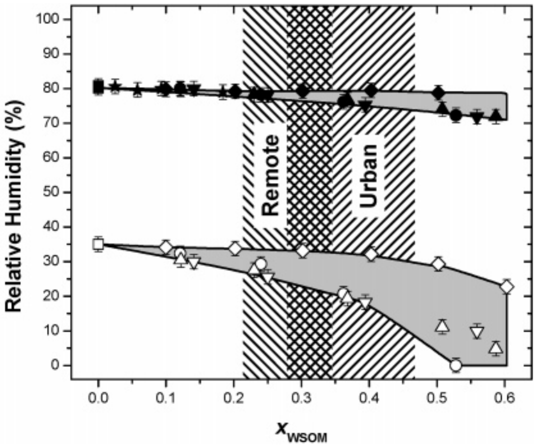


Figure 8. Summary of our DRH* (filled symbols) and 50% CRH (open symbols) results for AS + organic systems from the current study and our previous work:[21] (squares) pure AS; (circles) AS + Mal; (up triangles) AS + Gly; (down triangles) AS + Lev; (stars) AS + Ful; (diamonds) AS + Glut. Data are plotted in terms of water-soluble organic material (WSOM) mole fraction, x_{WSOM} = moles of WSOM/(moles of WSOM + moles of inorganic). The two overlapping hatched regions correspond to WSOM mole fraction in remote and urban aerosol particles as discussed within the text. Shaded regions show variation of data between each system.

0.6, the maximum deviation between the systems is approximately 10% RH. This is discussed in more detail below.

3.2. Thermodynamic Calculations of DRH* as a Function of Composition. In addition to measuring DRH*, we also compared our results with thermodynamic calculations. This comparison provides a test of the accuracy and validity of these calculations for predicting the thermodynamic properties of inorganic−organic particles in the atmosphere.

As discussed above, our DRH* results for AS + Mal and AS + Gly correspond to total deliquescence of AS. We assume that our DRH* results for AS + Lev and AS + Ful also correspond to total deliquescence of AS. This assumption is reasonable considering the range of concentrations studied and the trend in our DRH* data (DRH* either remains constant or decreases monotonically with the addition of organic material). We calculated total deliquescence of ammonium sulfate as a function of composition by first determining the concentrations of the liquid ternary solutions that are saturated with respect to ammonium sulfate, and then by predicting the relative humidities above these saturated solutions (see below for more details).

In the first series of calculations we assumed the solutes behave ideally. In this case, the solubility of ammonium sulfate (in terms of molality) in the liquid ternary solutions equals the solubility of ammonium sulfate in pure water. Also assuming ideality of the solutes, the RH above the saturated solutions, and hence DRH* of ammonium sulfate, can be predicted with the following equation:[20]

$$\mathrm{RH} = 100\% \cdot a_w = 100\% \cdot \exp\left(-M_w \sum_j m_j\right) \tag{1}$$

where a_w is the water activity, M_w is the molecular mass of water (0.018 kg mol^{-1}), and m_j is the molality of the solute j in the solution. Here we assume the inorganic salt is completely dissociated in the mixed solutions. Shown in Figures 2−5 (labeled calculation 1) are predictions of DRH* as a function of composition calculated with eq 1 and assuming the solutes behaved ideally. For these calculations a solubility of 5.71 mol kg^{-1} at 293.15 K was used on the basis of the Aerosol Inorganics Model by Clegg et al.[45−47]

Clearly, calculation 1 substantially underestimates DRH* for all systems even when the organic mole fraction is zero (pure ammonium sulfate particles). This is not surprising as electrolyte solutions depart significantly from ideality even in dilute solutions.

The second set of calculations was based on a simplified version of a recent model by Clegg et al.[1] Their model relies upon existing models of inorganic−water[45−47] and organic−water[48] solutions in combination with thermodynamically consistent terms that take into account the interactions between ions and organic molecules. In their model, the molal activity coefficients of an ion (γ_i) and an organic solute (γ_n) in a liquid ternary solution are given as follows:[1]

$$\ln(\gamma_i) = \Delta\ln(\gamma_i[\text{ion} - \text{water}]) + \Delta\ln(\gamma_i[\text{ion} - \text{organic}]) \tag{2}$$

$$\ln(\gamma_n) = \Delta\ln(\gamma_n[\text{organic} - \text{water}]) + \Delta\ln(\gamma_n[\text{ion} - \text{organic}]) \tag{3}$$

Each Δ term can be calculated independently and represents the contribution to the activity coefficient from ion−water, organic−water, or ion−organic terms.[1] The relationship for the water activity is given with respect to the osmotic coefficient of the solution, ϕ:[1]

$$\phi - 1 = (\phi' - 1)\left(\sum_i m_i\right)/\left(\sum_j m_j\right) + (\phi'' - 1)\left(\sum_n m_n\right)/\left(\sum_j m_j\right) + (\phi''' - 1) \quad (4)$$

Here, ϕ' is the osmotic coefficient contribution from the ionic−water interactions of the solution, ϕ'' is the contribution from the organic−water interactions, and ϕ''' is the contribution from ion−organic interactions.[1]

Equations 2−4 can be used to calculate the activity coefficients and osmotic coefficients for the liquid ternary solutions saturated with respect to ammonium sulfate. Then the RH above the liquid ternary solutions at total deliquescence of ammonium sulfate can be calculated with the following equation:

$$\mathrm{RH} = 100\%\cdot a_{\mathrm{w}} = 100\%\cdot \exp\left(-M_{\mathrm{w}}\phi\sum_j m_j\right) \quad (5)$$

where ϕ is given by eq 4. Shown in Figures 2−5 are predictions based on eqs 4 and 5. For these calculations (labeled calculation 2) we set the ion−organic interactions terms in eqs 2−4 to zero, as these parameters are not known for the systems studied. In this case, the solubility of ammonium sulfate in the liquid ternary solutions used in eq 5 equals the solubility in pure water (5.71 mol kg^{-1}). The first term in eq 4 was determined with the mole fraction based model of Clegg et al.,[46] and the second term in eq 4, which is the contribution from the organic solute to the osmotic coefficient, was set to zero. This is equivalent to assuming that the organic−water mixtures form ideal solutions.

As shown in Figures 2−5, calculation 2 reproduces our data up to 0.4 organic mole fraction. At higher organic mole fractions, the calculations slightly underpredict the measurements.

The third set of calculations was similar to the second set of calculations except that the second term in eq 4, $(\phi'' - 1)$, was calculated with the UNIFAC (Universal Quasi-Chemical Functional Group Activity Coefficients) model.[48] UNIFAC is a group contribution method that can be used for predicting thermodynamic properties of nonideal aqueous organic solutions. Interaction parameters from Reid et al.[49] were used in the UNIFAC calculations. Shown in Figures 2 and 3 (labeled calculation 3) are predictions based on this method. This procedure was not used to predict DRH* of AS + Lev and AS + Ful as the original UNIFAC model does not include interaction parameters for ring structures.

We also applied calculations 1−3 to our previous measurements of DRH* of the AS + Glut system.[21] Shown in Figure 6 are our previous results as well as these thermodynamic calculations. We have also included experimental results from other groups for completeness.[28,50] Similar to the other organic systems studied, calculation 1 deviates significantly from measurements of DRH*. Both calculations 2 and 3 agree with the measurements up to about 0.2 Glut mole fraction but underestimate the measurements at higher Glut mole fractions.

Within the uncertainty of the measurements calculations 2 and 3 reproduce our data up to an organic mole fraction of 0.4 for AS + Mal, AS + Gly, and AS + Lev. The maximum deviation between our measurements and the calculations occurs for the AS + Glut system. For this system, calculations 2 and 3 were approximately 7 and 5% RH below the measurements, respectively. Also, for all the systems we considered calculation 3 was slightly better than calculation 2.

3.3. Crystallization of Ammonium Sulfate in Aqueous Organic Solutions. Parts A−C of Figure 7 show our CRH measurements of AS + Mal, AS + Gly, and AS + Lev. Also shown in Figure 7D, for comparison purposes, are data for AS + Glut particles from our previous study.[21] The data points in Figure 7 correspond to 50% CRH and the vertical bars associated with each point correspond to the range over which crystallization was observed.

CRH data for the AS + Ful system were not measured because of experimental difficulties. For particles of pure AS, AS + Mal, AS + Gly, and AS + Lev, the contact angle with the PTFE surface was approximately 90°. In contrast, the contact angle between AS + Ful particles and the PTFE surface was close to 0° at relative humidities less than approximately 50% RH, which is close to the expected CRH values for this system. Because of this, we were unable to accurately determine the CRH values for these particles.

As shown in Figure 7A−D, pure AS (organic mole fraction = 0) crystallized over the range 37.1−34.3% RH, and half the particles were crystalline at 35.0% RH in this study. This is in good agreement (within 3% RH) with most previous studies measuring homogeneous crystallization of pure AS using various techniques (see for example, refs 51−53). On the basis of this, we suggest the crystallization of AS is not affected by the presence of the PTFE surface supporting the particles in our experiments and crystallization occurred by homogeneous nucleation.

Also shown in Figure 7 are measurements of crystallization reported by other groups. Choi and Chan[28] studied crystallization of AS + Mal, AS + Gly, and AS + Glut particles and obtained values significantly above our results. This difference cannot be explained by particle size, as similar sizes were used in both experiments. One explanation is that the particles in the Choi and Chan[28] experiments may have contained trace amounts of contamination that acted as a heterogeneous nucleus for crystallization. Braban[50] and Braban and Abbatt[22] studied the CRH of AS + Glut and AS + Mal particles, respectively, and obtained results that are lower than ours; however, this difference can be explained by differences in particle size. Classical nucleation theory predicts that the crystallization relative humidity decreases with the volume of the particle, and the particle volume in the experiments by Braban[50] and Braban and Abbatt[22] were approximately 5 orders of magnitude less than the particle volume in our studies.

Not included in Figure 7 are results by Hämeri et al.[30] and Prenni et al.[34] Both groups studied crystallization of submicron AS + Mal particles using a tandem differential mobility analyzer. Hämeri et al.[30] did not observe crystallization of particles with a composition of 0.5 malonic acid mole fraction, and Prenni et al.[34] did not observe crystallization of particles with a composition of about 0.3 malonic acid mole fraction. These results are consistent with our measurements when the difference in particle size is taken into account.

As expected, our results in Figure 7A−D show that the crystallization relative humidity decreases with increasing organic mole fraction for all the mixed inorganic−organic systems studied. However, there are significant differences between each system. For example, at an organic mole fraction of about 0.5, AS + Mal particles did not crystallize even at 0% RH, whereas AS + Glut particles crystallize at approximately 30% RH.

In Figure 8 we compare our results of DRH* and 50% CRH for all the systems we studied. This figure clearly shows that the CRH results vary significantly from system to system at large organic mole fractions. Also the variation in the CRH results are considerably larger than the variation in the DRH* results. For example, at 0.6 organic mole fraction, DRH* varies by at most 10% RH, whereas the CRH results vary by 25% RH. This wide variation in CRH results can be reasoned with classical nucleation theory. As mentioned earlier, we suggest that our CRH results correspond to homogeneous nucleation. According to classical nucleation theory, the rate of homogeneous nucleation, J, in an aqueous solution can be expressed as the following:[54,55]

$$J = A \exp\left[-\frac{16\pi\gamma^3\nu^2}{3k^3T^3(\ln S)^2} + \frac{\Delta G'}{kT}\right] \qquad (6)$$

where A is the preexponential factor, ν is the molecular volume, γ is the interfacial tension, k is the Boltzmann constant, T is the temperature, S is the degree of supersaturation, and $\Delta G'$ is the activation energy for molecular motion across the embryo–matrix interface, which is a function of the viscosity of the solution.[54] Based on eq 6, one possible explanation for the variation in the CRH results is that the interfacial tension varies significantly from system to system at high organic mole fractions. This could lead to considerably different nucleation rates at similar relative humidities. Another possible explanation is that at low RH and high organic mole fractions, viscosity may be significant and vary from system to system. In this case, viscosity will limit the rate of nucleation (through $\Delta G'$). Yet another possible explanation is that the degree of supersaturation at a given relative humidity varies significantly with the type of organic material, due to nonideal behavior.

Colberg et al.[56] have shown that the CRH of $H_2SO_4/NH_3/H_2O$ aerosol particles can be estimated by subtraction of a constant relative humidity (ΔRH) from the DRH* curves. We have also recently used this procedure to predict the CRH of AS + Glut particles and found that this procedure works well for a Glut mole fraction of less than 0.4.[21] Shown as dashed lines in Figure 7A–D are predictions of CRH based on this procedure. For these predictions a ΔRH offset of 45.2% RH was used. Clearly, 50% CRH for AS + Mal, Gly, or Lev is significantly below these curves even with low organic content. We conclude that this procedure is not appropriate for most of the systems we studied.

3.4. Atmospheric Implications. Here we estimate the effect of organics on the deliquescence and crystallization of inorganic particles in remote and urban areas by comparing our DRH* and CRH results with literature estimates of the amount of water-soluble organic material (WSOM) in these areas.

On the basis of several field studies, Heintzenberg[6] estimated that the average composition of fine aerosol particles in remote areas is 11% organic carbon (by mass), 22% sulfate, and 3% nitrate, and the average composition of fine aerosol particles in urban areas is 31% organic carbon (by mass), 28% sulfate, and 6% nitrate. Furthermore, we estimate that the fraction of organic carbon that is water-soluble is between 41 and 80% (by mass) in remote areas and between 29 and 66% (by mass) in urban areas, on the basis of measurements of water-soluble organic carbon in the troposphere.[57−63] These values should be considered as rough estimates as they are based on limited data. From the numbers presented above we calculate that the average WSOM mole fraction is about 0.21–0.35 in remote areas and 0.28–0.47 in urban areas. (Here the WSOM mole fraction is defined as moles of WSOM/(moles of WSOM + moles of inorganic). To calculate the WSOM mole fraction from the % organic carbon, we followed the procedure outlined by Martin et al.[5] Briefly, the mass of ammonium was not considered when the WSOM mole fraction was calculated, as it was assumed that the sulfate and nitrate occur as molecular units combined with ammonium or protons. Also, it was assumed that each organic molecule contained an average of five carbon atoms, which is consistent with measured organic molecular masses in remote aerosol particles.[61] Nevertheless, further studies are needed to verify the accuracy of this number.

The two overlapping hatched regions in Figure 8 (labeled Urban and Remote) represent the range of WSOM mole fractions we calculated for urban and remote areas above. For the remote region, our measured DRH* values do not deviate significantly from the deliquescence relative humidity of pure ammonium sulfate (the difference is less than the uncertainty of the measurements). On the basis of this, we conclude the organics, on average, are only a minor perturbation on the DRH of the pure inorganic particles in remote areas. Even for the urban region the difference in DRH* from DRH of pure ammonium sulfate is small. This difference ranges from 0 to 7% RH, which is close to the uncertainty of our measurements. In contrast, the organics appear to have a larger effect on the crystallization of inorganic particles. For the remote region, the difference between the crystallization RH of pure AS and the mixed inorganic–organic ranges from about 0 to 15% RH and depends on the type of inorganic–organic particle. This difference is about 0–25% RH in the urban region. If we also consider the measurements by Braban[50] and Braban and Abbatt,[22] this difference is even larger. We conclude that the organics on average may decrease the CRH of pure inorganic particles significantly and this effect depends on the type of organic material.

Recently Martin et al.[5] estimated that an upper limit to the average mole fraction of WSOM in the atmosphere is approximately 0.27. This value was determined by converting atmospheric mass burdens of sulfate, nitrate, and organic material from the IPCC SC1 scenario for 2000[64] into relative global mole burdens. If we compare this value with our DRH* and CRH data, we obtain conclusions similar to the conclusions reached above for remote regions. That is, the organics are only a minor perturbation to the DRH of inorganic particles. This is the same conclusion reached previously by Martin et al.[5] on the basis of a more limited data set. In contrast, organics may decrease the CRH of inorganic particles slightly and this decrease will depend on the type of organic material.

Several limitations to the discussions above need to be considered. First, our discussions above are based on average organic mole fractions. In reality, atmospheric particles have a broad range of organic mole fractions, and some areas will have significantly higher water-soluble organic content than represented in Figure 8 (see for example, ref 65). For a more accurate description, this variable in the organic mole fraction needs to be considered. Second, the effect of surfactants, heterogeneous nucleation, and mass transfer were not considered. Studies are needed to determine if these factors can affect the phase transitions of mixed inorganic–organic particles in the atmosphere. Third, to determine the average organic mole fractions in the atmosphere, we assumed that each organic molecule contained five carbon atoms, as done previously.[5] As mentioned above, further studies are needed to verify the accuracy of this estimate. Fourth, as indicated above, particle size is important for crystallization. Our results of 50% CRH should be considered as upper limits for these systems because we use particle sizes greater than typically found in the atmosphere. The CRH of inorganic particles is not very sensitive to particle size, but initial comparisons suggest that the CRH of inorganic−organic particles vary significantly with particle size. Finally, our conclusions are still based on a limited data set. Studies of other inorganic−organic particles that are relevant to the atmosphere are needed.

4. Conclusions

We have measured DRH* of four atmospherically relevant internally mixed inorganic−organic systems. Our measurements agree well with previous results and show that DRH* has little dependence on the type of organic material. DRH* of AS decreases with increasing organic content but remains within 10% RH of pure AS for each of the systems we have studied up to an organic mole fraction of 0.6. The thermodynamic calculations based on a simplified version of the model from Clegg et al.[1] are in agreement with measured values of DRH* up to organic mole fraction of approximately 0.4 for most of the systems studied.

Our conclusions from crystallization measurements made for AS + Mal, AS + Gly, and AS + Lev show that even for particles with organic mole fraction as low as 0.2, crystallization behavior for internally mixed inorganic−organic particles depends on the type of organic material. Therefore, mixed inorganic−organic systems may be more likely to exist as liquid particles. This is in agreement with previous conclusions.[20−22] Predictions of crystallization from the method presented by Colberg et al.[56] have been shown to reproduce measured CRH values for some combinations of substances, but it does not reproduce the data for all systems considered here and should not be applied to inorganic−organic systems in general.

In terms of atmospheric implications, we estimate that organics on average are only a minor perturbation on the DRH* of the pure inorganic particles; whereas the organics on average may decrease the CRH of pure inorganic particles significantly and this effect depends on the type of organic material.

Acknowledgment. We thank S. T. Martin for numerous helpful discussions regarding the effects of organic molecules on the phase transitions of inorganic particles. We appreciate A. Pant for discussions about atmospheric implications of mixed inorganic-organic particles. We also thank J. P. D. Abbatt and C. F. Braban for sharing their data prior to publication and for helpful discussions on phase transitions of organic-inorganic particles. This research was supported by the Natural Sciences and Engineering Research Council of Canada, the Canadian Research Chair Program, and the Canadian Foundation for Innovation.

References and Notes

(1) Clegg, S. L.; Seinfeld, J. H.; Brimblecombe, P. *J. Aerosol Sci.* **2001**, *32*, 713.

(2) *Air Quality Criteria for Particulate Matter*; United States Environmental Protection Agency: Washington, DC, EPA/600/P-95/001, 1996.

(3) Finlayson-Pitts, B. J.; Pitts, J. N. *Science* **1997**, *276*, 1045.

(4) Thornton, J. A.; Braban, C. F.; Abbatt, J. P. D. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4593.

(5) Martin, S. T.; Hung, H.-M.; Park, R. J.; Jacob, D. J.; Spurr, R. J. D.; Chance, K. V.; Chin, M. *Atmos. Chem. Phys.* **2004**, *4*, 183.

(6) Heintzenberg, J. *Tellus* **1989**, *41B*, 149.

(7) Middlebrook, A. M.; Murphy, D. M.; Thomson, D. S. *J. Geophys. Res.* **1998**, *103*, 16475.

(8) Murphy, D. M.; Thomson, D. S.; Mahoney, T. M. J. *Science* **1998**, *282*, 1664.

(9) Jacobson, M. C.; Hansson, H.-C.; Noone, K. J.; Charlson, R. J. *Rev. Geophys.* **2000**, *38*, 267.

(10) Saxena, P.; Hildemann, L. M. *J. Atmos. Chem.* **1996**, *24*, 57.

(11) Fuzzi, S.; Decesari, S.; Facchini, M. C.; Matta, E.; Mircea, M.; Tagliavini, E. *Geophys. Res. Lett.* **2001**, *28*, 4079.

(12) Parsons, M. T.; Mak, J.; Lipetz, S. R.; Bertram, A. K. *J. Geophys. Res.* **2004**, *109*, art. no. D06212, doi: 10.1029/2003JD004075.

(13) Prenni, A. J.; DeMott, P. J.; Kreidenweis, S. M.; Sherman, D. E.; Russell, L. M.; Ming, Y. *J. Phys. Chem. A* **2001**, *105*, 11240.

(14) Braban, C. F.; Carroll, M. F.; Styler, S. A.; Abbatt, J. P. D. *J. Phys. Chem. A* **2003**, *107*, 6594.

(15) Choi, M. Y.; Chan, C. K. *J. Phys. Chem. A* **2002**, *106*, 4566.

(16) Peng, C.; Chan, M. N.; Chan, C. K. *Environ. Sci. Technol.* **2001**, *35*, 4495.

(17) Demou, E.; Visram, H.; Donaldson, D. J.; Makar, P. A. *Atmos. Environ.* **2003**, *37*, 3529.

(18) Hansen, A. R.; Beyer, K. D. *J. Phys. Chem. A* **2004**, *108*, 3457.

(19) Peng, C.; Chan, C. K. *Atmos. Environ.* **2001**, *35*, 1183.

(20) Marcolli, C.; Luo, B. P.; Peter, T. *J. Phys. Chem. A* **2004**, *108*, 2216.

(21) Pant, A.; Fok, A.; Parsons, M. T.; Mak, J.; Bertram, A. K. *Geophys. Res. Lett.* **2004**, *31*, art. no. L12111, doi: 10.1029/2004GL020025.

(22) Braban, C. F.; Abbatt, J. P. D. *Atmos. Chem. Phys.* **2004**, *4*, 1451.

(23) Brooks, S. D.; DeMott, P. J.; Kreidenweis, S. M. *Atmos. Environ.* **2004**, *38*, 1859.

(24) Brooks, S. D.; Garland, R. M.; Wise, M. E.; Prenni, A. J.; Cushing, M.; Hewitt, E.; Tolbert, M. A. *J. Geophys. Res.* **2003**, *108*, art. no. 4487, doi: 10.1029/2002JD003204.

(25) Brooks, S. D.; Wise, M. E.; Cushing, M.; Tolbert, M. A. *Geophys. Res. Lett.* **2002**, *29*, art. no. 1917, doi: 10.1029/2002GL014733.

(26) Chan, M. N.; Chan, C. K. *Environ. Sci. Technol.* **2003**, *37*, 5109.

(27) Chen, Y.-Y.; Lee, W.-M. G. *J. Environ. Sci. Health A* **2001**, *36*, 229.

(28) Choi, M. Y.; Chan, C. K. *Environ. Sci. Technol.* **2002**, *36*, 2422.

(29) Cruz, C. N.; Pandis, S. N. *Environ. Sci. Technol.* **2000**, *34*, 4313.

(30) Hämeri, K.; Charlson, R.; Hansson, H.-C. *AIChE J.* **2002**, *48*, 1309.

(31) Hansson, H.-C.; Rood, M. J.; Koloutsou-Vakakis, S.; Hämeri, K.; Orsini, D.; Wiedensohler, A. *J. Atmos. Chem.* **1998**, *31*, 321.

(32) Lightstone, J. M.; Onasch, T. B.; Imre, D.; Oatis, S. *J. Phys. Chem. A* **2000**, *104*, 9337.

(33) Mikhailov, E.; Vlasenko, S.; Niessner, R.; Pöschl, U. *Atmos. Chem. Phys.* **2004**, *4*, 323.

(34) Prenni, A. J.; De Mott, P. J.; Kreidenweis, S. M. *Atmos. Environ.* **2003**, *37*, 4243.

(35) Wise, M. E.; Surratt, J. D.; Curtis, D. B.; Shilling, J. E.; Tolbert, M. A. *J. Geophys. Res.* **2003**, *108*, art. no. 4638, doi: 10.1029/2003JD003775.

(36) Graedel, T. E.; Hawkins, D. T.; Claxton, L. D. *Atmospheric Chemical Compounds: Sources, Occurrence, and Bioassay*; Academic Press: Orlando, 1986.

(37) Havers, N.; Burba, P.; Lambert, J.; Klockow, D. *J. Atmos. Chem.* **1998**, *29*, 45.

(38) Kawamura, K.; Seméré, R.; Imai, Y.; Fujii, Y.; Hayashi, M. *J. Geophys. Res.* **1996**, *101*, 18721.

(39) Nolte, C. G.; Schauer, J. J.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1999**, *33*, 3313.

(40) Simoneit, B. R. T.; Schauer, J. J.; Nolte, C. G.; Oros, D. R.; Elias, V. O.; Fraser, M. P.; Rogge, W. F.; Cass, G. R. *Atmos. Environ.* **1999**, *33*, 173.

(41) Goff, J. A.; Gratch, S. *Trans. Am. Soc. Heat. Ventil. Eng.* **1946**, *52*, 95.

(42) Kirgintsev, A. N.; Trushnikova, L. N. *J. Russ. Inorg. Chem.* **1968**, *13*, 600.

(43) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 82nd ed.; CRC Press: Cleveland, OH, 2002.

(44) Aiken, G. R.; Brown, P. A.; Noyes, T. I.; Pinckney, D. J. Molecular Size and Weight of Fulvic and Humic Acids from the Suwannee River. In *Humic Substances in the Suwannee River, Georgia: Interactions, Properties, and Proposed Structures*; Averett, R. C., Leenheer, J. A., McKnight, D. M., Thorn, K. A., Eds.; U.S. GPO: Denver, 1994; pp 89−97.

(45) Clegg, S. L.; Brimblecombe, P.; Wexler, A. S. Aerosol Inorganics Model, URL: http://www.hpc1.uea.ac.uk/∼e770/aim.html, 2002.

(46) Clegg, S. L.; Brimblecombe, P.; Wexler, A. S. *J. Phys. Chem. A* **1998**, *102*, 2137.

(47) Wexler, A. S.; Clegg, S. L. *J. Geophys. Res.* **2002**, *107*, art. no. 4207.

(48) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.

(49) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(50) Braban, C. F. Laboratory Studies of Model Tropospheric Aerosol Phase Transitions. Ph.D. Thesis, University of Toronto, 2004.

(51) Cziczo, D. J.; Nowak, J. B.; Hu, J. H.; Abbatt, J. P. D. *J. Geophys. Res.* **1997**, *102*, 18843.

(52) Tang, I. N.; Munkelwitz, H. R. *J. Geophys. Res.* **1994**, *99*, 18801.

(53) Martin, S. T. *Chem. Rev.* **2000**, *100*, 3403.

(54) Mullin, J. W. *Crystallization*, 4th ed.; Butterworth-Heinemann: Oxford, Boston, 2001.

(55) Turnbull, D.; Fisher, J. C. *J. Chem. Phys.* **1949**, *17*, 71.

(56) Colberg, C. A.; Luo, B. P.; Wernli, H.; Koop, T.; Peter, T. *Atmos. Chem. Phys.* **2003**, *3*, 909.

(57) Balasubramanian, R.; Qian, W. B.; Decesari, S.; Facchini, M. C.; Fuzzi, S. *J. Geophys. Res.* **2003**, *108*, art. no. 4523.

(58) Decesari, S.; Facchini, M. C.; Matta, E.; Lettini, F.; Mircea, M.; Fuzzi, S.; Tagliavini, E.; Putaud, J.-P. *Atmos. Environ.* **2001**, *35*, 3691.

(59) Kleefeld, S.; Hoffer, A.; Krivácsy, Z.; Jennings, S. G. *Atmos. Environ.* **2002**, *36*, 4479.

(60) Krivácsy, Z.; Hoffer, A.; Sárvári, Z.; Temesi, D.; Baltensperger, U.; Nyeki, S.; Weingartner, E.; Kleefeld, S.; Jennings, S. G. *Atmos. Environ.* **2001**, *35*, 6231.

(61) Krivácsy, Z.; Gelencsér, A.; Kiss, G.; Mészáros, E.; Molnár, A.; Hoffer, A.; Mészáros, T.; Sárvári, Z.; Temesi, D.; Varga, B.; Baltensperger, U.; Nyeki, S.; Weingartner, E. *J. Atmos. Chem.* **2001**, *39*, 235.

(62) Zappoli, S.; Andracchio, A.; Fuzzi, S.; Facchini, M. C.; Gelencsér, A.; Kiss, G.; Krivácsy, Z.; Molnár, Á.; Mészáros, E.; Hansson, H.-C.; Rosman, K.; Zebühr, Y. *Atmos. Environ.* **1999**, *33*, 2733.

(63) Maria, S. F.; Russell, L. M.; Turpin, B. J.; Porcja, R. J. *Atmos. Environ.* **2002**, *36*, 5185.

(64) Penner, J. E.; Andreae, M.; Annegarn, H.; et al. Aerosols, their Direct and Indirect Effects. In *Climate Change 2001: The Scientific Bases: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*; Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., van der Linden, P. J., Dai, X., Maskell, K., Johnson, C. A., Eds.; Cambridge University Press: Cambridge; New York, 2001; pp 289−348.

(65) Aklilu, Y. A.; Mozurkewich, M. *Aerosol Sci. Technol.* **2004**, *38*, 140.

(66) Leenheer, J. A.; McKnight, D. M.; Thurman, E. M.; MacCarthy, P. Structural Components and Proposed Structural Models of Fulvic Acid from the Suwannee River. In *Humic Substances in the Suwannee River, Georgia: Interactions, Properties, and Proposed Structures*; Averett, R. C., Leenheer, J. A., McKnight, D. M., Thorn, K. A., Eds.; U.S. GPO: Denver, 1994; pp 195−211.