Deliquescence and crystallization of ammonium sulfate-glutaric acid and sodium chloride-glutaric acid particles

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[1] In the following, we report the deliquescence relative humidities (DRH) and crystallization relative humidities (CRH) of mixed inorganic-organic particles, specifically ammonium sulfate-glutaric acid and sodium chloride-glutaric acid particles. Knowledge of the DRH and CRH of mixed inorganic-organic particles is crucial for predicting the role of aerosol particles in the atmosphere. Our DRH results are in good agreement with previous measurements, but our CRH results are significantly lower than some of the previous measurements reported in the literature. Our studies show that the DRH and CRH of ammonium sulfate and sodium chloride only decreased slightly when the mole fraction of the acid was less than 0.4. If other organics in the atmosphere behave in a similar manner, then the DRH and CRH of mixed inorganic-organic atmospheric particles will only be slightly less than the DRH and CRH of pure inorganic particles when the organic mole fraction is less than 0.4. Our results also show that if the particles contain a significant amount of organics (mole fraction > 0.5) the crystallization relative humidity decreases significantly and the particles are more likely to remain in the liquid state. Further work is needed to determine if other organics species of atmospheric importance have a similar effect. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation:** Pant, A., A. Fok, M. T. Parsons, J. Mak, and A. K. Betram (2004), Deliquescence and crystallization of ammonium sulfate-glutaric acid and sodium chloride-glutaric acid particles, *Geophys. Res. Lett.*, *31*, L12111, doi:10.1029/2004GL020025.

1. Introduction

[2] Aerosol particles play several key roles in the atmosphere. For example they influence the chemistry of the atmosphere by providing a medium for heterogeneous reactions, they decrease visibility in both urban and rural areas, and they affect climate by scattering and absorbing solar and terrestrial radiation. 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.

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[3] It is now well established that atmospheric aerosols consist of both organic and inorganic material. For example, an average composition of urban fine particles, based on measurements at several sites, is 37% sulfate, 24% organic carbon, 11% ammonium, 5% elementary carbon, and 4% nitrate by weight [*Heintzenberg*, 1989]. Single particle measurements have also shown that mixed organic-inorganic particles are abundant in the atmosphere [*Middlebrook et al.*, 1998; *Murphy et al.*, 1998].

[4] The phase and hygroscopic properties of pure inorganic particles, such as ammonium sulfate, have been studied extensively and are relatively well understood [*Martin*, 2000]. In contrast, very little is known about the phase and hygroscopic properties of organic and mixed organic-inorganic particles. Significantly more research is needed on this topic in order to predict accurately the role of aerosol particles in the atmosphere.

[5] In the following, we report measurements of the deliquescence and crystallization of ammonium sulfate-glutaric acid and sodium chloride-glutaric acid particles. Glutaric acid, which is a dicarboxlyic acid, has been identified as a component of atmospheric particles [*Kawamura et al.*, 1996; *Kerminen et al.*, 1999], and ammonium sulfate and sodium chloride are two of the major inorganic species found in atmospheric particulate material [*Finlayson-Pitts and Pitts*, 2000]. This study offers insight into the phase and hygroscopic properties of mixed organic-inorganic particles found in the atmosphere.

2. Experimental

[6] The apparatus has been described in detail elsewhere [*Parsons et al.*, 2004]. Briefly, the particles of interest were deposited on the bottom surface of the flow cell using a glass nebulizer. The bottom surface, which supported the particles, consisted of a hydrophobic polytetrafluoroethylene (PTFE) film annealed to a plain glass cover slide. The relative humidity in the cell, which was measured with a dew point hygrometer, was controlled by the continuous flow of a mixture of dry and humidified N_2. Flow rates ranged from 150 to 500 standard cm^3 min^{-1}.

[7] The size of particles monitored in the deliquescence experiments ranged from 2–20 μm, and the size of the particles monitored in the crystallization experiments were limited to diameters between 10–20 μm. Deliquescence and crystallization of the particles was monitored with a reflected-light microscope. Polarized light was used to enhance the contrast between solid and liquid particles. This technique is sensitive to small amounts of crystalline material present in the aqueous droplets. As an example, in the deliquescence experiments, we could identify solid

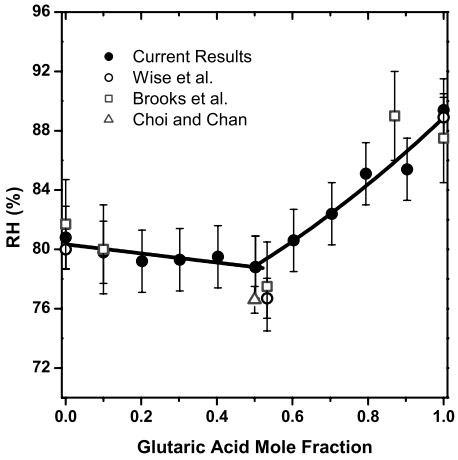

Figure 1. DRH of ammonium sulfate-glutaric acid particles. The data correspond to full deliquescence. See color version of this figure in the HTML.

inclusions present in the liquid droplets when the diameter of the solid inclusions was less than 1 μm in size. A 1 μm solid inclusion corresponds to less than 0.1% of the total mass of a 20 μm liquid droplet.

[8] During a deliquescence experiment the relative humidity was increased at a rate of 0.1–0.3% minute^{-1}, and during a crystallization experiment the relative humidity was reduced at a rate of 0.2–0.4% minute^{-1}. The temperature of the cell was maintained at 20.0 ± 0.1°C for all experiments. Typically 10–20 particles were monitored in a single experiment.

3. Results and Discussion

[9] *Deliquescence*. Shown in Figures 1 and 2 are the relative humidities at which ammonium sulfate-glutaric acid and sodium chloride-glutaric acid particles deliquesced. The results we report refer to when the particles fully deliquesced (and no solid remains) rather than the onset of water uptake. This is an important point as a solid can remain in equilibrium with an aqueous solution over a range of relative humidities in a multicomponent particle.

[10] The minimum deliquescence relative humidity for the ammonium sulfate-glutaric acid system and the sodium chloride-glutartic acid system occurred at 0.5 ± 0.1 mole fraction and 0.3 ± 0.1 mole fraction, respectively. These compositions correspond to the isothermal invariant points, which are also called the eutonic compositions [*Kirgintsev and Trushnikova*, 1968]. In Figure 1, the results to the left of the eutonic composition corresponds to full deliquescence of ammonium sulfate and the results to the right corresponds to full deliquescence of glutaric acid. In Figure 2, the results to the left of the eutonic composition corresponds to full deliquescence of sodium chloride; whereas the results to the right of the eutonic corresponds to full deliquescence of glutaric acid.

[11] Also included in Figures 1 and 2 are results from other groups. The work by *Wise et al.* [2003] and *Brooks et al.* [2002] were carried out with bulk solutions and the results from *Choi and Chan* [2002] were carried out with a single particle suspended in an electrodynamic trap. In all cases our results agree within experimental uncertainty with the previous measurements.

[12] The results shown in Figures 1 and 2 indicate that the deliquescence relative humidity of pure glutaric acid is suppressed when either ammonium sulfate or sodium chloride is added. Similarly the deliquescence relative humidity of pure ammonium sulfate and pure sodium chloride decreases when glutaric acid is added. The deliquescence relative humidity of ammonium sulfate and sodium chloride, however, only decreased slightly (within the uncertainty of the measurements) when the mole fraction of the acid was less than 0.4. *Brooks et al.* [2002] observed a similar trend for a series of dicarboxylic acids (malonic acid, glutaric acid, maleic acid, and L-malic acid) with ammonium sulfate.

[13] *Crystallization*. Shown in Figures 3 and 4 are the relative humidities at which the inorganic-organic liquid droplets crystallized. Due to the stochastic nature of nucleation, all the particles did not crystallize at the same relative humidity. The open circles correspond to where 50% of the

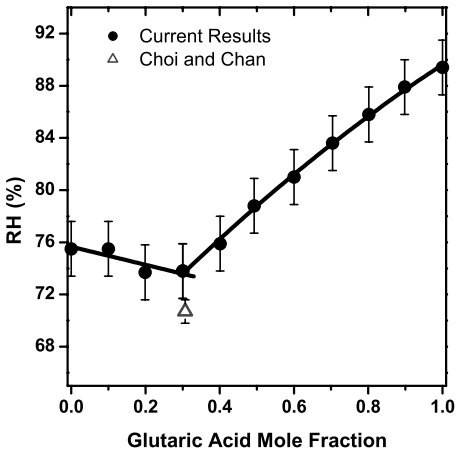

Figure 2. DRH of sodium chloride-glutaric acid particles. The data correspond to full deliquescence. See color version of this figure in the HTML.

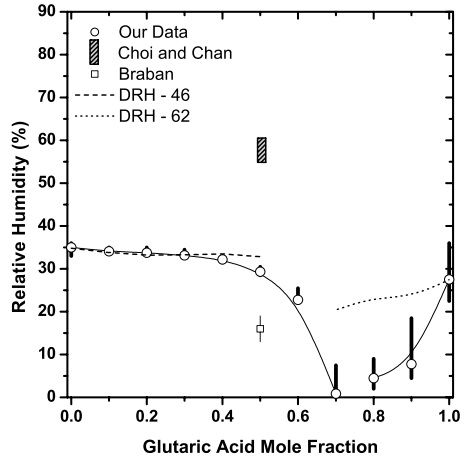

Figure 3. CRH of ammonium sulfate-glutaric acid particles. See text for details.

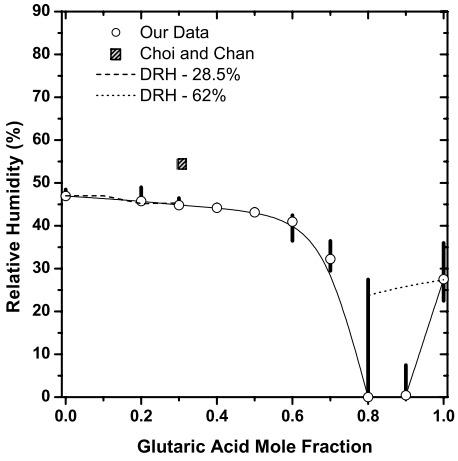

Figure 4. CRH of sodium chloride-glutaric acid particles. See text for details.

particles crystallized, and the vertical bars associated with the open circles correspond to the range over which we observed crystallization. For the remainder of the document we will refer to the relative humidity at which 50% of the particles crystallized as the crystallization relative humidity (CRH). We were unable to determine from the images of the particles if they were completely or partially solid after crystallization had occurred.

[14] The CRH results for pure ammonium sulfate and pure sodium chloride (mole fraction = 0.0 in Figures 3 and 4) are within 3% RH of most previous measurements (see for example *Martin* [2000] and *Tang and Munkelwitz* [1994]). This good agreement suggests that our technique is capable of measuring homogeneous nucleation of $(NH_4)_2SO_4$ and NaCl from aqueous solutions. In other words, the PTFE substrate supporting the particles does not influence the nucleation of these salts.

[15] Our crystallization results for pure glutaric acid particles (mole fraction = 1.0) are compared with measurements by other groups in Table 1. Also included in Table 1 are the observation times and particle sizes used in the experiments. Our results are in excellent agreement with measurements by *Peng et al.* [2001] but do not agree with the results from *Prenni et al.* [2001] and *Braban* [2004]. The difference between our results and the results presented by Prenni et al. and Braban may be due to differences in particle volume. Classical nucleation theory predicts th crystallization relative humidity decreases with the volume of the particle, and the particle volume in the experiments by Prenni et al. and Braban was approximately 6 orders of magnitude less than the particle volume in our studies.

[16] We have also included in Figures 3 and 4 results from other groups that have studied the CRH of ammonium sulfate-glutaric acid and sodium chloride-glutaric acid particles. The hatched bars represents the range over which Choi and Chan observed crystallization [*Choi and Chan*, 2002]. Clearly, Choi and Chan observed crystallization at significantly higher relative humidities than observed in our experiments. The 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 experiments contained trace amounts of contamination that acted as a heterogeneous nucleus for crystallization. Regardless, our experiments indicate that the CRH of these particles is significantly lower than previously suggested by Choi and Chan.

[17] Using an aerosol flow tube, Braban investigated the CRH of 0.5 mole fraction ammonium sulfate-glutaric acid particles [*Braban*, 2004]. The square in Figure 3 represents where ammonium sulfate crystallized in approximately 50% of the particles in their experiments. (From the IR spectrum they were able to conclude that only ammonium sulfate crystallized in the particles in their experiments.) The associated vertical line represents the range over which they observed crystallization. Our results are higher than the measurements by Braban; however, this difference may be due to a difference in particle size, as Braban studied submicron particles.

[18] Our results in Figures 3 and 4 show that the addition of small amounts of glutaric acid (mole fraction < 0.4) to pure ammonium sulfate or pure sodium chloride only lowers the CRH by less than 2% RH, which is within the uncertainty of our experiments. However, if the mole fraction is greater than this value, the CRH decreases significantly.

[19] Recently it was 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 deliquescence relative humidity (DRH) curves [*Colberg et al.*, 2003]. This was motivated by the procedure by *Koop et al.* [2000] who suggested that homogeneous nucleation of ice from aqueous solutions occurs at a concentration differing by a constant RH from the melting point curve. In contrast, *Martin et al.* [2003] studied the CRH of H_2SO_4–NH_3–HNO_3–H_2O particles, and they observed that the difference between the DRH and CRH varied from 40–55%. Here we investigate whether or not the CRH in our experiments can be predicted by subtraction of a constant relative humidity from the DRH curves. The dashed line in Figure 3 was calculated by subtracting 46% RH from the $(NH_4)_2SO_4$ deliquescence curve; the dashed line in Figure 4 was calculated by subtracting 28.5% RH from the NaCl deliquescence curve, and the dotted lines in Figures 3 and 4 were calculated by subtracting 62% RH from the glutaric acid deliquescence curves. The dashed lines overlap the measurements suggesting that this method is valid for predicting the crystallization relative humidity of

Table 1. CRH of Pure Glutaric Acid Particles

Reference	Temperature	Observation Time	Diameter	CRH
Current data	293 K	60 minutes to scan from 45–20% RH	10–20 μm	36–22.5%
Peng et al. [2001]	298 K	40 minutes to scan from 93–5% RH	10–20 μm	33–29%
Prenni et al. [2001]	303 K	<1 minute at fixed RH	0.1–0.05 μm	no[a]
Braban [2004]	293 K	<1 minute at fixed RH	submicron	no[a]

[a]Phase transition not observed when the particles were dried to less than 5% RH.

$(NH_4)_2SO_4$ and NaCl in these aqueous solutions (at least up to a mole fraction of 0.4). The dotted lines, however, do not reproduce the CRH values, suggesting that this procedure is not appropriate for predicting the CRH of glutaric acid in these aqueous solutions. One possible explanation is that at low RH and high mole fractions the solutions become highly non-ideal, and hence the thermodynamic properties of glutaric acid, such as supersaturation, are a strong function of both ΔRH and composition. Another possible explanation is that at low RH and high mole fractions viscosity becomes important and limits the rate of nucleation. This may also explain why crystallization occurred over a wide range when the composition was greater than 0.6 mole fraction. Further work is needed to understand this behavior.

[20] As mentioned above, the CRH results shown in Figures 3 and 4 correspond to when we first saw crystallization in the liquid droplets. We also observed a second phase transition at relative humidities below the CRH values when the composition was between approximately 0.2 and 0.6 mole fraction. This suggests that the individual particles did not completely crystallize at the CRH values when the composition was between 0.2 and 0.6 mole fraction. The second phase transition was clearly discernable from the images of the particles as this phase transition resulted in a sudden increase in the intensity of the particles when polarized light was used. The second phase transition will be the focus of a future publication.

4. Conclusions and Atmospheric Importance

[21] Our measurements of full deliquescence are in good agreement with previous measurements. These studies show that the addition of glutaric acid to ammonium sulfate or sodium chloride only decreases the DRH slightly if the mole fraction of the acid is less than 0.4. Our measurements of CRH are significantly lower than previous measurements by *Choi and Chan* [2002], and our results show that the addition of glutaric acid to either ammonium sulfate or sodium chloride only decreases the crystallization relative humidity slightly if the mole fraction is less than 0.4. If other organics in the atmosphere behave in a similar manner, then the DRH and CRH of mixed inorganic-organic atmospheric particles will only be slightly less than the DRH and CRH of pure inorganic particles when the organic mole fraction is less than 0.4. This conclusion is similar to previous conclusions concerning the effects of organics on inorganic phase transitions [*Braban*, 2004; *Brooks et al.*, 2002; *Martin et al.*, 2004].

[22] A large fraction of the particles in the atmosphere are sub-micron in size. Since the relative humidity at which particles crystallize decreases with particle volume, our CRH results provide an upper limit to the crystallization relative humidities of sub-micron particles with similar chemical compositions. Our results also show that if the particle contains a significant amount of organics (mole fraction > 0.5) the crystallization relative humidity decreases significantly and is more likely to remain in the liquid state. This conclusion, however, is based on one organic species, glutaric acid. Hundreds of different organic species have been identified in the atmosphere, and these species may have a range of chemical and physical properties [*Finlayson-Pitts and Pitts*, 2000]. Research on other organic species typically found in the atmosphere is needed.

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