Ammonium Bisulfate/Water Equilibrium and Metastability Phase Diagrams

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Though ammonium bisulfate is one of the most common of atmospheric hygroscopic aerosols, knowledge of its interaction with water has, until now, been extremely limited. This paper presents our observations on single isolated ammonium bisulfate aerosol particles, as they interact with water vapor at temperatures ranging from −40 to 30 °C. The complete phase diagram in the temperature/composition as well as the pressure/temperature domains has been derived here for the first time, mapping out equilibrium and metastable to stable phase transitions. A new low-temperature crystalline hydrate phase that might have an important role in processes occurring in the upper troposphere has been discovered.

Introduction

Hygroscopic aerosols, both natural and anthropogenic, are ubiquitous in the atmosphere. They serve as cloud condensation nuclei, redistribute atmospheric radiation, and provide sites for condensed phase reactions. These aerosols influence the climate either directly by scattering solar radiation back to space or indirectly by changing the optical properties and frequency of clouds.1

Sulfates, which have both natural and anthropogenic sources, are one of the most important atmospheric aerosols. They originate from sulfuric acid molecules which are produced by gas phase photochemical processes. These acidic aerosols are neutralized very rapidly in the lower atmosphere by reactions with ammonia. At low altitudes, therefore, where ammonia concentrations are high, the most common aerosol forms are (NH₄)₂SO₄ and (NH₄)₃H(SO₄)₂, while above the boundary layer the composition is closer to NH₄HSO₄. Under strong convective conditions NH₄HSO₄ aerosols can also be found at cirrus cloud altitudes where they could serve as ice-forming nuclei (IFN).

We present in this article, a brief summary of our observations on single suspended NH₄HSO₄ particles and their interaction with water vapor, at temperatures ranging from −40 to 30 °C. We have generated the NH₄HSO₄/H₂O phase diagram, and discovered a new crystalline hydrate phase that is stable at temperatures below −30 °C. We have been able to map out deliquescence, efflorescence, and solid-solid phase transitions and show that, unlike most hygroscopic aerosols, NH₄HSO₄ exhibits a strong temperature-dependent deliquescence behavior.

Experimental Section

The single particle levitation technique which was used for these studies has been described in detail elsewhere. It is essentially a low-temperature version of the one used in earlier studies.3,4 A single electrostatically charged 5−10 μm (diameter) NH₄HSO₄/H₂O droplet is suspended in an electrodynamic balance. First, the NH₄HSO₄ droplet is dried under vacuum at −260 K. Once dry, the particle is balanced in a dc field, and the voltage required to position the particle at the null point is noted. Water vapor is introduced gradually, and the pressure is monitored continuously using a capacitance manometer. The change in the particle’s composition as the temperature or relative humidity (RH) is varied is determined by measuring the mass-to-charge ratio (with an accuracy of ∼1%).

A vertically polarized HeNe laser is focused on the particle. The intensity of the scattered light is continuously monitored at a 90° angle from the incident laser, and the phase (solid or liquid) is determined from the Mie scattering.

To assure uniform temperature, the electrodynamic trap and the interaction chamber are constructed of copper. The chamber is insulated with a vacuum shroud and is in contact with a liquid nitrogen reservoir via heat transfer straps. An automated feedback heating loop is used to control the temperature to better than 0.2 K. The temperature is monitored at two points, above and below the particle, with the difference kept to less than 0.3 K. The reported temperature is the average between the two points. The system can be used to perform experiments at constant temperature or to scan temperature at a prescribed rate. Both modes were utilized to obtain the data presented here. When the temperature was scanned, the water vapor pressure was maintained at equilibrium with ice, by coating the cell walls with ice. The entire pressure and temperature monitoring system was calibrated against the ice frost line. The results reported here represent observations of over ∼20 particles.

Experimental Results

Figure 1 illustrates a hydration and dehydration cycle in a plot of particle mass expressed as the mole ratio H₂O/NH₄HSO₄ vs RH. (The RH throughout this paper is always calculated with respect to liquid water according to Tabata.)5 The cycle in Figure 1 is typical and, qualitatively, is much like the one observed at 25 °C,6 except that it was carried out at −25 °C. The path A to B represents the anhydrous NH₄HSO₄; at point B, the deliquescence point at −25 °C, the particle absorbs water rapidly to form the saturated NH₄HSO₄ solution droplet at point C. Based on the particle mass, the saturated solution concentration at −25 °C is 41% NH₄HSO₄ by mass. At this temperature the deliquescence point is at 58% RH compared to 40% RH at 25 °C.6,7 Increasing the RH beyond the deliquescence point produces a more dilute solution droplet at point D. The dehydration path (D−E) shows typical hysteresis, with the range C to E representing the metastable supersaturated solution. At this temperature efflorescence (point E) occurs at 34% RH.
A hydration (A→B→C→D→E→F) dehydration (F→G→A) cycle at 
\(-31.5^\circ C\) is shown in Figure 2. The path A to B is the 
anhydrous \(\text{NH}_4\text{HSO}_4\). At 52.5% RH a new feature appears 
where the solid particle absorbs exactly eight water molecules 
per molecule of \(\text{NH}_4\text{HSO}_4\) (B→C) to form a new solid of 
composition \(\text{NH}_4\text{HSO}_4\cdot8\text{H}_2\text{O}\). The stable phase between 
52.5% RH and 64% RH (C→D) is \(\text{NH}_4\text{HSO}_4\cdot8\text{H}_2\text{O}\). At 64% RH, \(\text{NH}_4\text{HSO}_4\cdot8\text{H}_2\text{O}\) deliquesces to form the \(34%\) \(\text{NH}_4\text{HSO}_4\) (by mass) solution droplet (E), the 
composition \(\text{NH}_4\text{HSO}_4\cdot8\text{H}_2\text{O}\). At 64% RH, \(\text{NH}_4\text{HSO}_4\cdot8\text{H}_2\text{O}\) deliquesces, forming an octahydrate phase at 
\(-31.5^\circ C\). On the reverse cycle (F→G) the efflorescence transition (G) occurs at a RH that is lower than 
the anhydrous to octahydrate transition, and consequently the 

guaze phase does not form along this dehydration path.

To complete the section of the phase diagram in which ice is 
the stable precipitate, we performed the experiment in the 
temperature scanning mode. Figure 3 illustrates this procedure. 
First, the particles were deliquesced at \(-10^\circ C\) (path \(\text{A}→\text{B}→\text{C}\)), and the water vapor pressure was increased to the point 
where it became constant, indicating that it is in equilibrium 
with the ice vapor pressure at this temperature (path \(\text{C}→\text{D}\)). The chamber was then sealed and the temperature decreased, 
as illustrated by path \(\text{D}→\text{E}→\text{F}\). This procedure assured that, 
along the \(\text{D}→\text{E}→\text{F}\) path, the water vapor pressure was mainta
ined equal to that of ice. The particle composition along the 
\(\text{D}→\text{E}\) path as a function of temperature is that of an \(\text{NH}_4\text{HSO}_4\) 
solution at equilibrium with ice. Note that, along this path of 
decreasing RH, efflorescence occurs (transition \(\text{E}→\text{F}\) at \(-35.1^\circ C\)) to form \(\text{NH}_4\text{HSO}_4\cdot8\text{H}_2\text{O}\).

Discussion

Equilibrium Phase Diagram. Data such as those shown in 
Figures 1→3 were used to construct the \(\text{NH}_4\text{HSO}_4/\text{H}_2\text{O}\) phase 
diagram. Figure 4 shows the \(\text{NH}_4\text{HSO}_4/\text{H}_2\text{O}\) equilibrium phase diagram in the composition—temperature domain. The pure 
solution region is designated by the striped area and the three 

solid phases: (1) anhydrous \(\text{NH}_4\text{HSO}_4\), and octahydrate are 
labeled. Two eutectic points at \(-33.5^\circ C\) and \(-30^\circ C\) for the 

octahydrate—ice and the anhydrous—octahydrate phases, re-

spectively, were determined. The narrow stability range for the 

octahydrate phase may explain why it has thus far escaped.
detection. The only data point that was available prior to the present work labeled a in Figure 4 is from Tang et al. 

Since atmospheric conditions are specified in terms of temperature and RH, from the perspective of understanding atmospheric processes, phase diagrams presented in the water vapor pressure–temperature domain are much more useful. Figure 5A shows the observed equilibrium phase transition in this system in a log($p_w$) vs 1/T plot; Figure 5B is an expanded view of the low temperatures. As in Figure 4, the striped area designates the pure solution region and the deliquescence transition lines are marked by a thick solid line. The solid—solid anhydrous to octahydrate phase transition line is indicated by clear squares. For reference, the water–ice frost line and the liquid water vapor pressure are also shown.

In the expanded view (Figure 5B) all four phases can be found. The shaded area marks the range of conditions where the octahydrate is the equilibrium phase. The rest of the symbols are as indicated in Figure 5A.

In the log($p_w$) vs 1/T plot the deliquescence points of the anhydrous NH$_4$HSO$_4$ (solid circles) form a nearly straight line. As shown in Figure 6 in a plot of RH vs temperature, the deliquescence transitions in this system exhibit a strong dependence on temperature, from 40% RH at 25 °C to 70% RH at −33.5 °C.

We have previously reported on the unique nonequilibrium crystalline phases that form in all of the bisulfate aerosol systems. The single particle room temperature experiments$^9$ have shown that in NH$_4$HSO$_4$ the equilibrium and the metastable phase form with equal probability. These two distinct crystalline anhydrous NH$_4$HSO$_4$ forms have different deliquescence points at 37% RH and 40% RH. Of the two, the second was shown to be the room temperature equilibrium phase. The fact that all the observed deliquescence points in the present experiments, conducted at lower temperatures, fall on a single line indicates that only one of these forms is accessible at low temperatures. To determine which of the two phases is the low-temperature form, a linear fit to the low-temperature data alone was extrapolated to 25 °C, yielding a deliquescence point of 40.5 ± 0.5% RH, consistent with the equilibrium phase.

**Metastability Phase Diagram.** In hygroscopic aerosols a useful rule of thumb is that phase transformations along the path of increasing RH occur at equilibrium, while phase transformations encountered along the reverse path commence from a metastable state.$^9$ To characterize the metastable transformations, we need a different type of (nonequilibrium) phase diagram, the boundaries of which define the boundaries of the metastable state(s). We can think of this as a “metastability phase diagram” whose boundaries mark the fundamental limit to metastability due to homogeneous nucleation. For example, measurements of the temperature at which homogeneous nucleation of supercooled liquid water occurs as a function of external pressure between 0 and 3 kbar$^{10}$ define the metastable phase boundary for pure supercooled water and provide a very valuable reference for understanding the single component nucleation mechanism. In this paper we have examined the effects of composition on homogeneous nucleation as a function of temperature.
Boundaries in equilibrium phase diagrams indicate the conditions of coexistence of two (or more) phases, and by analogy, boundaries in the metastability phase diagram indicate the conditions of coexistence (unstable equilibria) of the metastable phase with the critical nucleus (or nuclei) under conditions that the nucleation threshold is reached (rates of nucleation near unity). The metastability phase diagram represents a map of conditions where metastable to stable phase transformations occur, as such it is expected to be somewhat dependent on particle size. It is thus somewhat remarkable that distinct and reproducible boundaries to metastability are observed—given that the nucleation rate is controlled by kinetic as well as thermodynamic conditions. Nevertheless, observed homogeneous nucleation conditions are reproducible and appear to fall on continuous, well-defined boundaries. Roughly we understand that this behavior results because the rate of nucleation (in theory) has a characteristic exponential-prefactor structure with the thermodynamics in the exponent, which greatly dominates the nucleation rate.

A second important distinction is that equilibrium is a thermodynamic condition that applies between two or more extended phases, while the metastability equilibrium is between an extended supercooled phase and a nanoscale critical nucleus. Thus, surface free energy, which plays no role in the equilibrium phase diagram, is of vital importance to defining the boundaries of the metastable phase.

From the experimental standpoint, much of what we know about such transitions from the metastable phase is derived from...
experiments on bulk samples in contact with container walls. Under these conditions nucleation is most often initiated by a heterogeneous process involving either surface or interior impurity sites whose presence is generally random and not easily subject to experimental control. Impurity-induced nucleation occurs under different levels of supercooling for the simple reason that different impurity sites have different abilities to initiate the process. In contrast, both theory and experiments on ultrapure phase samples show very well-defined phase transition points. The freezing of pure water droplets, for example, shows that the nucleation rate changes 4 orders of magnitude over a span of 2 °C.11

In a recent study of the freezing of sulfuric acid droplets, it was found that the observed freezing points form a line in the temperature—composition domain not unlike the equilibrium ice/solution coexistence line, except that it is shifted by some 40 °C.12 This behavior is not limited to ice formation. We have recently investigated a variety of hygroscopic salts, all of which show that efflorescence occurs along well-defined lines.13,14

The metastability phase diagram for NH₄HSO₄ is constructed by combining our experimentally observed efflorescence points such as E and G in Figures 1 and 2, respectively, or E in Figure 3. The resultant phase diagram is presented in Figures 7 and 8 in the temperature/composition and water—pressure/temperature domains, respectively. We have observed three distinct types of metastable to stable transformations in this system. Upon efflorescence the supersaturated solution droplets can transform to either the anhydrous or the octahydrate phases. At all temperatures above −32.5 °C, the anhydrous phase forms, while below −32.5 °C the efflorescence process produced only the octahydrate phase. Metastability in this system is not limited to the solution phase. The equilibrium region where the octahydrate phase is stable is extremely limited, but once formed, this phase remains stable even at 0 RH, as long as the temperature remains below −27 °C (as observed for over 24 h). At temperatures below −38 °C—the freezing point of pure water droplets—and high RH, ice is the expected solid phase.

Conclusion

We have for the first time derived the phase diagram for the NH₄HSO₄/H₂O system and observed a new, low-temperature crystalline phase composed of NH₄HSO₄ with eight water molecules. The temperature dependence of the phase transitions either solid—solid or solid—liquid have been mapped, and the metastable, supersaturated solution efflorescence conditions have also been identified.

The phase diagrams presented in Figures 4, 5, 7, and 8 can now be used to predict the phase and composition of an NH₄HSO₄ aerosol under any atmospheric condition, provided the history of the air parcel is known. An anhydrous particle will not deliquesce as long as its temperature is kept below −33.5 °C. It can, however, increase in size (roughly double its mass) as its RH is increased due to the absorption of water and transform from the anhydrous to the octahydrate phase. At temperatures between −30 and −33.5 °C an increase in RH would first induce a transition from the anhydrous to the octahydrate state and eventually lead to deliquesce. Metastable solution droplets can be found at temperatures lower than −33.5 °C, but only if initially formed at a higher temperature.

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References and Notes

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