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The Search for Sulfuric Acid Octahydrate: Experimental Evidence

Keith D. Beyer,* Anne R. Hansen, and Michael Poston

Department of Chemistry, Wisconsin Lutheran College, Milwaukee, Wisconsin 53226

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We have investigated the H_2SO_4/H_2O binary liquid/solid phase diagram using a highly sensitive differential scanning calorimeter (DSC) and infrared spectroscopy of thin films. In particular we have sought to investigate the region from pure ice to sulfuric acid tetrahydrate (SAT), including a detailed look at the sulfuric acid octahydrate (SAO). Our studies have found that there is a unique, repeatable IR spectrum for SAO. Our spectrum is not merely a combination of spectra of ice and sulfuric acid tetrahydrate (SAT), as has been previously suggested could be the case by Zhang et al. (Zhang, R.; Wooldridge, P. J.; Abbatt, J. P. D.; Molina, M. J. *J. Phys. Chem.* **1993**, *97*, 7351). From our thermal analysis experiments, we have identified the melting transition of SAO. We report for the first time in the literature the enthalpy of fusion of SAO. We have also determined from our studies using the energies of fusion of ice and the various hydrates of H_2SO_4 that SAO is a major component of H_2SO_4 solutions in the range 20−40 wt % when they freeze. Our results indicate that SAO could be present in solid or partially frozen polar stratospheric and upper tropospheric cloud particles. Finally, we make a comment based on our results regarding the stoichiometric composition of SAO.

Introduction

Many researchers have investigated the H_2SO_4/H_2O liquid/solid phase diagram over the past 110 years.[1−9] Nucleation in H_2SO_4/H_2O aerosols has also been studied with respect to the formation of ice or other hydrates in laboratory studies.[10−18] When stratospheric and upper tropospheric sulfate aerosols cool, solids may nucleate in the droplets. This can have an impact on heterogeneous chemistry under various conditions in the atmosphere. It has been shown that reactions on polar stratospheric clouds (PSCs) are dependent on the water content of the surfaces.[19] The higher the water content the faster the reaction, so, for example, reactions on sulfuric acid octahydrate (SAO) would be expected to be faster than reactions on sulfuric acid tetrahydrate (SAT). Therefore, if sulfuric acid octahydrate (SAO) is a solid that forms in PSCs, this water-rich solid could be very efficient at promoting stratospheric heterogeneous reactions. Alternatively, if upper tropospheric sulfate aerosols freeze they can promote cirrus cloud formation. To better understand both these possibilities, one must know which solids are thermodynamically stable when sulfate aerosols freeze or partially freeze, thus requiring an accurate knowledge of the H_2SO_4/H_2O phase diagram, particularly in the region where ice, SAO, and sulfuric acid hemihexahydrate (SAH) can form.

While the hydrates of sulfuric acid have been well defined in the past, conclusive evidence for the octahydrate has been somewhat elusive. Hulsmann and Biltz[3] first reported an octahydrate, but Gable et al.[4] found no evidence for it. Hornung et al.[8] reported evidence for the octahydrate, but were only able to speculate about its thermodynamic properties. Later, Giaque et al.[9] reported it as an unstable phase between 37 and 58 wt % H_2SO_4. Mootz and Merschenz-Quack[20] reported the crystal structure of the octahydrate, but the region of thermal stability was not defined. In a comprehensive review by Zeleznik[21] the octahydrate was not discussed, nor was it studied by Bandy and Ianni[22] using density functional theory, though they studied all the other hydrates of sulfuric acid. Zhang et al.[23] reported an infrared spectrum for the octahydrate, but stated they could not conclude their spectrum was unique from a combination of ice and SAT. Clapp et al.[14] reported a similar IR spectrum for aerosols. Imre et al.[15] generated aerosols that transformed into solids with a vapor pressure consistent with the octahydrate, but others have not seen evidence of freezing to the octahydrate in their aerosol experiments, though not all investigators analyzed for the presence of SAO.[10−13,16−18]

In the experiments described here, we have reinvestigated the H_2SO_4/H_2O solid/liquid phase diagram over the entire range of compositions, but we focused mainly on the region from ice to SAT. In particular we have measured the transition temperatures of sulfuric acid octahydrate (SAO), sulfuric acid hemihexahydrate (SAH), sulfuric acid tetrahydrate (SAT), and ice using differential scanning calorimetry (DSC). We have measured the energies of transitions and report for the first time the enthalpy of fusion of SAO. Using fusion enthalpy values of the various hydrates, we have determined the amount of each solid present when a liquid sample freezes. Using Fourier Transform Infrared Spectroscopy on thin film samples, we have determined the identity of solids present in liquid samples when they freeze and report a unique spectrum corresponding to SAO. We also discuss the composition of SAO, and whether it is, in fact, an octahydrate or another stoichiometric composition.

Experimental Section

Sample Preparation. Acid samples were prepared by diluting 98 wt % ACS reagent grade H_2SO_4 supplied by Fischer with Culligan purified water. The concentrated acid was standardized by acid−base titration and the concentration of all samples is known to ±0.40 wt %.

Infrared Spectra. The sample cell used for infrared spectra is shown schematically and explained in detail in previous literature.[23] Briefly, a small drop of H_2SO_4 solution was placed

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* Author to whom correspondence should be addressed at Department of Chemistry, Wisconsin Lutheran College, 8800 W. Bluemound Rd., Milwaukee, WI 53226. E-mail: Keith_Beyer@wlc.edu.

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between two AgCl windows, which were held in the center of an aluminum block by a threaded metal ring. Sample volumes were 1−2 μL. On each side of the aluminum block a Pyrex cell was purged with dry nitrogen gas. KBr windows were placed on the end of each cell, sealed with O-rings, and held in place by metal clamps. Heat tape was wrapped around the purge cells to prevent condensation on the KBr windows. The sample was cooled by immersing the end of the aluminum block in liquid nitrogen and warmed by resistive heaters connected to a temperature controller. Temperature was measured by a copper/constantan thermocouple placed at the edge of the AgCl windows and connected to the temperature controller. The temperature of the cell was calibrated using Culligan purified water and high purity organic solvents (Aldrich): decane, octane, and acetic anhydride of which the melting points are 243.5, 216.4, and 200.2 K, respectively.[24] The IR cell temperatures are known on average to within ±1.3 K of the transition temperatures measured with the DSC.

Spectra were obtained with a Mattson Instruments Galaxy 4020 FTIR with 16 cm^{-1} resolution. Each spectrum is the average of 4 scans. Before spectra were taken of a sample, a reference scan was obtained from a dry, purged sample cell. Samples were cooled to 192 K at 3 K per minute and then allowed to warm to room temperature without resistive heating, typically this was ~1 K/min. If acid samples did not freeze while cooling, they were held at ~145 K for up to an hour and the samples would crystallize upon warming. In all cases our spectra compare well for ice, SAH, SAT, sulfuric acid trihydrate (SATri), and sulfuric acid monohydrate (SAM) with those previously published[21] (detailed comparison of SAO spectra with those previously published will be given in the results section.)

Differential Scanning Calorimeter. Thermal data was obtained with a Mettler Toledo DSC 822e with liquid nitrogen cooling. Industrial grade nitrogen gas was used as a purge gas with a flow rate of 50.0 mL per minute. The temperature reproducibility of this instrument is better than ±0.05 K. Our accuracy is estimated to be ±0.9 K with a probability of 0.94 based on a three-point temperature calibration[25] using indium, HPLC grade water, and anhydrous high-purity (99%+) octane from Aldrich, the latter two stored under nitrogen. The sensitivity of our instrument to thermal signals is high. Previously, we have calculated our sensitivity to detecting a component undergoing a thermal transition to be <50 ppm.[26]

Samples were contained in a 30 μL platinum pan and typically had a mass of ~22 mg. In cases where samples did not freeze upon repeated runs, we used larger samples ranging from 60 to 130 mg contained in 70 μL platinum pans. Each sample was weighed before and after the experiment using a Mettler-Toledo AT20 microgram balance. The average mass loss from evaporation during the experiment was less than 1%. A typical sample was cooled to 173 K at 10 K/min, held at that temperature between 5 and 30 min, warmed to 183 K at 10 K/min, and held there for 0−30 min, and then finally warmed at a rate of 1 K/min until 298 K. We will refer to this as the 173 K method. When samples did not freeze using the 173 K method a second method was attempted where samples were cooled to 138 K and then warmed using the same procedure as described in the 173 K method. We will refer to this method as the 138 K method.

Results

Phase Diagram. Figure 1 shows the phase diagram of the H_2SO_4/H_2O system with the following data plotted: historic data of Hulsman and Biltz,[3] Gable et al.,[4] and Kunzler and Giauque.[6] We have also plotted our data from two types of experiments. Data in red are samples from experiments using the 173 K method and data in blue are from experiments using the 138 K method. A summary of the eutectic and peritectic transitions measured is given in Table 1 with a comparison to literature data. As can be seen from Figure 1, samples were difficult to freeze in the composition range 55−85 wt % H_2SO_4 (region of SAT, SATri, SAD, and SAM stability), and for a few samples around the ice/SAT eutectic. This is in agreement with bulk and aerosol studies that had difficulty freezing aerosols of composition greater than 35 wt % H_2SO_4.[4,10,12,14] In general, it is seen that our data are in good agreement with the historic work. We will now discuss specific transitions that are relevant to atmospheric aerosols.

Ice/SAT Eutectic. This eutectic spans the composition range from 0 to 57.7 wt % H_2SO_4 (SAT stoichiometric composition). However, we have observed this transition up to 65 wt %, indicating small amounts of ice can form up to this composition. An average of all samples with this transition yields the temperature to be 199.32 ± 0.43 K. There has not been agreement in the literature on this eutectic temperature (see Table 1). The most recent work on this system did not even measure this eutectic, but rather calculated it to be 198.6 K.[8] Other earlier workers assigned this eutectic a value between 198 and 201 K.[1−4] The rationale for assigning this eutectic will be given below since it is very close to the SAO transition.

Sulfuric Acid Octahydrate. As indicated above, there has been much disagreement over whether the octahydrate even exists. We provide here strong evidence for the existence of a low-temperature hydrate, though our evidence suggests that it is at least a nonahydrate rather than an octahydrate; however, for simplicity we will refer to this hydrate throughout as "SAO." We have seen transitions in the DSC and IR experiments corresponding to SAO. The average temperature of this transition from DSC experiments is 200.37 ± 0.36 K. This transition occurs over a range of concentrations, from our most dilute sample at 2.2 wt % up to 60.4 wt %, thus showing the broad concentration region where this hydrate can occur (see Figure 1). That the signals for several hydrates can be clearly seen and identified is illustrated in Figure 2. The various transitions observed in this thermogram will be discussed below.

In Figure 3 we demonstrate the uniqueness of the SAO IR spectrum. Previously published spectra for SAO are those of Zhang et al.[23] for thin films and Clapp et al.[14] for aerosols. The published spectra of both groups are quite similar; however, Zhang et al. stated that they could not differentiate between the SAO spectrum and a spectrum of ice mixed with SAT. Our spectrum for SAO in Figure 3 was generated by freezing a thin film of liquid with composition 39.2 wt % H_2SO_4 (in general, we observed an identical spectrum for films in the concentration range 20−45 wt %). Our ice spectrum is that of a frozen film of distilled water, and our SAT spectrum is that of a frozen film of liquid with composition 4:1 H_2O/H_2SO_4, each consisting of the same volume of sample. Spectrum A in Figure 2 is that of ice + SAT while spectrum B is our spectrum of SAO. For comparison purposes, an initial spectrum was generated using the following method. By the lever rule if a 40.5 wt % liquid sample froze completely to produce a mixture of ice + SAT, the solid would be composed of 70.2% SAT and 29.8% ice, thus the SAT/ice ratio would be 2.35. However, when we produced a spectrum by multiplying our SAT spectrum by 2.35 and adding it to ice, it was found to be identical to our spectrum for SAT. Therefore, to enhance the ice features, we produced spectrum A by a 1:1 addition of the SAT and ice spectra. Even in this case, it is readily seen that our spectrum for SAO is not

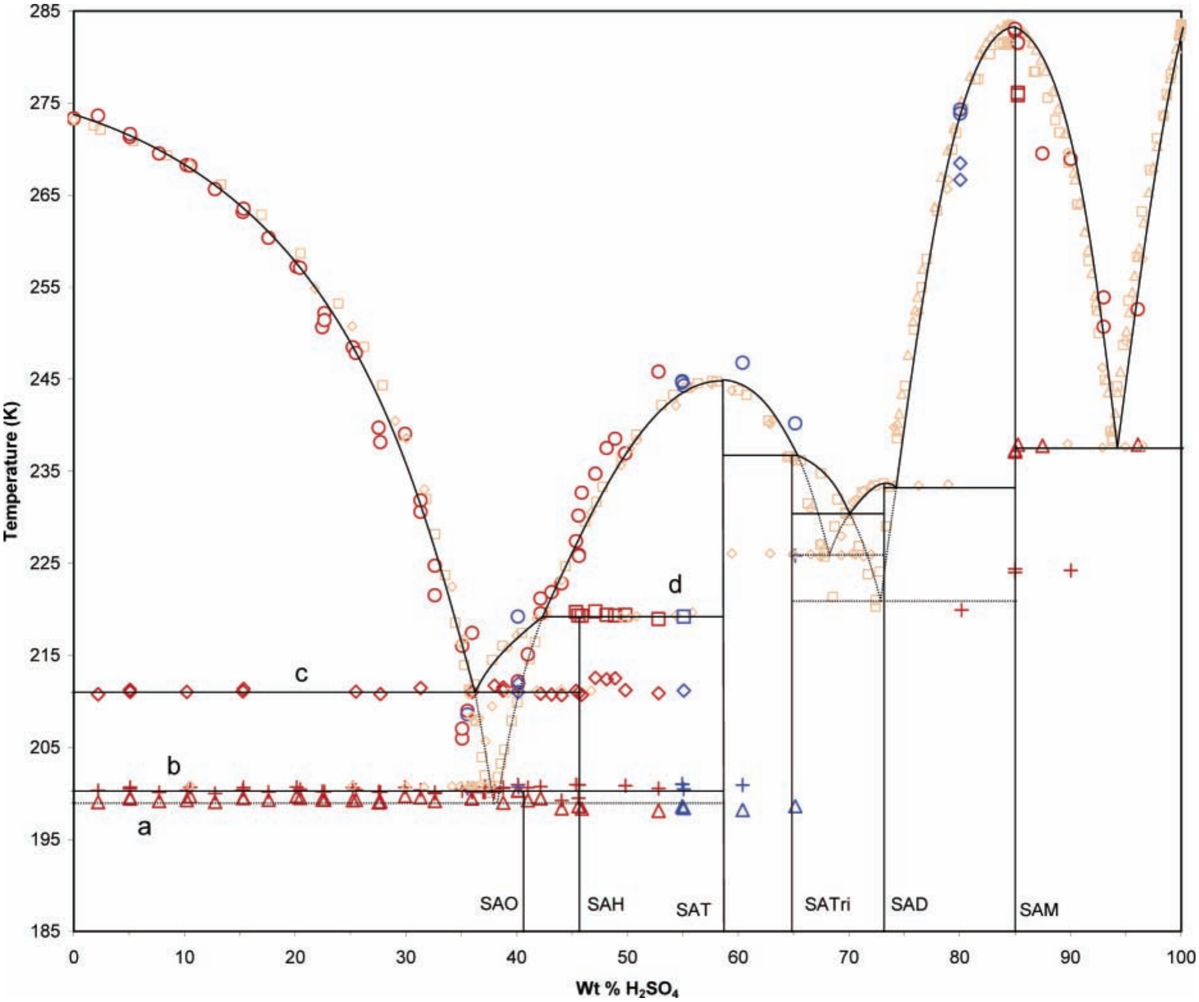

Figure 1. Phase diagram of sulfuric acid/water. Data points in gold are from Hulsmann and Biltz[3], Gable et al.,[4] and Kunzler and Giaque.[6] All other data points are from our DSC work. Red data are samples cooled to 173 K, blue data are samples cooled to 138 K to induce nucleation by passing through the glass transition. For concentrations less than 70 wt % H_2SO_4, symbols are: triangles, ice/SAT eutectic melting; crosses, SAO transition; diamonds, ice/SAH eutectic; squares, SAH peritectic melting; circles, final melting. Letters refer to transitions listed in Table 1; vertical lines indicate exact composition of each hydrate.

TABLE 1: Summary of Transition Temperatures and Enthalpies of Fusion

area in Figure 1	phase transition	this work	literature values
a	ice−SAT eutectic	199.32 ± 0.43 K	198.15−201.15 K[a]
b	SAO melting	200.37 ± 0.36 K	200.6−200.8 K[b]
c	ice−SAH eutectic	211.26 ± 0.56 K	211−211.28 K[c]
d	SAH−SAT peritectic	219.38 ± 0.28 K	219.15−220.28 K[c]
	ΔH_f (SAH)	32.77 ± 3.75 kJ/mol	31.99−34.15 kJ/mol[d]
	ΔH_f (SAO)	31.76 ± 0.37 kJ/mol	n/a

[a] Refs 1−4,8. [b] Refs 3,8. [c] Refs 3,4,8. [d] Refs 8,21.

merely a mixture of the spectra of SAT and ice. While the peaks at ∼626, ∼1079, and ∼2351 cm^{-1} match reasonably well, there are significant differences among all the other peaks in the fingerprint region. Especially of note are the peaks at 845 and 1313 cm^{-1} in our SAO spectra where there are minimum values in the SAT + ice spectrum. We have also performed spectral subtractions of ice and SAT from our SAO spectrum and compared them to SAT and ice spectra, respectively. They also do not match. It should be noted that our spectrum of SAO is different from that of Zhang et al. We found that a spectrum similar to that of Zhang et al. is generated upon the initial freezing of a sample in the range 20−40 wt % H_2SO_4 (spectrum C in Figure 3). However, over a period of 5 to 15 min at temperatures between 173 and 200 K, the spectrum slowly changes into spectrum B. Spectrum B persists for indefinite periods of time below the SAO transition at 200.4 K. However, other samples did not first pass through this “metastable” state, but rather immediately formed the “stable” state shown in spectrum B. Also, the state of frozen SAO did not appear to depend on the freezing temperature of the sample, or the composition of the liquid it formed from. We cannot rule out the possibility that spectrum C represents another hydrate that is less stable than, but similar to, SAO such that it reverts to SAO over time.

As seen in Figure 1, there are two transitions quite close together (199.3 and 200.4 K). The question arises, which transition is SAO melting and which is the ice/SAT eutectic? We have assigned the higher transition to SAO melting based on the DSC and IR experiments. From 2.25 to 32 wt % the 199.4 K transition is a very weak signal in the DSC experiments

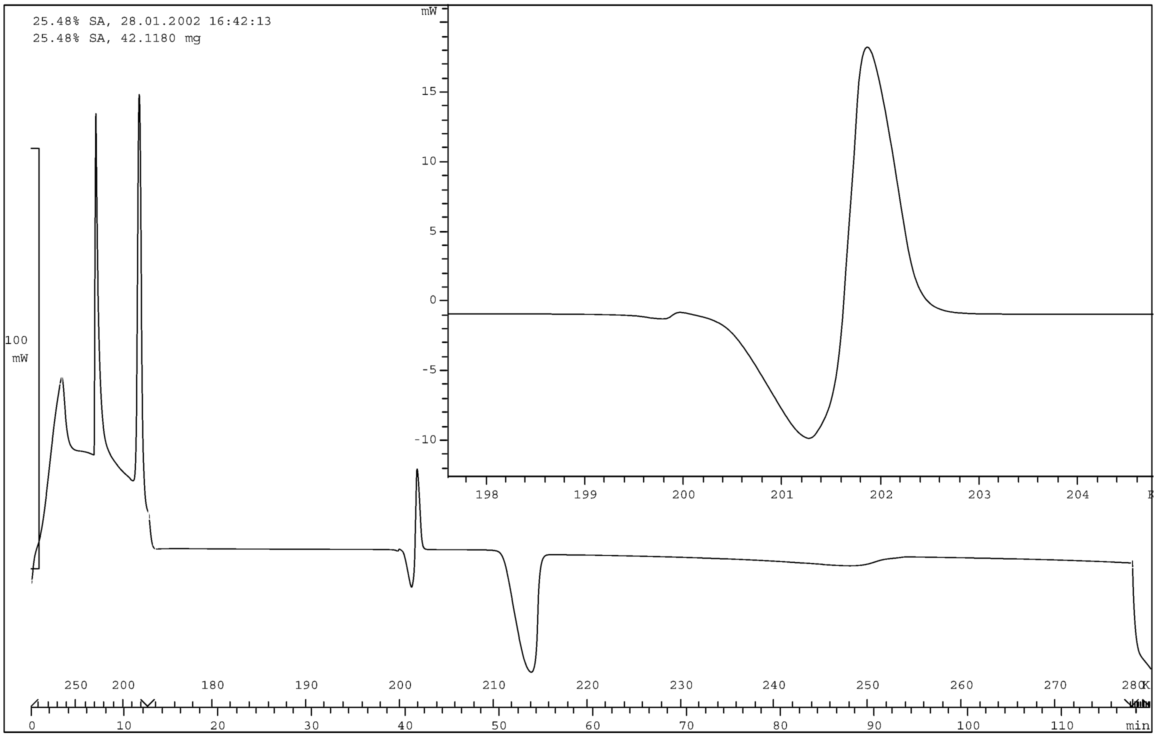

Figure 2. Thermogram of 25.5 wt % H_2SO_4 sample cooled using 173 K method. Thermogram is an energy flow vs time (temperature) sequence. The thermogram illustrates two freezing events on cooling to 173 K. Upon warming a small melt at 199.4 K (SAT) is followed by a larger melt at 200.4 K (SAO) and then a recrystallization of this melt. At 211 K the eutectic melting of SAH in contact with ice is seen followed by the final melting of ice at 248 K. A portion of the thermogram from 198 to 204 K is expanded for ease of observing the small SAT peak.

(see Figure 2) and is absent for some samples in the concentration range 32−40 wt %. This indicates that the corresponding solid is a very minor phase in the sample, whereas the 200.4 K signal grows to be a major fraction of the phases present in the DSC samples (the fraction of solid in each phase is discussed below). In fact it is the only peak present for some samples in the concentration range 35−37 wt %. Throughout this concentration region our IR samples indicate that the only major phases present are ice (0−18 wt %) and SAO (8−40 wt %, see Table 2 for a summary of phases present in our IR experiments.) In some IR samples the only phase present was SAO, in agreement with our DSC results. Thus, the larger thermal transition at 200.4 K must correspond to the melting of SAO, and the minor transition at 199.4 K corresponds to the eutectic melting of SAT below ∼37 wt % or ice above ∼37 wt % in contact with each other. This assignment also agrees with Hornung et al.[8] who calculated the SAT/ice eutectic to be 198.6 K. The most recent DSC work on this system did not discern between these two transitions but rather interpreted a single transition at 200 K in 20 and 50 wt % samples to be the conversion of octahydrate with either ice (20 wt %) or SAT (50 wt %) into hemihexahydrate.[23] Most likely their instrument did not have the sensitivity to observe the small thermal signal due to melting of ice or SAT at the ice/SAT eutectic. Also, they did not correlate their IR studies with the DSC experiments to determine the identity of phases present. We feel the SAO transition at 200.4 K is not a true eutectic (melting of SAO with another phase) as we do not have evidence of a SAO melting envelope and the 200.4 K transition exhibits very little temperature variation over a wide composition range. Therefore 200.4 K is likely the temperature at which SAO becomes unstable and thermally decomposes to the liquid.

We have also measured and report here for the first time the enthalpy of fusion for SAO. Our value is the average of 5 samples in the range 36−38 wt %. In each case SAO was the only solid present as indicated by a single melting peak in the thermogram corresponding to the melting temperature of SAO. This was confirmed by our IR experiments indicating SAO as the only phase detected for samples of the same concentration. An average of the thermal melting signature from these samples gives an enthalpy of fusion: $\Delta H_f = 31.76 \pm 0.37$ kJ/mol for SAO.

Finally, we wish to discuss the evidence for the stoichiometric composition of this hydrate. Our evidence to discern the stoichiometry comes from the DSC experiments. When a solution is prepared of the exact composition of the hydrate, there theoretically will be only one solid formed upon freezing, thus only one melting signal should be observed corresponding to the melting of the pure hydrate. For SAO this should occur at 40.50 wt %, but we do not observe this to be the case. Our samples at ∼40 wt % show transitions corresponding to SAO, SAT, ice, and SAH. Several samples in the range 36−37 wt % composition, had a single melting transition corresponding to the SAO melting temperature. If we take this to be an indication that these samples are very near the hydrate stoichiometric composition, then we note that 35.3 wt % corresponds to 1:10 H_2SO_4:H_2O and 37.7 wt % corresponds to 1:9 H_2SO_4/H_2O. The most plausible composition between 36 and 37 wt % is 36.4 wt % corresponding to 1:9.5 H_2SO_4/H_2O. A strong piece of evidence for the existence of SAO would seem to be the crystal structure determined by Mootz and Merschenz-Quack.[20] However, they did not use a 1:8 H_2SO_4/H_2O solution to make single-crystal SAO. Instead they used a 37.7 wt % solution to produce the crystals used in their experiments. This corresponds exactly to 1:9 H_2SO_4/H_2O as stated above. Their explanation for using 1:9 H_2SO_4/H_2O was to prevent the formation of SAH which they felt was more stable than SAO. They indicated observing ice formation along with SAO in their experiments.[27] Other observers have reported evidence for an octahydrate. The first was Hulsmann and Biltz;[3] however, they mistakenly assigned

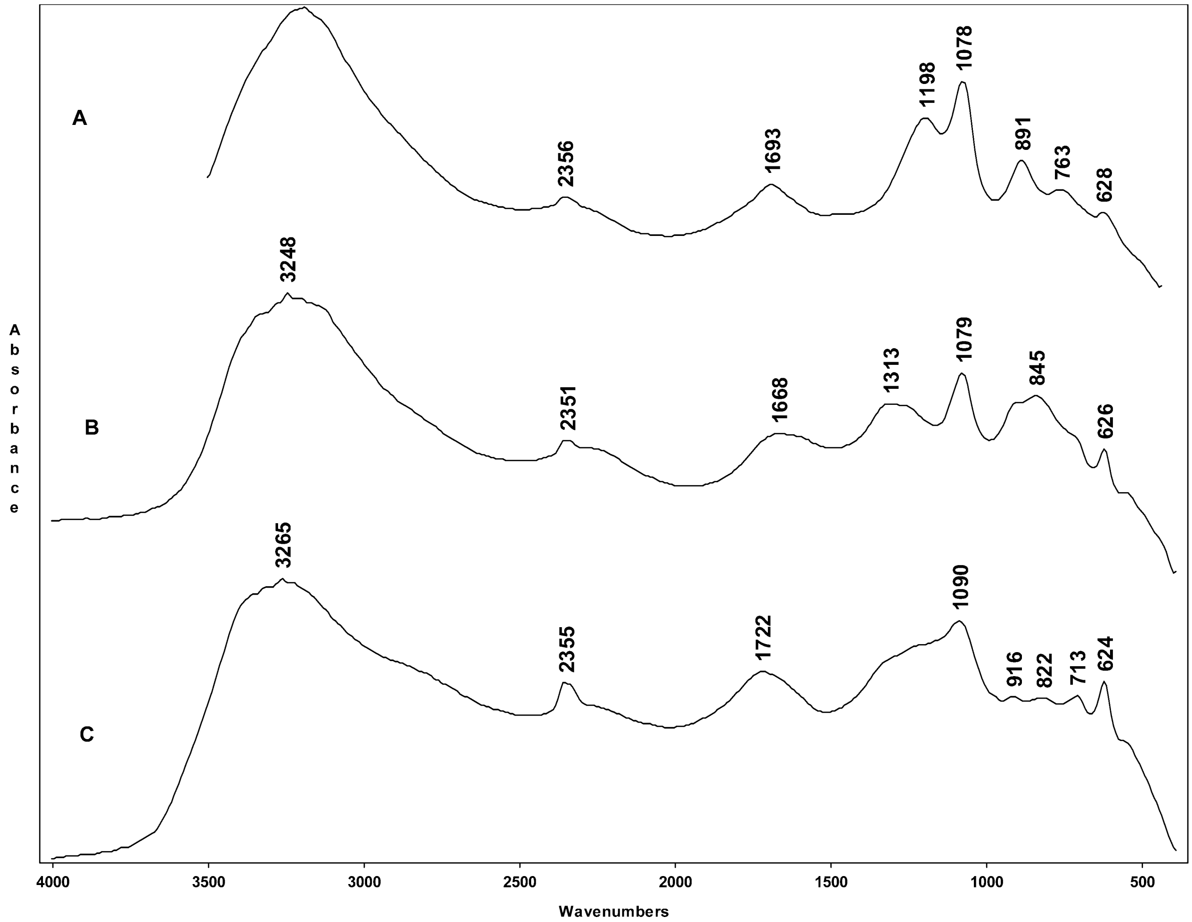

Figure 3. Infrared spectra of thin films: (a) spectral addition of ice + SAT spectra; (b) SAO produced from 39.2 wt % H_2SO_4, (c) "metastable" SAO spectrum similar to that observed by Zhang et al.[23]

TABLE 2: Summary of Infrared Thin Film Experiments

phase	concentration of samples in which phase was detected	concentration of samples in which phase was the only solid detected
ice	0−17.6	0−5.11
SAO	7.7−45.6	20.4−36, 38−40, 40[a], 45.6[a]
SAH	37−45.6	37, 45.6[a]
SAT	40−65	57.6
SATri	65	
SAM	82−85	82−85

[a] Phase indicated was initially the only one present, but converted to a mixture of phases upon melting.

the octahydrate transition as a peritectic at 211 K. This transition is in fact the eutectic between ice and SAH as was first pointed out by Gable.[4] The second finding is that of Hornung et al.[8] They reported the observation of two temperatures, 200.60 K, which they assign to the eutectic of ice and octahydrate, and 201.03 K, which they assign to a peritectic transition between SAO and SAT. We have no evidence for a transition at 201.03 K. Based on thermodynamic data, they calculate the ice/SAT eutectic to be 198.6 K, but did not measure this temperature. We speculate that a correct interpretation of their data is that their measured temperatures are slightly too high; therefore, their transition at 200.6 K is actually a high measurement of the ice/SAT eutectic, and likewise the 201.03 K measurement is actually a high measurement of the melting of SAO. As stated above, we have no evidence for a melting *envelope* of SAO.

Hence, we are unable to confirm that SAO is exclusively an octahydrate. Our results disagree with the crystal structure measurements of Mootz and Merschenz-Quack,[20] and seem to indicate that SAO is really at least a nonahydrate, or possibly as high as a decahydrate, or some composition between these two. We feel this water-rich, low-temperature hydrate needs to be investigated further.

Sulfuric Acid Hemihexahydrate. In agreement with previous investigators,[8,20] we have not observed the formation of SAH exclusive of all other solids in any of our experiments. Because this solid has a peritectic transition with SAT, we always observe SAT in samples more concentrated in sulfuric acid than the peritectic concentration. Additionally, we also observe a signal corresponding to the eutectic melting of ice in contact with SAH, small signals due to the SAO transition at 200.4 K, and the eutectic melting of ice in contact with SAT at 199.3 K. We have observed transitions of SAH in the concentration range 2−55 wt % H_2SO_4. Average temperatures for the ice/SAH eutectic and SAH/SAT peritectic are given in Table 1. For samples below 35 wt % in the DSC experiments, we have observed that in every case where a recrystallization event occurred after the melting of SAT and SAO at 199.4 and 200.4 K, respectively, there was also a eutectic melting of SAH at 211 K. Likewise, where this recrystallization event was lacking, there was no SAH eutectic melting—hence, no SAH in the sample (down to our detection limit of <50 ppm.) This leads us to conclude that for solutions below 35 wt % H_2SO_4, SAH is most likely to grow from the melt of SAT/SAO (either from nucleation from the liquid or growth on nuclei formed at lower temperatures) and seems unlikely to grow in the initial crystallization of the liquid. Possibly this is because SAH has a higher barrier to nucleation or crystal growth than SAO, ice, or SAT at these concentrations. We also report the enthalpy of fusion

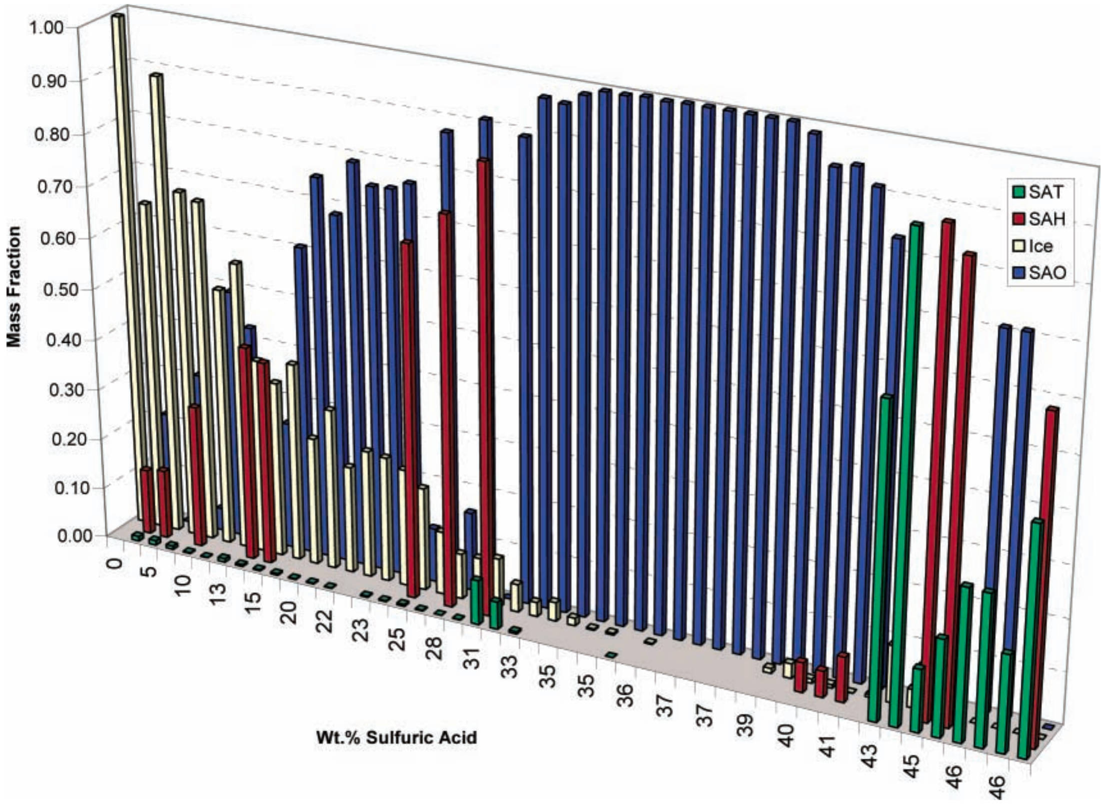

Figure 4. Content of frozen samples expressed as mass fraction in each solid phase. Each set of columns along the *x* axis represents a single sample with the concentration given. Columns represent solids as follows: blue, SAO; yellow, ice; red, SAH; green, SAT.

for SAH as given in Table 1. It is seen that our value is within the range of that previously measured. Our error bars on the value are large because we were unable to get good separation of the SAH peak from the peaks of other transitions, thus leading to uncertainty in the energy values for SAH. The value listed is the average of three samples.

Content of the Solid Phase. The content of the solid phase can be determined from the fusion enthalpies of the various solids present. The mass fraction of each phase in a sample is calculated using the following equation:

$$y_i = \frac{E \times M_i}{\Delta H_i^{fus} \times m_T} \tag{1}$$

where y_i is the mass fraction of species i, E is the energy of the transition as measured by the DSC, M_i is the molar mass of solid i, $\Delta H_i^{\mathrm{fus}}$ is the molar enthalpy of fusion of species i, and m_T is the total mass of the sample; where i represents SAO, SAT, etc. Figure 4 is a plot of the results for each sample in our DSC experiments in the range 0−50 wt % H_2SO_4. All possible solids did not appear in each sample since nucleation is a stochastic process. Also note there is more than one sample at many concentrations. Figure 4 demonstrates several things about the content of frozen samples. Ice is initially the dominant phase at low H_2SO_4 concentration, but then diminishes with SAO becoming dominant throughout the range 15−41 wt %. The amount of SAT present is minimal until the concentration reaches about 43 wt %. Finally, for various samples SAH concentration is significant; however, it must be remembered that for samples more dilute than 35 wt %, SAH was only seen to form from the recrystallization of melted SAT and SAO. At ∼45 wt % SAH is the dominant phase as expected since this corresponds to the 6.5:1 H_2O/H_2SO_4 exact composition. Clearly the extent of growth of a phase is dependent on its nucleation kinetics. As various phases nucleate they begin to grow and compete for liquid molecules to add to their crystalline lattice.

Comparison with Aerosol Experiments

A number of investigators have attempted to determine the freezing temperatures of H_2SO_4/H_2O aerosols using flowing aerosol or single particle experiments[10−12,14,15,17,18] while others studied aerosols deposited on a surface.[13,16] However, results have been mixed. Generally, aerosols more concentrated in sulfuric acid than 35 wt % did not freeze even at the lowest temperatures. This leaves only the region under the ice melting envelope where crystallization has been detected, and we shall limit our discussion to aerosols that may freeze in this concentration regime. All studies that explored this region have detected the nucleation of ice. However, conclusive evidence regarding sulfuric acid hydrate formation cannot be garnered from these experiments. Martin et al.[13] saw evidence of SAT formation. They detected formation of SAT by observing the sulfate peak at 1060 cm^{-1}; however, SAO and SAH also have this peak in their respective spectra. Imre et al.[15] and Clapp et al.[14] reported evidence for SAO formation in laboratory aerosol particles based on vapor pressure measurements of a single particle and IR spectra measurements of flow tube aerosols, respectively. Anthony et al.[10] could not rule out the crystallization of H_2SO_4 hydrates in small amounts; however, they had no indication of homogeneous freezing or heterogeneous freezing on ice at temperatures down to 193 K. Prenni et al.[18] did not have temperatures below the SAO or SAT melting points in this region, thus they only detected ice in coexistence with H_2SO_4 liquid. Koop et al.[16] did not report the onset of melting in their particles, only temperatures of freezing and the final melting of ice, thus we do not know if they detected a melting corresponding to the SAO transition or ice/SAT, ice/SAH eutectic temperatures, which would indicated the presence of these solids.

The lever rule necessitates that at least two solids be present when a binary system completely freezes except at the exact composition of a molecular solid. Our results demonstrate that completely frozen samples in the composition range 8−46 wt % H_2SO_4 contain some SAO, and is seen to be the major solid present near its exact crystal composition. We surmise that some aerosol studies may not have analyzed specifically for the presence of SAO in their respective experimental techniques. For example, Bertram[28] noted that they did not specifically analyze for SAO in their study.[11] Limits of other studies have been noted above. Therefore, it is possible, in light of our results, that SAO was present when particles froze in some of the previous investigations, but its presence went undetected.

In our experiments with sample concentrations less than 30 wt % we observed ice freezing first as indicated by the first crystallization temperature always being >215 K (see, for example, Figure 2.) At these temperatures and on the water-rich side of the ice/SAH eutectic at 211 K, the only stable phase with respect to the liquid is ice. A second crystallization occurs that is always <189 K, which could be formation of SAT, SAO, or SAH. However, our results on the content of the solid phase show that even in the presence of SAT (and possibly SAH nuclei), SAO crystals grow preferentially in samples under the ice melting envelope. This could be the result of heterogeneous nucleation on ice. We cannot determine whether heterogeneous nucleation is occurring in our samples at the interface with our platinum crucibles. Martin et al.[13] determined that a gold surface enhances nucleation of ice but not of SAT and interpreted the formation of SAT in their experiments as heterogeneous nucleation on ice. We observe the nucleation of ice, SAO, SAH, and SAT in nearly all samples in the concentration range under the ice melting envelope, thus any heterogeneous effect of the crucibles would seem to be enhancing the nucleation of all solids, rather than one selectively. We know nucleation is enhanced by the larger volumes and lower minimum temperatures in our experiments when compared to aerosol experiments as predicted by theory. But again, this should affect the nucleation of all solids rather than one selectively. Regardless of the nucleation mechanism, clearly SAO crystals grow preferential to the other hydrates that may be present.

Atmospheric Implications and Conclusions

While the H_2SO_4/H_2O system is a reasonable representation of upper tropospheric aerosols, it is only an approximation of stratospheric aerosols that will incorporate HNO_3 at low temperatures. Therefore, it is a limiting case for polar stratospheric clouds (PSCs). If atmospheric aerosols completely freeze at low temperatures and form some combination of ice/SAT/SAO/SAH, the melting points of the respective solids in contact with each other can be taken as the point at which its stability envelop or eutectic transition coincides with the composition of atmospheric aerosols as given by model calculations.[29] SAO undergoes a thermal decomposition to the liquid at 200.4 K, apparently irrespective of other solids present; therefore, if it is present in atmospheric aerosols, it will decompose to the liquid at this temperature. It is also possible that after SAO melts at its decomposition temperature and SAT or ice melts at the ice/SAT eutectic, the resulting liquid may simply recrystallize into SAH and ice. Ice can coexist with SAH up to 211 K at which point ice or SAH melts at the eutectic depending on the ratio of ice/SAH. SAT seems to be extremely difficult to form as observed by previous work and in our experiments. Therefore, we would not expect an ice/SAH particle to undergo a solid−solid-phase transition to SAT upon warming into the SAT stability region or above the SAH peritectic temperature. In our opinion, SAT at most will be a very minor component of any frozen sulfate aerosol in the atmosphere.

We have provided evidence for a water-rich, low temperature hydrate which has commonly been referred to as the sulfuric acid octahydrate (SAO). However, we are unable to provide supporting evidence for the exact stoichiometry of this hydrate. Our calorimetry results indicate the composition may be between 9:1 to 10:1 H_2O/H_2SO_4, but this is in contradiction to the crystallography results on SAO indicating it is 8:1 H_2O/H_2SO_4.[20] However, we have made several measurements of the physical chemistry of this hydrate (referred to as “SAO”). We observed a unique infrared spectrum for stable SAO which has not been previously reported in the literature. We are able to generate the spectrum reported by Zhang et al.[23] and Clapp et al.[14] upon initial freezing of some of our samples. This spectrum then converted to the unique spectrum we have shown over a period of minutes, which then persisted indefinitely. We report for the first time a direct measurement of the SAO melting temperature over a broad range of composition and the enthalpy of fusion for SAO. We have also clarified and assigned the two very close transitions of the ice/SAT eutectic at 199.3 K and the SAO melting transition at 200.4 K. We have observed that in solutions more dilute than the ice/SAH eutectic, SAH only grows from the re-crystallization of melted SAO and SAT. Our observations also demonstrate that when samples completely freeze in the concentration range 20−41 wt %, SAO is the major phase present, and for samples in the range 36−38 wt % SAO is essentially the only phase present. This is the same concentration range that experiments have demonstrated freezing occurs in sulfuric acid aerosols. Our final melting temperatures and various other transition temperatures for the H_2SO_4/H_2O system are in good agreement with the results of previous investigators.

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