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PREPARATION AND CHARACTERISATION OF THE NONAHYDRATE AND PENTAHYDRATE OF ALUMINUM SULFATE

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ABSTRACT

Crystalline $Al_2(SO_4)_3 \cdot 9\ H_2O$ has been synthesized by thermal dehydration of a higher hydrate at a constant total water vapor pressure of one atmosphere. X-Ray diffraction analysis shows the compound to be identical to its only previous preparation by crystallization from solution. The pentahydrate of aluminum sulfate was also synthesized using the dehydration technique. Its X-ray diffraction pattern has been determined for the first time. Doubt is cast upon the existence of the hexahydrate. The rate of vapor rehydration for both $Al_2(SO_4)_3 \cdot 9\ H_2O$ and $Al_2(SO_4)_3 \cdot 5\ H_2O$ was measured. $Al_2(SO_4)_3 \cdot 9\ H_2O$ is metastable under the conditions employed.

INTRODUCTION

Several references have been made over the years to a hexahydrate of aluminum sulfate, but there appears to be insufficient proof of its existence. Young [17], for example, produces the "correct" amount of water balance through dehydration of a higher hydrate, but offers no proof that the resulting material is a unique, stable compound having characteristic features such as an X-ray diffraction pattern. A classic paper by Taylor and Bassett [15] discloses a hexahydrate, and publishes for the first time an X-ray diffraction pattern of the preparation. The method of synthesis, however, suggests that the actual material produced was partially converted to an alunitic type structure. The evidence for this is the known alunitic content of the nonahydrate which was prepared in a companion experiment. In a series of papers by Barret and Thiard [1,2], the most definitive thermal analysis of aluminum sulfate hydrates to date identifies a hexahydrate, but uncertainty is expressed as to whether there are actually 6 or 4.5 moles of water per mole of aluminum sulfate. At any rate, the compound was amorphous as shown by X-ray diffraction analysis. Incidentally, an allusion is made by Barret and Thiard to a pentahydrate which had been prepared by Erdey and Paulik, but no reference was given. Indeed, a recent search of works by Erdey and co-workers fails to disclose the purported synthesis.

A paper by Zapol'skii and Fedoritenko [18] claims synthesis of a hexahydrate, but an examination of their weight loss vs. time curves reveals that the dehydration process under study with temperature parametric was never carried to steady-state, let alone thermodynamic equilibrium. No X-ray diffraction data were given. Drobot et al. [6] likewise did not ensure thermodynamic equilibrium had been reached before they reported a hexahydrate. And while some X-ray diffraction spectra are published, they do not definitively establish the existence of the hexahydrate. No reference to the spectrum of Taylor and Bassett [15] was made.

Gitis et al. [8] report a dehydration study, and claim the hexahydrate on the basis of differential thermal analysis and differential thermal gravimetry. An analysis of their data shows that the purported compound contained 5.6 moles of water. As for crystalline structure, they report that the compound "bears a definite similarity to" the results of Taylor and Bassett [15]. Again, the work is not definitive based upon the relatively rapid rate of heating specimens, 10°C min^{-1}.

In a more recent work Sato et al. [11,12] report the hexahydrate. Weight loss was used as the sole criterion in the dehydration of higher hydrates. Their numbers show, however, enough uncertainty in the composition of the starting material as to vitiate their final conclusions. Again, temperature programming was too rapid to allow definitive conclusions to be drawn.

Serious doubt is thus cast on the existence of an aluminum sulfate hexahydrate. Furthermore, there is only an allusion to the pentahydrate, with no tangible reference to support it.

The first mention of a nonahydrate comes from the work of Taylor and Bassett [15] who adjusted the water content of a solid and equilibrated it at 160°C for nine weeks in a sealed capsule. An X-ray diffraction pattern for the resultant crystals was obtained. The solid was later found to contain a small amount of insoluble alunite. Also, only 8.7 moles of water were included within the capsule.

Exploratory work in this laboratory on hydrothermal formation of aluminum sulfate hydrates indicated a definite nonahydrate. Its X-ray diffraction pattern bore little resemblance to that of Taylor and Bassett. It was identical, however, to a pattern published in a Japanese patent application [14], where no attempt had been made to determine the composition of what was then considered to be a novel compound.

Barrett and Thiard [1,2] also reported a definite nonahydrate as a result of thermal dehydration, but their compound was amorphous. A definite crystalline nonahydrate with a good X-ray diffraction pattern was first reported by Bretsznajder and Rojkowski [4]. They had crystallized the material out of an aluminum sulfate solution containing sulfuric acid at 85°C [5]. Their diffraction pattern did not agree with that of Taylor and Bassett, but was very close to the one obtained by us in the exploratory runs. In another paper, Bretsznajder and Rojkowski [3] made a thermoanalytical study of the hydrates, and report the nonahydrate as a decomposition product of the hexadecahydrate. They claim that a trihydrate is formed upon continued dehydration, but, interestingly enough, the hexahydrate seems not to have appeared. The latter only appears upon dehydration of crystalline nonahydrate prepared from solution as described earlier; this continued process led to a trihydrate and a monohydrate as well. No corroborating evidence was given in support of these compounds. Also, by the authors' own admission, successive dehydration stages overlapped due to the rapid heating rates employed and conditions were far from equilibrium.

It is interesting that the hexahydrate but no nonahydrate is reported in the thermoanalytical work of Drobot et al. [6], Zapol'skii and Fedoritenko [18], Gitis et al. [8], and Sato et al. [11,12].

In summary, there is strong evidence for the existence of a stable, crystalline nonahydrate. In the present work we prepare the material by a novel method and substantiate the work of Bretsznajder and Rojkowski using analytical, gravimetric and X-ray diffraction techniques.

EXPERIMENTAL

The starting material for all experiments performed in this work was Mallinckrodt reagent grade aluminum sulfate containing roughly 16 moles of hydrate water. Such materials are made by freezing a concentrated liquor, contain more than one hydrate species, and are normally not highly crystalline. They are usually slightly basic. Duplicate analyses for both sulfate and aluminum gave the average result 16.74% Al_2O_3, 46.31% SO_4. This translates to the empirical formula $[Al_2(SO_4)_3 \cdot 15.42\ H_2O] \cdot 0.0206\ Al_2O_3$. In the interpretation of hydration data it has been assumed that the basicity of all products is the same as that of the starting material. Only hydrate water content varies. X-Ray diffraction analysis of the starting material showed $Al_2(SO_4)_3 \cdot 16\ H_2O$ to be the preponderant phase with some $Al_2(SO_4)_3 \cdot 14\ H_2O$ and $Al_2(SO_4)_3 \cdot 9\ H_2O$ present.

Dehydration/equilibration

Starting material was screened and the −10, +40 U.S. Standard Sieve fraction was used for all runs. Approximately 30 g were tightly packed into each screw-top wide-mouth bottle. A large hole was drilled in the center of the plastic screw-tops. A temperature-resistant rubber gasket about 1/16 in. in thickness was held tightly in place by the screw-tops. A razor slit was made in the gasket about $\frac{1}{2}$ in. in length. This arrangement assured that internal water vapor in excess of one atmosphere pressure would escape, i.e. the solid sample could dehydrate. At the same time, water vapor transpiration was so restricted that equilibrating solids were assured of contacting a virtual barometric pressure of water vapor throughout a run.

Exploratory experiments were carried out over a range of times and temperatures. Surprisingly, only two weight loss plateaux occurred over a rather wide range of temperature in each case. One corresponded roughly to the nonahydrate product and the other to a pentahydrate. A more careful series of experiments was then made in which the temperature selected for each plateau situation was taken from approximately mid-range of the exploratory runs. These temperatures were 120 and 160°C.

Weight loss data were carefully recorded on samples after having conditioned the empty sample holders at the highest temperature employed in the series, 160°C. Products were also analyzed for aluminum. All samples were analyzed by X-ray diffraction. Some products were set aside for later rehydration experiments.

X-Ray diffraction

Samples were examined on a Norelco X-ray Diffractometer in rate meter mode and parafocus geometry using CuK_α radiation. A slow scan of 1° min^{-1} was used in order to obtain accurate *d*-spacings.

Vapor re-hydration

Selected products of the dehydration/equilibration runs were exposed to 50% relative humidity at 70°F for several days and the weight changes frequently recorded. Approximately 1 g samples were spread thinly in glass weighing bottle tops for these experiments and weight changes due to adsorption of water on glass were found to be negligible.

RESULTS

Dehydration of the "hexadecahydrate" starting material was tracked using weight loss and analysis for aluminum. Table 1 shows the results. Note especially the transition sample (sample 6) which represents about 3 h of dehydration after the

TABLE 1

Dehydration of $[Al_2(SO_4)_3 \cdot 15.42\ H_2O] \cdot 0.0206\ Al_2O_3$ under 1 atm water vapor pressure

Temp. (°C)	Sample no.	Time (h)	Water of crystallisation (moles)	
			By wt. loss	By Al_2O_3 analysis
120	1	0		15.42 [a]
	2	9	9.53	9.36
	3	20	9.45	9.39
	4	30	9.07	8.90
	5	48	9.07	9.03
160 [b]	6	53	7.21	7.14
	7	58.5	5.25	5.27
	8	63.5	5.17	5.26
	9	68.5	4.98	5.01
	10	75.5	5.13	5.3

[a] By analysis for Al_2O_3 and sulfate.

[b] Temperature increased to 160°C at 50 h.

temperature had been raised from 120 to 160°C. This sample plays an important role in the proof of a pentahydrate, as discussed under the section on X-ray diffraction.

Table 1 shows slightly less scatter in the weight loss data than in the analytical results. Nonetheless, there is good agreement between the two sets of data. Certainly the two sets overlap well within the estimates of error. The two distinct plateaux

TABLE 2

X-Ray diffraction analysis of apparent nonahydrate of aluminum sulfate

d	I/I_0	Moles water [a]	d	I/I_0	Moles water [a]
6.423	23	9	2.002	9	9
5.563	13	9	1.980	1	9
5.448	1	9	1.949	6	9
4.887	10	9	1.908	4	
4.678	2	14, 16	1.892	1	
4.469	100	9	1.864	2	9
4.205	64	9	1.854	1	
3.897	7	16, 14	1.833	3	
3.708	11	9	1.816	3	
3.673	11	9	1.807	2	
3.490	20	9	1.788	4	
3.219	6	9	1.759	6	
3.198	4	9	1.746	9	
3.066	38	9	1.725	2	
2.956	32	9	1.686	2	
2.853	1	9	1.658	2	
2.771	8	9	1.644	1	
2.722	6	9	1.631	1	
2.642	14	9, 16, 14	1.614	2	
2.614	5	9	1.608	2	
2.558	5	9	1.596	2	
2.507	3	9	1.580	1	
2.483	3	9	1.548	2	
2.446	4	9	1.535	2	
2.423	4	16, 14	1.521	4	
2.389	4	9	1.492	2	
2.351	1	9	1.480	1	
2.268	2	9	1.463	1	
2.241	4	14	1.443	2	
2.196	1	9	1.438	2	
2.180	6	9	1.427	3	
2.116	3	9	1.415	3	
2.065	1	14, 16	1.405	3	
2.032	7	9	1.393	3	

[a] Patterns used for identification of 16, 14, and 9-hydrates of $Al_2(SO_4)_3$ all taken from Bretsznajder and Rojowski [4].

mentioned earlier are clearly evident and it is apparent that equilibrium had been achieved at 120°C prior to the increase to 160°C. Equilibrium was reached again at 160°C.

Examining only weight loss data for the moment, the water of crystallization at 120°C stabilizes within 1% of 9.00 moles (samples 4 and 5). At 160°C, the value falls within 1% of 5.00 moles (samples 9 and 10).

All samples were analyzed by X-ray diffraction. Patterns for samples 4 and 5 were virtually identical and match very closely with the published pattern of Bretsznajder and Rojkowski [4] as seen in Table 2. The patterns for samples 7–10 were also virtually identical. Our diffraction pattern for sample 9 is given in Table 3. The match with the pattern of Taylor and Bassett [15] is so poor that the latter is not included in the table. Ours appears to be a new pattern. No lines for the 16, 14, or 9-hydrates appear in this pattern.

The diffraction pattern for sample 6 contains only nonahydrate and pentahydrate lines. Furthermore, there is a 1 : 1 correlation for the reduced or normalized relative intensities found from all non-overlapped reflections in both sample 6 and sample 9. This provides strong evidence that sample 9 is not a mixture of compounds containing waters of crystallization both higher than and lower than five, i.e. such that they average to exactly five as they must do according to the data given in Table 1. The evidence points to a definite pentahydrate compound.

Sample 4, representing the nonahydrate, and sample 8, representing the pentahy-

TABLE 3

X-Ray diffraction analysis of apparent pentahydrate of aluminum sulfate

d	I/I_0	d	I/I_0
7.487	6	2.315	6
7.149	13	2.265	6
6.159	69	2.204	3
5.810	2	2.034	11
4.732	67	1.949	6
4.069	13	1.866	6
3.826	7	1.829	5
3.735	10	1.762	3
3.527	43	1.705	2
3.406	61	1.688	4
3.276	9	1.627	2
3.074	7	1.546	3
3.040	100	1.539	2
2.969	7	1.521	4
2.797	4	1.493	4
2.706	3	1.475	3
2.679	4	1.443	3
2.560	3	1.225	3
2.356	7		

TABLE 4

Vapor rehydration of dehydration products at 50% relative humidity and 70°F

Time (h)	Water of crystallization
Aluminum sulfate nonahydrate	
0	9.07
7	9.13
23	9.21
31	9.23
88	9.38
Aluminum sulfate pentahydrate	
0	5.17
7	6.08
23	7.72
31	8.17
88	11.65
96	11.97
120	12.85
168	13.88
263	14.97

drate, were selected for vapor rehydration. Results are given in Table 4. The weight increase of the nonahydrate in over 85 h is so slight as to be considered possibly an adsorption rather than a chemical combination of water. By contrast, the pentahydrate begins picking up water immediately, i.e. without an incubation period. The experiment was terminated at 263 h, at which point the compound contained 15 waters of crystallization. A plot of the data points does not reveal any arrests in the weight gain curve. However, an insufficient number of data points were obtained in the close vicinity of a nonahydrate composition, where an arrest might have been expected.

CONCLUSIONS

The results of the present investigation confirm the existence of aluminum sulfate nonahydrate, as reported by Bretsznajder and Rojkowski [4,5]. More particularly, our X-ray diffraction pattern is in excellent agreement with that work. This resolves the uncertainty over whether Bretsznajder and Rojkowski or Taylor and Bassett reported the correct pattern for the nonahydrate. There is still a possibility that there are at least two polymorphs of the same hydrate. One would have to be stable at 120°C and the other at 160°C, a possible but not very probable occurrence. More likely, the Taylor and Bassett preparation was in transition to an alunitic structure. Additional research would be required to resolve the question.

It is interesting that the excellent thermal analysis by Barrett and Thiard [1,2] reveals a crystalline 16-hydrate transforming to a crystalline 14-hydrate and then on to a crystalline 12-hydrate. Continued dehydration results in an amorphous 9-hydrate. This is in line with the reported structure of the 17-water hydrate [10] which contains 5 zeolitic waters. As these 5 waters are gradually lost, there is a relatively minor structural transformation to crystalline lower hydrates. Loss of the next incremental mole of water now results in disruption of the original basic structure. The next stable hydrate, the nonahydrate, is therefore disordered as seen by X-ray diffraction. Our work shows that the presence of 1 atm water vapor pressure facilitates crystallization of the nonahydrate. The data demonstrate clearly that it is the water vapor atmosphere, and not the long equilibration time which is mainly responsible for the crystallization. This is reminiscent of earlier evidence of the converse phenomenon, viz. that deliberate lowering of the water vapor atmosphere during dehydration/decomposition of bicarbonates prevents crystallization of the product [7]. It is now clear that Barrett and Thiard did not produce a crystalline nonahydrate because the highest partial pressure of water employed was only 100 mmHg.

Taylor and Bassett started with an amorphous material having roughly the composition of a nonahydrate and sealed this in a glass tube which was then heated at 160°C for nine weeks. There certainly was a considerable pressure of water acting and equilibration times were certainly long enough. A visible recrystallization occurred as a result. Thus the problem was therefore not one of lack of crystallinity, but one of transformation to a compound(s) different from the one we report.

The method of producing the nonahydrate which we report is relatively simple and straightforward. Thus a ready source of seed material for phase equilibrium studies is now easily obtained. No doubt the process could be developed on an industrial scale if needs be.

In the introduction, we suggested that the evidence for the existence of a hexahydrate is not convincing. While the present work does not prove that a hexahydrate does not exist, it certainly proves that the pentahydrate does. The only other interpretation left open is that what we report as a single compound is a mixture of several hydrates, possibly including a pentahydrate. But this is highly unlikely due to the constancy in relative X-ray diffraction peak heights in proceeding from the transition sample to the final equilibrium sample. Our results are then not inconsistent with those of Barrett and Thiard [1] who report the number of water moles in their hexahydrate as "6 H_2O (or 4.5 H_2O)".

Our pentahydrate X-ray pattern is in disagreement with Taylor and Bassetts' "hexahydrate" pattern. This could mean that they indeed had a hexahydrate. More likely, however, their hexahydrate results were vitiated by the same factors discussed earlier in connection with their nonahydrate.

It is now evident that the novel compound of the above-cited Japanese patent application [14] was the nonahydrate. This is reasonable inasmuch as their synthesis solution temperature was 116°C, close to our 120°C. While their synthesis was conducted at a total pressure of 1 atm, the partial pressure of water over the solution is unknown; it could have been close to 1 atm.

Smith and Walsh [13] also reported an equilibrium solid of unknown composition obtained by refluxing an aluminum sulfate solution at 123°C. This compound was most likely the nonahydrate in the light of the evidence we present.

It is interesting that many of the reports on the thermoanalysis of aluminum sulfate hydrates show a distinct arrest in the TGA–DTA curves corresponding to a trihydrate composition [9]. We have made the same observation in our laboratory. Furthermore, we find that the dissolubility in water shows a distinct drop-off at roughly the trihydrate composition. Bretsznajder, furthermore, reports a monohydrate. It may now be possible to resolve these points by employing the same technique described in the present work, with appropriate adjustment of experimental temperature and water vapor pressure.

The vapor rehydration phenomena shown in Table 4 are interesting if only to illustrate the marked difference in behavior between the particular nonahydrate and pentahydrate employed. The results suggest that the nonahydrate is metastable in this particular atmosphere. The reason is that the pentahydrate absorbs water and the resultant compound passes through the nonahydrate composition and beyond until it contains 15 moles of water. Metastability is usually explained on the basis of kinetics (and surface phenomena [16]). It is conceivable that the pentahydrate preparation is the more porous, and therefore absorbs water more readily. Or it could mean that the driving force for pentahydrate rehydration, which has to be stronger than for the nonahydrate initially, provided the acceleration in the kinetics required to carry right through the nonahydrate zone and beyond. Further efforts in this direction could profitably employ the techniques used by Barrett and Thiard [2] to study metastability in a hydrate series.

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