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Solubility of Aluminum Sulfate in Aqueous Ethanol at 30 and 80 °C

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The solubility of aluminum sulfate in 85–100% by weight aqueous ethanol has been reexamined at 30 and 80 °C. A technique has been developed for producing a stable solution of ~1% $Al_2(SO_4)_3$ by weight in 97% ethanol relatively rapidly. Starting with this stock solution, we prepared lower concentration ethanol systems for equilibration by addition of water. Stock solution is also distilled azeotropically to produce aluminum concentrations in solution as high as ~4% by weight as aluminum. Such solutions are slightly deficient in sulfate due to volatilization of sulfuric acid esters during distillation. Solubilities of $Al_2(SO_4)_3$ are found to be higher than those reported earlier in the 95–100% ethanol region. This is explained by the observation that anhydrous (calcined) aluminum sulfate and aluminum sulfate hydrates equilibrated in ethanol by previous workers are extremely slow in dissolving. Solid phases in equilibrium with ethanolic solutions are found, in general, to be hydrated basic aluminum sulfates containing monoethyl sulfate.

Anhydrous aluminum sulfate is normally prepared by heating the corresponding hexadecahydrate in air in the vicinity of 400 °C. The resulting material has a characteristic X-ray diffraction pattern. Our interest was in determining whether a lower temperature polymorph existed. Whereas there are many potential routes to such a material, equilibration in the ethanol–water system seemed appropriate and convenient. Gee (*6*), for example, reported anhydrous aluminum sulfate in equilibrium with ethanol-water at temperatures as low as 30 °C. Exploratory experiments based upon Gee's work led to the finding that the system is more complex than earlier work had anticipated. Indeed, some of the discrepancies in the reported literature (*2*, *3*, *4*, *12*) on the solubility of aluminum sulfate in ethanol-water systems may have been the consequence of kinetic factors and failure to attain thermodynamic equilibrium.

In view of the apparent complexity of the aluminum sulfate–ethanol–water system, it was decided to approach equilibrium from a new direction and to pay special attention to the composition of solids in equilibrium with higher concentration ethanol solutions.

Experimental Section

The stock solution of aluminum sulfate was prepared by adding 10 mL of saturated aqueous reagent grade $Al_2(SO_4)_3$ solution to 450 mL of boiling USP absolute ethanol (99.8% by weight) in a Waring blender. The $Al_2(SO_4)_3$ solution had been adjusted to 0% basicity by adding sulfuric acid; i.e., the total molar sulfate concentration in solution was adjusted to exactly 1.50 times the molar aluminum concentration. After 5 min in the blender the slurry formed was allowed to equilibrate at room temperature. In approximately 5 h the coarse, gritty solids completely dissolved to give ~1% $Al_2(SO_4)_3$ in ~97% ethanol. One such stock solution, for example, contained 1.03% by weight aluminum as $Al_2(SO_4)_3$ after standing at room temperature for 6 months. Stock solution concentrations of $Al_2(SO_4)_3$ as high as 2.90% were achieved by equilibrating the Waring blender slurry at room temperature after having initially decanted off some of the clear liquor. These procedures for making stock solution are preferred over dissolution of crystalline hexadecahydrate in absolute alcohol, a process which takes several days at elevated temperature.

Table I. Equilibration Time in a Representative Ethanol-Water-Aluminum Sulfate System at 30 °C

time (after water introduction), days	Al concn in solution, wt % $Al_2(SO_4)_3$
0	1.04
3	0.33
4	0.085
5	0.05
6	0.045
7	0.04
10	0.04

Table II. Estimated Precision of Analytical Data

anal. for	coef of variation
Al	2
SO_4	1
H_2O[a]	1.5
C	7

[a] By Karl Fischer titration.

Deionized water was added slowly to $Al_2(SO_4)_3$ stock solution at room temperature with vigorous agitation to produce the solid–liquid systems to be equilibrated. All such systems were equilibrated a minimum of 6 days. Equilibration temperatures were 30 ± 1 and 80 ± 1 °C.

Gee (*6*) equilibrated ethanol–water–aluminum sulfate systems for a minimum of 4 days. In the present investigation a 6-day minimum time was required, as illustrated in the following example. To a sample of 1% $Al_2(SO_4)_3$ stock solution was added sufficient water to produce a 93% by weight ethanol concentration in the final equilibrium clear liquor. Ethanol concentrations are always based upon the ethanol and water contents, to the exclusion of soluble aluminum and sulfate. The system was equilibrated at 30 °C, and uniform slurry samples were withdrawn periodically. Solids were separated by centrifuge, and the clear liquor was analyzed for aluminum. Results are given in Table I.

In order to obtain data for a more concentrated ethanol system, 1% $Al_2(SO_4)_3$ stock solution was distilled in the presence

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Table III. Solubility of $Al_2(SO_4)_3$ in Ethanol: Solution- and Solid-Phase Compositions

	solution phase		solid phase			
% EtOH[a]	% $Al_2(SO_4)_3$	% H_2O	% Al_2O_3	% SO_4	% C	% H_2O
		30 °C				
87.1	0.01	12.9	16.15	45.17	0.26	45.8
93.4	0.04	6.6	21.12	36.47	0.94	–[b]
94.2	0.57	5.8				
94.6	1.24	5.4				
95.0	1.98	4.95				
99.5	14.80[c]	0.4				
		80 °C				
87.3	0.01	12.7	25.48	67.23	0.09	–[b]
93.7	0.01	6.3	27.51	51.63	0.89	–[b]

[a] Weight % ethanol by using ethanol and water solvent components only, assuming solute is $Al_2(SO_4)_3$. [b] Karl Fischer titration gives generally low results due to relative insolubility of solids in methanol titration medium. [c] Stock solution concentrated by azeotropic distillation and then titrated with water. SO_4/Al mole ratio in final solution is 1.4, indicating volatilization of sulfuric acid esters.

Table IV. Empirical Composition of Solids in Equilibrium with Ethanolic Solutions, $Al(OH)_x(C_2H_5SO_4)_y(SO_4)_z \cdot wH_2O$

% EtOH	x	y	z	w
		30 °C		
87.1	0.06	0.034	1.45	8.03
93.4	1.26	0.095	0.82	5.68
		80 °C		
87.3	0.20	0.008	1.40	1.91
93.7	1.07	0.069	0.93	2.35

Table V. Solubilization of Anhydrous $Al_2(SO_4)_3$ in Ethanol at 30 °C

	solution phase	
% EtOH	% $Al_2(SO_4)_3$	% H_2O
97.1	0.026	2.92
97.5	0.045	2.53
99.8	0.005	0.18
99.9	0.002	0.12

of spectrophotometric grade cyclohexane by using a bubble-cap column. Two distinct azeotropes exist for the ethanol-cyclohexane-water system (*14*). Resulting still bottoms were clear and did not exhibit a Tyndall effect. They contained no water (Karl Fischer titration) and no cyclohexane (infrared absorption). This solution contained over 15% $Al_2(SO_4)_3$ and was apparently stable. It was also titrated with water in order to produce solids in preparation for equilibration.

Equilibrium solids and solution phases were analyzed for aluminum by using EDTA titration. Sulfate was measured by using the gravimetric barium sulfate method. Water content was analyzed by Karl Fischer titration. Carbon content of solids was found by combustion. Solids were washed with absolute ethanol and then dried under vacuum at room temperature for a minimum of 2 h.

Replicate analyses were performed in order to estimate the precision of the analytical data. Results are given in Table II.

Some experiments were performed by equilibrating ethanol-water solutions with anhydrous aluminum sulfate which was made by using the minimum temperature-time condition required to drive all the water from the hexadecahydrate, 330 °C for 2 h. Such systems were equilibrated for 2 weeks at room temperature, followed by a minimum of 4 days of equilibration at 30 °C.

Results and Discussion

Table III shows the results of equilibrating $Al_2(SO_4)_3$ stock solution to which varying amounts of water had been added. Soluble aluminum is expressed as $Al_2(SO_4)_3$. The 99.5% ethanol point represents the system concentrated by distillation. The SO_4/Al mole ratio in solution was found to be 1.4 instead of the expected 1.5 indicating perhaps a volatilization of sulfuric acid esters. When this solution was slowly evaporated over sulfuric acid, a clear solution containing at least 25% $Al_2(SO_4)_3$ was obtained. Whether such solutions are at thermodynamic equilibrium is unknown.

The empirical composition of solid phases is assumed to be $Al(OH)_x(C_2H_5SO_4)_y(SO_4)_z \cdot wH_2O$ where the actual composition in each case is a function of both temperature and ethanol concentration. The values for y and z are determined from analyses for aluminum, carbon, and sulfate, and the value for x is computed from the equation $x = 3.00 - y - 2z$. Ethyl sulfate anion is formed according to eq 1 and 2 (*5*). Empirical

$$\tfrac{1}{2}Al_2(SO_4)_3 + mH_2O \rightleftharpoons Al(OH)_m(SO_4)_{(3-m)/2} + (m/2)H_2SO_4 \quad (1)$$

$$C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5SO_4^- + H^+ + H_2O \quad (2)$$

compositions are given in Table IV. The coefficient for water of hydration, w, is calculated. Only in one instance, where the empirical composition closely approaches that of $Al_2(SO_4)_3 \cdot 16H_2O$ did the calculated value for w agree with that found by Karl Fischer titration. This particular solid dissolved completely in the methanol titration medium whereas the others did not. Table IV shows that solids are hydrated to a greater degree at 30 °C than at 80 °C, consistent with expectations. Also, compounds in equilibrium with more concentrated ethanol solutions are the more basic and contain more ethyl sulfate, consistent with eq 1 and 2.

Results of the anhydrous $Al_2(SO_4)_3$ equilibration experiments are shown in Table V. Solids showed the same well-defined X-ray diffraction pattern before and after equilibration. Under these conditions at least, there is no evidence of a polymorphic or a compositional transformation.

The large differences between the solubilities in Table V and those shown in Table III are undoubtedly due to an activation energy barrier in the dissolution of the anhydrous compound. Note also from Table V that dissolution rates are faster in 97% ethanol than in absolute ethanol. It must be concluded that thermodynamic equilibrium has not been reached in the anhydrous $Al_2(SO_4)_3$ system. Raising the temperature from 30 to 80 °C apparently did not accelerate the process appreciably according to visual observation.

Results of the present work are compared with those of Gee (*6*), de le Paulle (*4*), and Barber and Ali (*2*) in Table VI. At the lower temperatures it is evident that solubilities reported in the earlier work are all lower than our equilibrium solubilities. Some of these data are in fair agreement with our $Al_2(SO_4)_3$ solubilization values, however. This is to be expected inasmuch as a calcined aluminum sulfate was used as the starting material solid phase in all cases, including the work of Gee (*7*). Neither

Table VI. Solubility of $Al_2(SO_4)_3$ in Ethanol; Comparison with Earlier Work

de le Paulle (*4*)

% EtOH[a]	wt % $Al_2(SO_4)_3$	starting material
	20 °C, approximately	
100	0.023	not specified

Barber and Ali (*2*)

% EtOH[a]	wt % $Al_2(SO_4)_3$	starting material
	Room Temperature	
96	0.01	$Al_2(SO_4)_3 \cdot 18H_2O$
96	0.025	$Al_2(SO_4)_3$[b]
	~78 °C	
95.9	0.15	$Al_2(SO_4)_3 \cdot 18H_2O$
96.0	0.10	$Al_2(SO_4)_3$

Gee (*6*)

% EtOH[a]	wt % $Al_2(SO_4)_3$	equilibrium solid phase
		30 °C
83.5	0.0	$Al_2(SO_4)_3 \cdot 10H_2O$
90.8	0.0	
92.6	0.0	
95.2	0.1	$Al_2(SO_4)_3$[c] and $Al_2(SO_4)_3 \cdot 10H_2O$
96.1	0.1	$Al_2(SO_4)_3$[c]
99.9	0.1	
		80 °C
86.6	0.3	$Al_2(SO_4)_3$[c]
92.6	0.7	
99.8	0.9	

This Work

% EtOH[a]	wt % $Al_2(SO_4)_3$	equilibrium solid phase
		30 °C
87.1	0.01	$Al(OH)_{0.06}(C_2H_5SO_4)_{0.034}(SO_4)_{1.45} \cdot 8.03H_2O$
93.4	0.04	$Al(OH)_{1.26}(C_2H_5SO_4)_{0.095}(SO_4)_{0.82} \cdot 5.68H_2O$
94.2	0.57	-
94.6	1.24	-
95.0	1.98	-
99.5	14.80	-
97.1	0.026	$Al_2(SO_4)_3$[d]
97.5	0.045	
99.8	0.005	
99.9	0.002	
		80 °C
87.3	0.01	$Al(OH)_{0.20}(C_2H_5SO_4)_{0.008}(SO_4)_{1.40} \cdot 1.91H_2O$
93.7	0.01	$Al(OH)_{1.07}(C_2H_5SO_4)_{0.069}(SO_4)_{0.93} \cdot 2.35H_2O$

[a] Weight % ethanol by using ethanol and water solvent components only. [b] Produced by heating $Al_2(SO_4)_3 \cdot 18H_2O$ at 400 °C for several hours. [c] Calcined aluminum sulfate hydrate (*7*). [d] Starting material produced by heating $Al_2(SO_4)_3 \cdot 16H_2O$ at 330 °C for 2 h.

anhydrous $Al_2(SO_4)_3$ nor $Al_2(SO_4)_3 \cdot 10H_2O$ equilibrium solid phases reported by Gee were found in the present work. Smith and Walsh (*12*) also did not find the decahydrate reported by Gee.

At 80 °C our equilibrium solubilities are much lower than those reported by Gee and are closer to the values obtained by Barber and Ali. It is to be expected that as the alcohol concentration increases to the vicinity of 93–94%, the $Al_2(SO_4)_3$ solubility will rise sharply, in analogy with the 30 °C behavior. While we do not report equilibrium values in this region, the distillation experiments tend to support this expectation; i.e., the hot still bottoms were highly concentrated in $Al_2(SO_4)_3$.

The unexpectedly high $Al_2(SO_4)_3$ solubilities measured in the present work are more in line with what is known about the solubilities of $Cr_2(SO_4)_3$ (*11*) and of $Fe_2(SO_4)_3$ (*15*) in ethanol. On the other hand, the Waring blender technique developed here was not effective in solubilizing $ZnSO_4$ or $MgSO_4$. Solubilities of these salts in ethanol evidently are low as reported by Gibson, Driscoll, and Jones (*8*). This suggests that the higher solubilities of the Al, Fe^{III}, and Cr^{III} salts may be related to their tendency to form polynuclear complexes.

It has been generally accepted that the solubility of $Al_2(SO_4)_3$ in ethanol is low, and indeed the term "insoluble" has been used (*10*, *13*). The present work provides evidence that this is attributable to the very slow dissolution rates of both hydrated and calcined aluminum sulfates in ethanol. The Waring blender technique employed here converts aqueous $Al_2(SO_4)_3$ solution directly to an amorphous metastable lower hydrate solid which readily dissolves in concentrated ethanol. Such solutions now undoubtedly contain ethyl sulfate species, and the aluminum ion is most probably ethanolated in analogy with the Cr^{III} system (*9*). We show that equilibria are critically dependent upon the water concentration in high concentration ethanol solutions, consistent with the more complex interactions expected here. As to the vastly differing rates of dissolution of the various $Al_2(SO_4)_3$ solids, one can speculate that this is due to differing degrees of anion penetration of the inner coordination sphere of the aluminum ion, in analogy with "green" vs. "violet" forms of $Cr_2(SO_4)_3$, for example (*1*, *11*).

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