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AM(III) HYDROLYSIS CONSTANTS AND SOLUBILITY OF AM(III) HYDROXIDE

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## Am(III) Hydrolysis Constants and Solubility of Am(III) Hydroxide

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*Solubility Americium hydroxide/Solubility product/Hydrolysis constants*

### Summary

Americium(III) hydroxide solubility was measured in dilute salt solutions under an argon atmosphere. The equilibrium, attained in < 23 days, was approached from both over and undersaturation. Thermodynamic equilibrium constants ( $K_{S10}^0$ ) for the solubility of  $\text{Am}(\text{OH})_3$  (amorphous) [ $\text{Am}(\text{OH})_3$  (amorphous) +  $3\text{H}^+$  +  $\text{Am}^{3+}$  +  $3\text{H}_2\text{O}$ ] and the cumulative Am hydrolysis ( $\beta_n^0$ ) constants [ $\text{Am}^{3+}$  +  $n\text{H}_2\text{O}$   $\rightleftharpoons$   $\text{Am}(\text{OH})_{3-n} + n\text{H}^+$ ] were calculated from the solubility data. The measured value of  $\log K_{S10}^0$  was  $17.5 \pm 0.3$ . The values of  $\log \beta_1^0$ ,  $\log \beta_2^0$ , and  $\log \beta_3^0$  were  $\leq -8.2$ ,  $-17.1 \pm 0.5$ , and  $\leq -27.0$ , respectively. Contrary to predictions in the literature, Am(III) does not show amphoteric behavior in the pH range studied (i.e., no evidence for the existence of  $\text{Am}(\text{OH})_4^-$  species).

### Introduction

Determining the mobility of hazardous elements contained in nuclear wastes is central to assessing the long-term safety of various disposal methods. To assess the amount of an element available for transport and its potential mobility, the solubility of its compounds under geochemical environments must either be known or predictable. This paper reports the measured solubility product of

Am(III) hydroxide and the Am(III) hydrolysis constants, some of the parameters necessary for predicting the nature of Am aqueous species and Am(III) hydroxide solubility under geologic environmental conditions.

Americium can exist in four different oxidation states (III, IV, V, VI) [1]. Under Eh-pH conditions of natural aqueous environments [2], Am is expected to be present primarily as Am(III) [3]. However, complete experimental data are not available for the solubility products of Am(III) solids or the formation constants of Am(III) with even the most common and important ligands (such as hydroxide and carbonate). The estimated values of the solubility product ( $K_{S10}$ ) of  $\text{Am}(\text{OH})_3$  (*s*, *s* = solid) are reported in Table 1, along with the estimated and experimental values of some of the hydrolysis constants. The estimated values for the  $\log K_{S10}$  and hydrolysis constants differ by several orders of magnitude. As a result, the previously available thermodynamic data (Table 1) could not be used to accurately predict the dominant Am hydroxy species and the concentrations of Am expected to be present in equilibrium with  $\text{Am}(\text{OH})_3$  (*s*). Therefore, experiments were conducted to determine the solubility product of  $\text{Am}(\text{OH})_3$  (*s*) and the hydrolysis constants of Am(III) species from solubility measurements.

Table 1. Am(III) hydrolysis constants

$\log K_{S10}$ $\text{Am}(\text{OH})_3$ ( <i>s</i> )	Log $\beta_n$ <sup>b</sup> of different species				Ionic strength ( $\mu$ )	Reference
	$\text{AmOH}^{2+}$	$\text{Am}(\text{OH})_2^+$	$\text{Am}(\text{OH})_3^0$	$\text{Am}(\text{OH})_4^-$		
14 <sup>a</sup>	-5.8	-13	-21	-31	0	ALLARD <i>et al.</i> [4] <sup>c</sup>
18.7 <sup>a</sup>	-8.0	-16.9	-26.5	-37.1	0	PHILLIPS [5] <sup>d</sup>
	-3.3	-7.1			0.005	SHALINETS and STEPANOV [6], KOROTKIN [7] <sup>e</sup>
	-2.7				0.005	MARIN and KIKINDAI [8]
	-6.97				1.0	NAIR <i>et al.</i> [9]
	-5.92				0.1	DESIRE <i>et al.</i> [10]
$17.5 \pm 0.3$	$\leq -8.2$	$-17.1 \pm 0.5$	$\leq -27.0$	NE <sup>f</sup>	0	This study

<sup>a</sup> Estimated values for  $\text{Am}(\text{OH})_3$  (*s*) +  $3\text{H}^+$   $\rightleftharpoons$   $\text{Am}^{3+}$  +  $3\text{H}_2\text{O}$ .  
<sup>b</sup> Equilibrium constants ( $\beta_n$ ) for  $\text{Am}^{3+}$  +  $n\text{H}_2\text{O}$   $\rightleftharpoons$   $\text{Am}(\text{OH})_{3-n} + n\text{H}^+$   
<sup>c</sup>  $\beta_1$  is based on experimental value of literature, all others are estimated.  
<sup>d</sup> Based on estimated values by BAES and MESMER [11] for Nd.  
<sup>e</sup>  $\beta_1$  is estimated by SHALINETS and STEPANOV.  
<sup>f</sup> No evidence was found for the existence of  $\text{Am}(\text{OH})_4^-$  in solutions of pH values < 13. If we assume this species becomes dominant past pH 13,  $\log \beta_4$  should be  $\leq -40$ . Experiments are in progress to determine whether  $\text{Am}(\text{OH})_4^-$  becomes dominant past pH 13.

## Materials and methods

<sup>241</sup>Am (III) hydroxide

In this study, a filtered (0.0018  $\mu\text{m}$ ) Am(III) stock solution (nearly 100% <sup>241</sup>Am)<sup>a</sup> was used. Portions of this solution containing approximately 5 mg <sup>241</sup>Am were rapidly titrated with NaOH to pH values of approximately 10 to precipitate <sup>241</sup>Am(III) hydroxide. These suspensions were then centrifuged (6000 g for 40 min) and the supernatant solution discarded. The precipitates were washed twice with 0.0015 M CaCl<sub>2</sub> solutions by centrifuging suspended precipitates and discarding of the supernatant solution. Thirty milliliters of 0.0015 M CaCl<sub>2</sub> solutions, previously adjusted to a range in pH values (1.9 to 9.3) with HCl or NaOH, were then added to the precipitates. The suspensions were equilibrated under air at room temperature and shaken for various periods of time. Periodically, the pH of the suspensions was measured and readjusted because of the time-dependent decrease in pH values due to radiolytic effects of <sup>241</sup>Am [12]. Calcium carbonate (10 mg) was added to two suspensions to neutralize radiolytically produced H<sup>+</sup> and buffer the pH values around 8.

At various times, the pH was measured, the suspensions were centrifuged at  $\sim$ 1900 g for 20 min and small aliquots of the supernate were withdrawn for filtration. Filters of 0.1 and 0.015  $\mu\text{m}$  pore sizes were more effective in separating suspended solids from solution than centrifugation alone at forces of approximately 6000 g for 40 min [13]. In the present study, Amicon type CF25 Centriflo<sup>®</sup> membrane filter cones (Amicon Corp., Lexington, Massachusetts) having an approximate 0.0018  $\mu\text{m}$  pore size were used. These filters were checked to determine whether they adsorb significant quantities of Am. The filters did not adsorb significant amounts of Am (Table 2), as solutions, both filtered and the centrifuged, contained similar Am concentrations. These results placed confidence in the routine use of 0.0018  $\mu\text{m}$  filters. As an added precaution, an aliquot of the sample was filtered and filtrate discarded before filtering the sample for analysis. This technique was used to saturate any possible adsorption sites of the filter and the filtrate collection container.

<sup>243</sup>Am (III) hydroxide

<sup>243</sup>Am(III) hydroxide preparation and solubility measurements were done with solutions sparged with argon and in an argon-filled Model HE-43-2 glove box (Vacuum Atmospheres Corp., Hawthorne, California) equipped with a recirculating oxygen removal system, pressure controller, and evacuable antechamber. An analysis of the glove box atmosphere by gas chromatography indicated 8% N<sub>2</sub>, 92% Ar, and less than 0.02% CO<sub>2</sub>. The O<sub>2</sub> content was less than 0.01% as determined by a fuel-cell type O<sub>2</sub> sensor.

Portions of <sup>243</sup>Am stock (nearly 100% <sup>243</sup>Am) in HNO<sub>3</sub> each containing approximately 16.6 mg <sup>243</sup>Am were rapidly titrated with tetrapropylammonium hydroxide. The precipitates were then washed (see above for details) with deionized water previously adjusted to pH 8.5 with tetrapropylammonium hydroxide. Twenty milliliters of deionized water, previously adjusted to different pH values (7 to 13) with HCl or tetrapropylammonium hydroxide, were added to the precipitates and the suspensions shaken for various lengths of time at room temperatures (22  $\pm$  2 °C). The pH of the suspensions was periodically measured and the suspensions filtered through 0.0018  $\mu\text{m}$  filters before Am analyses.

## Approaching solubility of Am(III) hydroxide from oversaturation

Essentially all of the Am used in precipitating <sup>241</sup>Am(III) and <sup>243</sup>Am(III) hydroxides was present in solution at pH values < 6.5. Radiolysis caused the pH of both the <sup>241</sup>Am and <sup>243</sup>Am solutions to decrease with time, much more rapidly for <sup>241</sup>Am than for <sup>243</sup>Am. Am(III) hydroxide samples with pH values < 6 were used to approach the solubility from oversaturation. In this approach the pH of the above samples was adjusted to higher values (> 7.0) where most of the Am is expected to be present as a solid. These suspensions were equilibrated as previously discussed.

## Analytical measurements

The pH of the suspensions was measured with a combination glass electrode. The <sup>241</sup>Am concentrations in the filtered solutions (0.0018  $\mu\text{m}$ ) were determined by gross alpha counting with a liquid scintillation detector. The <sup>243</sup>Am concentrations were determined by counting the 74.67 keV gamma peak with a high purity germanium planar detector. Aliquots of the filtered <sup>243</sup>Am solutions (0.0018  $\mu\text{m}$ ) were diluted to a fixed volume with 1 M HCl and set aside for approximately 30 days to allow the <sup>239</sup>Np daughter, produced from the total <sup>243</sup>Am solid

Table 2. Comparison of <sup>241</sup>Am concentrations in 0.0018  $\mu\text{m}$  filters and centrifuged supernates from samples of Am contaminated sediment suspensions in 0.0015 M CaCl<sub>2</sub>

Sample pH	dpm/ml		Ratio
	0.0018 $\mu\text{m}$ Centrifuged <sup>a</sup>	(0.0018 $\mu\text{m}$ /Centrifuged)	
1000-25 4.3	1461	1520	0.96
1002-25 4.5	506	537	0.94
1004-25 4.7	283	300	0.94
1006-25 4.9	119	132	0.90
1008-25 5.4	47	55	0.86
1010-25 5.8	18.4	20.7	0.89
1012-25 6.0	7.4	7.7	0.96

<sup>a</sup> Centrifuged at  $\sim$ 6000 g for 40 min.

<sup>a</sup>  $\alpha$  spectroscopy analysis indicated no detectable  $\alpha$  impurities above background ( $\sim$  0.4 cpm).

in the original suspensions, to decay to near secular equilibrium with the  $^{243}\text{Am}$  present in each vial. A waiting period was necessary to resolve the 74.67 keV gamma of  $^{243}\text{Am}$  from the large Compton edge of the PuK X-rays coming from the  $^{239}\text{Np}$  decay. X-ray diffraction patterns of Am solids were obtained with a Gandolfi Camera using  $\text{CuK}\alpha$  radiation [14].

## Results and discussion

### $^{241}\text{Am}$ (III) hydroxide

The pH values of  $^{241}\text{Am}$  (III) hydroxide suspensions were adjusted between approximately 2 and 9 to bracket the pH range of interest. This bracketing was necessary because of the lack of experimental information on the solubility of  $\text{Am}(\text{OH})_3$  (s) and the wide variation in the reported solubility product (Table 1). The measured Am concentration in filtered (0.0018  $\mu\text{m}$ ) solutions as a function of pH showed that  $\text{Am}(\text{OH})_3$  is very soluble; in suspensions of pH values  $< 6.5$ , essentially all of the added  $\text{Am}(\text{OH})_3$  dissolved (Fig. 1). Thus, pH should be greater than approximately 7 for these solubility measurements.

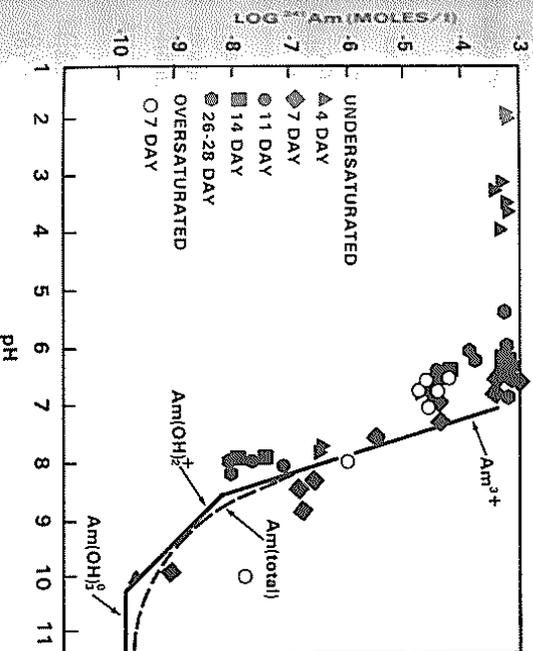


Fig. 1.  $^{241}\text{Am}$  concentrations contacting  $\text{Am}(\text{OH})_3$  (s) (at pH values  $\geq 7$ ) plotted with the lines representing the three parameter model (Table 5) that best fits the  $^{243}\text{Am}(\text{OH})_3$  (s) data (solid lines represent activities of different Am solution species and the dashed line represents the total Am activity in solution). Nearly constant Am concentrations at low pH values ( $\leq 7$ ) are due to complete dissolution of  $\text{Am}(\text{OH})_3$  (s).

Although the pH values of some of the original suspensions were adjusted as high as 9, the pH values of the neutral-to-alkaline suspensions were difficult to maintain. The pH values of some of the samples decreased by one unit even after one day of equilibration (Table 3). We attribute the rapid decrease in pH values to alpha-induced production of nitric acid by  $^{241}\text{Am}$ , an alpha emitting isotope with a 432 year half-life [12]. Only two samples stayed at pH values near 8 at the completion of the experiment (Fig. 1), and even in these cases it was necessary to add  $\text{CaCO}_3$  to buffer the pH values (Table 3).

Table 3. Effect of time on pH values of a few  $^{241}\text{Am}$  (III) hydroxide suspensions

Equilibration period (days)	pH Values of different samples			
	1	2	3	4
0	9.15 <sup>a</sup>	9.30 <sup>a</sup>	8.35	8.00
1	8.85	8.85	7.40	7.10
4	7.70	7.80	6.80	7.00
6	9.50 <sup>b</sup>	9.60 <sup>b</sup>	—	—
7	8.25	8.40	6.75	6.95
11	8.05	8.00	6.55	6.60
14	7.90	7.90	6.55	6.40
19	7.85	7.95	5.95	5.80
26	8.10	8.00	6.05	6.20

<sup>a</sup> Contained 10 mg  $\text{CaCO}_3$ .

<sup>b</sup> Added 10 mg  $\text{CaCO}_3$  and pH raised to the recorded value.

$^{241}\text{Am}(\text{OH})_3$  (s) solubility was also approached from oversaturation. In this case, the pH of solutions containing approximately  $10^{-3.2}\text{M}$   $^{241}\text{Am}$  was raised to values between 7 and 10. After seven days, the aqueous Am concentrations in these samples were similar to those where the  $\text{Am}(\text{OH})_3$  (s) solubility was approached from under-saturation, thus indicating that equilibrium had been reached in 7 days (Fig. 1).

As may be expected, the results indicate decreased  $\text{Am}(\text{OH})_3$  (s) solubility with increased pH (Fig. 1). However, these data are difficult to interpret because insufficient samples were in the pH range ( $> 7$ ) to provide accurate measurements of solubility and hydrolysis constants; also, atmospheric  $\text{CO}_2$  and  $\text{CaCO}_3$  additions may have interfered.

### $^{243}\text{Am}$ (III) hydroxide

Experiments with  $^{241}\text{Am}(\text{OH})_3$  (s) established that pH values  $> 7$  must be maintained for meaningful solubility measurements. Additionally,  $\text{CO}_2$  (g) interferences must be removed to determine hydrolysis constants. Therefore, experiments with  $^{243}\text{Am}$  (an alpha-emitting isotope with a 7380 year half-life) were conducted in an argon glove box over a range of pH values between 7 and 13.

Information on the dominant Am species in a given pH range was obtained through preliminary nonlinear least squares fitting parameters in an analogous fashion to that reported in Table 4. The ionic strength of these Am solutions is primarily due to the Am concentrations when pH values were  $< 10$  and tetrapropylammonium hydroxide when pH values were  $> 10$ . From the information on dominant Am species and the calculated ionic strength ( $\mu$ ), the activity coefficients ( $\gamma$ ) for different Am species (i) were calculated from the DAVIES [15] equation ( $\log \gamma_i = AZ_i^2 [( \sqrt{\mu} ) / (1 + \sqrt{\mu}) - (0.3\mu)]$ ), where  $A = 0.509$  at  $25^\circ\text{C}$  and  $Z_i$  is the valency of the species). The measured Am concentrations were multiplied by the activity coefficients to obtain Am activities. The calculated Am activities (Fig. 2) are  $< 0.2$  of a log unit lower than Am concentrations for four data points around  $10^{-4}\text{M}$ .

Table 4. Nonlinear least squares fitting parameters ( $K_j^0$ )<sup>a</sup>

Number of parameters:	4	3	2
Number of points:	34	34	34
$K_{S10}^0$	17.53 ± 0.39	17.54 ± 0.29	9.90 ± 0.23
$K_{S11}^0$	8.19 ± 8.48		
$K_{S12}^0$	0.47 ± 0.55	0.48 ± 0.41	
$K_{S13}^0$	-9.93 ± 0.33	-9.93 ± 0.33	-9.87 ± 0.28
Chi Square ( $\chi^2$ )		8.87	10.83
$F_x$ Test values		0 <sup>b</sup>	6.85 <sup>c</sup>
$F(5\%)$		4.17	4.16

$$a \quad \text{Log Am} = \log [10(\log K_{S10}^0 - 3\text{pH}) + 10(\log K_{S11}^0 - 2\text{pH}) + 10(\log K_{S12}^0 - \text{pH}) + 10(\log K_{S13}^0)]$$

b Between 4 parameter and 3 parameter functions.

c Between 3 parameter and 2 parameter functions.

The activity corrections for all of the other data points amounted to  $\leq 0.03$  of a log unit which is far less than the scatter in the data.

The  $^{243}\text{Am}$  activities in solutions contacting  $\text{Am}(\text{OH})_3(s)$  for up to 23 days are plotted versus pH in Fig. 2. A steady-state condition appears to have been reached within a few days because the activities are similar over time. As with  $^{241}\text{Am}$ , when the solubility limit was approached from oversaturation (Fig. 2), the  $^{243}\text{Am}$  activities in solutions were similar to the solutions originally contacting  $^{243}\text{Am}(\text{OH})_3(s)$  indicating that equilibrium was reached within 7 days.

The Am solution activity in equilibrium with  $\text{Am}(\text{OH})_3(s)$  decreased with the increase in pH values of up to  $\sim 11$  and appeared to be constant thereafter. The changes can be attributed to  $\text{Am}(\text{III})$  hydrolysis species. Different Am hydroxy species [ $\text{Am}^{3+}$ ,  $\text{AmOH}^{2+}$ ,  $\text{Am}(\text{OH})_2^+$ ,  $\text{Am}(\text{OH})_3^0$ ,  $\text{Am}(\text{OH})_4^-$ ] are predicted to be dominant at different pH values [4, 5]. The  $\text{Am}(\text{OH})_3(s)$  reactions involving these species are given in Eq. (1–5).

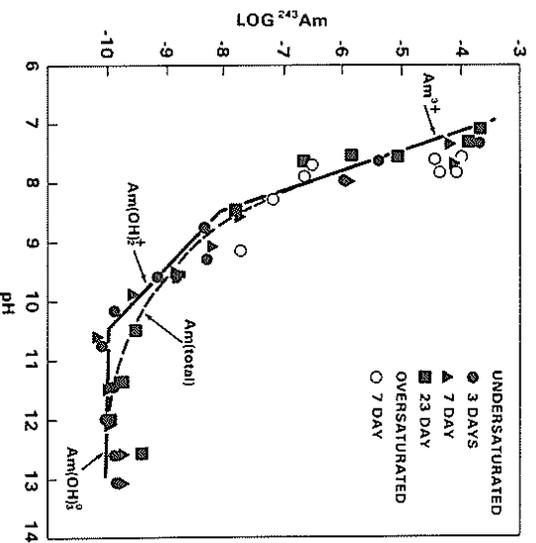
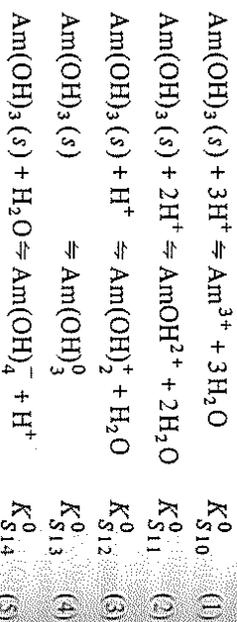


Fig. 2.  $^{243}\text{Am}$  activities in filtrates (0.0018  $\mu\text{m}$ ) from Argon-equilibrated  $\text{Am}(\text{OH})_3(s)$  suspensions in pH adjusted distilled water. Lines represent the three parameter model (Table 5) that best fits the undersaturated data (the solid lines represent activities of different Am solution species and the dashed line represents the total Am activity in solution).



These reactions indicate that for each Am solution species in Eq. (1–5) a line representing the log Am activity versus pH will have a slope of  $-3, -2, -1, 0, +1$ , respectively, in the regions of dominance for each hydrolyzed species. The data in Fig. 2 show that the Am concentration does not ever increase, even at high pH. This indicates that  $\text{Am}(\text{OH})_4^-$  does not have a region of dominance below pH 13; thus, the reaction indicated in Eq. (5) can be ignored.

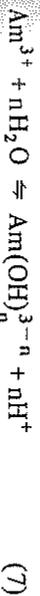
Assuming that Am species represented by Eq. (1–4) are the only species present in significant amounts in solution, we can express the total activity of Am in equilibrium with  $\text{Am}(\text{OH})_3(s)$  as,

$$\begin{aligned} \log \text{Am}(\text{total}) &= \log [(\text{Am}^{3+}) + (\text{AmOH}^{2+}) + (\text{Am}(\text{OH})_2^+) \\ &\quad + (\text{Am}(\text{OH})_3^0)] & (6) \\ \log \text{Am}(\text{total}) &= \log [10(\log K_{S10}^0 - 3\text{pH}) + 10(\log K_{S11}^0 - 2\text{pH}) \\ &\quad + 10(\log K_{S12}^0 - \text{pH}) + 10(\log K_{S13}^0)] \end{aligned}$$

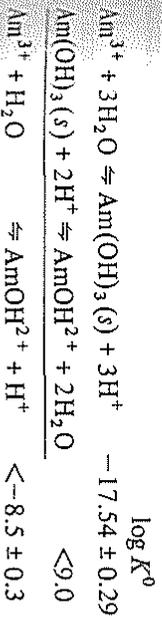
where  $K_{S10}^0$  to  $K_{S14}^0$  represent the equilibrium constants for Eq. (1–4), respectively. A non-linear least squares program, CURFIT [16] with no-weighting option, was used to derive the values of  $K_{Sxy}^0$  parameters from the data in Fig. 2. In addition to fitting the data to the full model (Eq. (6)) with four parameters, truncated models (either three or two parameters) were also applied (Table 4). Statistical  $F_x$  test values using four and three parameter fits as well as three and two parameter fits were calculated from the chi-square ( $\chi^2$ ) values of the individual fits. If  $F_x < F(5\%)$  [17], the additional term is not justified (i.e., a model with fewer parameters fits best) and should not be used in the fitted function. If  $F_x > F(5\%)$ , the additional parameter does significantly

improve the fit and should be included in the function (1c), a model with fewer parameters does not fit as well). Results in Table 4 show that the experimental data is best fitted by the three parameter model which incorporates Eq. (1, 3, and 4). The calculated  $\log K_{S10}^0$ ,  $\log K_{S12}^0$ , and  $\log K_{S13}^0$  values for these reactions, therefore, are  $17.54 \pm 0.29$ ,  $0.48 \pm 0.41$ , and  $-9.93 \pm 0.33$ , respectively (Table 4). The calculated activities of different species along with total Am activity using these three  $\log K_{Sxy}^0$  values are plotted in Fig. 2. Although there were many uncertainties in the  $^{241}\text{Am}$  data, the three-parameter model also described these data reasonably well (Fig. 1). The dominance of  $\text{Am}(\text{OH})_3$  species (Eq. (4)) at pH values  $> 10.5$  is consistent with the data in Fig. 2. However, Am concentrations at these pH values are at or near the detection limit. Therefore, the value of  $-9.93 \pm 0.33$  represents the upper limit for  $\log K_{S13}^0$ .

$\text{AmOH}^{2+}$  is not statistically (Table 4) needed to describe the data over any pH range. Therefore, Eq. (2) only contributes marginally, if at all, to total Am activity (Fig. 2). The maximum possible contribution of Eq. (2) would dictate that the Eq. (1, 2, 3) all intersect at one point (pH 8.53,  $\log \text{Am} = -8.05$ ). Based on this requirement, the upper limit of  $\log K^0$  value of Eq. (2) was calculated to be 9.0. Using the  $\log K^0$  values of Eq. (1-4),  $\log \beta_n^0$  of the hydrolysis constants (Eq. (7)) were calculated.



The  $\log \beta_n^0$  was calculated to be  $\leq -8.2$  by combining Eqs. (1) and (2) in the following manner:



Similarly, the value of  $\log \beta_2$  was calculated to be  $-17.1 \pm 0.5$  and of  $\log \beta_3$  to be  $\leq -27.0$ .

The nature of the solid phase is important in understanding the solubility data. Freshly precipitated  $\text{Am}(\text{OH})_3(\text{s})$  was used in these studies. MILLIGAN *et al.* [18] state that neutralization of acidic Am solutions with a base produces hydrous americia gel. Although  $\text{Am}(\text{OH})_3(\text{c})$ ,  $\text{c} = \text{crystalline}$  was detected in the samples, the solubilities reported here are for  $\text{Am}(\text{OH})_3(\text{a})$ ,  $\text{a} = \text{amorphous}$  because  $\text{Am}(\text{OH})_3(\text{a})$  was the initial precipitated compound [18] that stayed amorphous with time at pH values  $< 9.6$  (Table 5) and was the most soluble phase of the two (most soluble phase controls the solubility). In addition, the solubility stayed nearly constant (Fig. 2) with time (3 to 23 days) indicative of the initial compound [ $\text{Am}(\text{OH})_3(\text{a})$ ]. Because of these reasons and the similarity in solubility between  $^{241}\text{Am}(\text{OH})_3$  and  $^{243}\text{Am}(\text{OH})_3$  with markedly different energy dissipation in the solid, we believe that the activity of the solid phase with aging (3 to 23 days) over a range of pH values is nearly constant.

Table 5. X-ray diffraction data of solids from aged suspensions of  $^{243}\text{Am}(\text{III})$  hydroxide

Standard $\text{Am}(\text{OH})_3(\text{c})^a$	d(A°)	(I/I <sub>0</sub> )	pH Adjusted distilled water- $\text{Am}(\text{OH})_3(\text{s})$ suspensions <sup>b</sup>		
			pH 7.54	pH 9.61	pH 12.97
			Interplanar spacings, d(A°) <sup>c</sup>		
5.565	4	'	'	'	
3.217	10	'	'	'	
3.105	10	'	'	'	3.074
2.783	1	'	'	'	2.797
2.441	1	'	'	'	2.462
2.102	7	'	'	'	2.227
1.850	3	'	'	'	2.040
1.832	8	'	'	'	1.845
1.734	7	'	'	'	
1.619	1	'	'	'	1.771
1.605	2	'	No peaks		1.614
1.545	1	'	No peaks		1.549
1.425	1	'	'	'	1.427
1.397	0.5	'	'	'	
1.320	2	'	'	'	1.315
1.278	2	'	'	'	
1.214	1	'	'	'	

<sup>a</sup> MILLIGAN *et al.* [18].

<sup>b</sup> 23-day equilibration period.

<sup>c</sup> All the observed spacings in the quoted region ( $> 1.214$ ) are listed.

The values obtained for different thermodynamic constants from solubility measurements are summarized in Table 1. These experimentally determined values will help determine Am hydrolysis species to be expected in different ground-water conditions.

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