

《Original》

States of Am in Aqueous Solution

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수용액중의 Am의 상태

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Abstract

The state of Am in the concentration of 10^{-5} M has been studied in the pH range of 5 to 10 by filtration and centrifugation method. By the experiments, we could estimate possible Am hydrolysis products and solubility constants. If the solubility of Am $(\text{OH})_3$ estimated by Baes and Mesmer is increased about a factor of 10, i.e. changing $\log k = -18.7$ to $\log k = -17.5$ it was found that the calculated curve of Am concentration versus pH agreed completely with experimental values.

요 약

pH 변화 5~10 범위에서 10^{-5} M Am 수용액의 상태를 여과법 및 원심분리법에 의하여 조사하였다. 이 실험에서 Am의 가능한 가수분해 생성물 및 용해도 상수를 추정할 수 있었다. 이때 Baes 및 Mesmer에 의하여 이론적으로 계산한 Am $(\text{OH})_3$ 의 용해도를 약 10배 증가하면 즉 $\log k = -18.7$ 를 $\log k = -17.5$ 로 변화시키면 계산에 의한 pH 변화에 따른 Am 농도곡선은 실험치와 완전히 일치하였다.

1. Introduction

Several investigations (1, 2, 3) have been devoted to the study of the states of Am in aqueous solution at trace concentrations as a function of pH. A dispute followed the publication of the results and explanation of the nature of possible colloidal forms and the conditions for their formation (4, 5), e.g. adsorption of Am on near colloidal size particles of foreign

material (pseudo colloids) versus the formation of colloids by Am itself (true colloids).

From the results of studies on the behavior of ^{241}Am at a concentration of 10^{-9} M as a function of pH using ultrafiltration, centrifugation, electro-migration and direct adsorption techniques, Starik and Ginsburg (1) concluded that the colloidal behavior of Am in aqueous solution at pH values between 6 and 8 resulted from the sorption of positively charged Am species on particles of foreign material, e.g. silicic acid

particles, to form pseudo colloids while true Am predominated at pH values greater than pH 9 where the solubility product for the formation of Am (OH)₃ appeared to be exceeded.

In the present study, we have examined the state of Am in the concentration of 10⁻⁵ M by filtration and centrifugation method. Measurements of the concentration of Am in aqueous 0.1N NaClO₄ solutions of the pH range 5 to 10 have been completed.

2. Experimental

2-1. Materials

All solutions were prepared with distilled deionized water from which CO₂ had been removed by boiling for about one hour followed by flushing with Ar. Ultra pure HCl, NaOH and NaCl₄ were used to prepare the Am solutions and to adjust pH.

2-2. Measurements

The pH measurements were made using an Orion model 399A pH meter with a Beckman model 39505 combination glass electrode. The ²⁴³Am content of the aliquots were determined by gross alpha counting using a Packard 460 liquid scintillation counter.

2-3. Purification of Am Ion

The purification of the Am³⁺ (Am Cl₃ in 0.1 M HCl) was accomplished by ionexchange chromatography. The ²⁴³Am³⁺ in 0.1 M HCl was loaded on a Dowex 50×8 cation-exchange resin (400 mesh) column. The column was first washed with 3 column volumes of 0.1M HCl and then 3 column volumes of 3 M HCl. The Am³⁺ was then eluted with 6 M HCl. The eluate was taken to near dryness and a stock solution of 1ml of 5.996×10⁻³M ²⁴³Am was prepared with 0.1 M HCl. Alpha pulse height analysis of samples taken from the stock solution showed that the isotopic composition was 99.8% ²⁴³Am, 0.15% ²⁴¹Am and <10⁻⁴% ²⁴⁴Cm by weight.

2-4. Exclusion of Carbon Dioxide

In order to exclude CO₂ from the system, the sample preparations and subsequent measurements were carried out in an inert atmosphere box under an Ar atmosphere. In addition, the box atmosphere was circulated through a canister containing soda lime to decrease the CO₂ content as low as possible. Unfortunately, we have no way to measure the exact CO₂ content. However, the O₂ content of the box atmosphere was measured periodically using a Teledyne model 310 oxygen analyzer. By purging the box with Ar, the oxygen content of the box atmosphere was maintained at less than 2,000ppm or ~1% of room air. Since nothing was done to remove O₂ in the box atmosphere except purging with Ar, an estimate of the upper limit to the CO₂ content could be made by assuming that the CO₂/O₂ ratio in the box atmosphere was the same as the room air. This estimate was <3×10⁻⁶ atmospheres CO₂. Circulation of the box atmosphere through the canister should have reduced the CO₂ content substantially below this limit.

2-5. Separation of ²⁴³Am from ²⁴³Am-²³⁹Np Mixture

Since the ²³⁹Np, daughter of ²⁴³Am, could contribute to the counting rate and was not necessarily in equilibrium with the Am, the ²⁴³Am was separated from the ²³⁹Np by cation-exchange chromatography before counting. One ml of the aliquots (0.1 M in HCl) was passed through 3mm diameter by 6 cm long Dowex 50×8 cation-exchange resin column and the Am was absorbed on the top of the column.

The column was then washed with 1ml of 1 M HCl to elute the Np; then the Am was eluted with 1ml of 6 M HCl. This procedure consistently gave greater than 95% recovery of the ²⁴³Am free of ²³⁹Np. Aliquots of the eluted Am solutions were made up to 1ml with 0.1 M HCl and 10ml of Packard insta-gel scintillating cocktail

was added. The ^{243}Am contents of the solutions were then determined by liquid scintillation counting.

2-6. Procedure

Duplicate samples (labelled AmI and Am II) of 100ml volumes, $1.023 \pm 0.031 \times 10^{-5}\text{M}$ in ^{243}Am and 0.1N in NaClO_4 , were prepared. The pH of these solutions was initially adjusted to 5 with dilute NaOH . The pH was then increased in steps of ~ 1 pH unit to pH 10.

At each new pH value, the solutions were allowed to sit for several days to reach equilibrium. The pH was checked nearly daily and readjustments were made if necessary. Initially it was planned to allow the solutions to sit at each pH for about 4 days. However, in the range 6~9, the pH tended to drift slowly, usually to lower values, with time. Therefore, waiting times were extended to longer periods to allow the pH to be more or less stabilized. However, even after the longer periods, some drift was observed at pH 7, 8 and 9.

At the end of the waiting periods, samples of the two solutions were taken and centrifuged at 15,000 RPM for 5 minutes.

One ml of the centrifuged solutions was taken directly for analysis of ^{243}Am content. Two mls of the centrifuged solutions were passed through 0.4 micron Gelman disposable filters. In an attempt to minimize the effect of possible sorp-

tion of Am by the filters, the first oneml of filtrate through the filters was discarded and the second one ml was taken for analysis for ^{243}Am . Since any precipitated Am could be in a finely divided form, at pH 8, 9, and 10 portions of the centrifuged solutions were also passed through 0.015 micron Nucleopore filters to determine if there might be an effect due to filter pore size. All aliquots of the centrifuged and filtered solutions were acidified to 0.1M with HCl solution before removal from the inert box for analyses.

3. Results and Discussion

The concentrations of ^{243}Am , expressed as moles/liter, in the various samples as a function of pH are given in Table 1. From a consideration of errors associated with counting and sampling, the precision of the reported values for the Am concentrations is 3%. The errors in the pH values were estimated from the inherent reproducibility of the pH meter and probe (~ 0.05 of a pH unit) and the observed drift in the pH during the waiting periods.

There was essentially no observed loss in Am from solution for both Am I and II at pH values of $\sim 5, 6$ and 7. Both the centrifuged and the 0.4 micron filtered samples gave nearly the same results. At pH 8, Am began to be lost

Table 1. Concentration of Americium in Solution as a Function of pH

pH	Time (days)	Am I(M)			Am II(M)		
		1	2	3	1	2	3
4.95 \pm 0.05	4	0.954 $\times 10^{-5}$	0.964 $\times 10^{-5}$		0.9451 $\times 10^{-5}$	0.913 $\times 10^{-5}$	
5.90 \pm 0.15	5	1.020 $\times 10^{-5}$	1.048 $\times 10^{-5}$		1.059 $\times 10^{-5}$	1.042 $\times 10^{-5}$	
6.85 \pm 0.20	7	0.873 $\times 10^{-5}$	0.912 $\times 10^{-5}$		0.921 $\times 10^{-5}$	0.936 $\times 10^{-5}$	
7.90 \pm 0.15	23	3.757 $\times 10^{-6}$	3.393 $\times 10^{-6}$	2.131 $\times 10^{-5}$	5.715 $\times 10^{-5}$	5.322 $\times 10^{-5}$	3.975 $\times 10^{-6}$
8.95 \pm 0.10	21	1.699 $\times 10^{-7}$	1.140 $\times 10^{-8}$	2.362 $\times 10^{-8}$	7.700 $\times 10^{-8}$	1.288 $\times 10^{-8}$	1.297 $\times 10^{-8}$
10.00 \pm 0.05	12	1.595 $\times 10^{-7}$	1.750 $\times 10^{-9}$	5.040 $\times 10^{-9}$	7.716 $\times 10^{-8}$	1.698 $\times 10^{-9}$	4.394 $\times 10^{-9}$

1-centrifugation; 2-centrifugation plus 0.40 micron filtration; 3-centrifugation plus 0.015 micron filtration

Initial Am concentration= $1.023 \pm 0.031 \times 10^{-5}\text{M}$

from solution and the centrifuged and the filtered samples began to give slightly different results. At pH values of 9 and 10, the centrifuged samples contained considerably more Am in solution than the filtered samples. These higher values, compared to the filtered solutions, could have resulted from finely divided Am(OH)₃ or Am sorbed on very small contaminant particles that were not centrifuged down at 15,000 RPM. They could also have resulted from sampling problems since it is possible that some of the centrifuged material could have been stirred up when the 1 ml samples were taken from the 1.5 ml centrifuge cones. However, the values obtained for the centrifuged samples do represent an upper limit to the solubility of Am under these conditions. At pH 9, the 0.4 micron and 0.015 micron filtered samples gave similar results but, at pH 10, the 0.4 micron filtered samples contained approximately a factor of three less Am than the 0.015 micron samples for both Am I and Am II. This leads one to suspect that the filtration process may have removed Am from solution. The 0.4 micron Gelman filters are more massive and probably present a larger possible sorption area to the solutions than the 0.015 micron Nucleopore filters. This is a problem that will have to be investigated further in the future. Since we do not know the source of the difference, between the 0.4 and 0.015 micron filtered samples, values of Am concentration in solution for both filter sizes and for both Am I and Am II were averaged for the pH values of 8, 9 and 10 and least square errors calculated. For pH values of 5, 6 and 7, the results for the 0.4 micron samples for both Am I and Am II were averaged. The results of these calculations are displayed in Figure 1 as the points.

Allard has reported estimates for the hydrolysis constants for Am³⁺ in aqueous solution as for the solubility product of Am(OH)₃(6). His

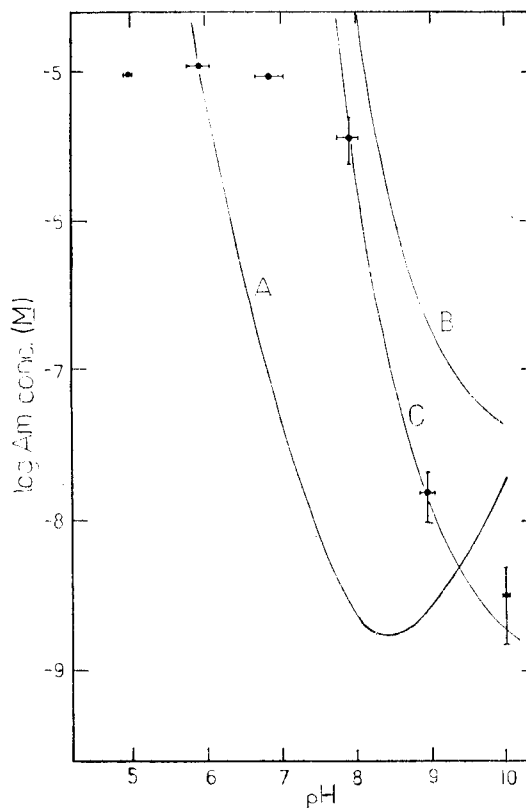


Fig. 1. Log of Am Concentration v.s. pH

estimates are given in Table 2. Using a computer program which includes corrections for ionic strength by the Davies equation (7), we have calculated the solubility limit for Am in a 0.1 N NaClO₄ solution as a function of pH from Allard's estimates. The results of the calculation are shown in Figure 1 as the curve marked A.

Baes and Mesmer (8) have also estimated the solubility product for Am(OH)₃ from a comparison with a lanthanide ion of nearly the same ionic radius, i.e. Nd³⁺, and their estimate is given in Table 2. It seems reasonable to go a step further and to use the measured or estimated values for the hydrolysis constants for Nd as estimates for Am. These values, taken from Baes and Mesmer, are also shown in Table 2. The solubility limits for Am(OH)₃ in 0.1 N

Table 2. Estimates of Hydrolysis and Solubility Constants of Am

Reaction		logK (Allard)	logK (Baes & Mesmer)	logK(OurWork)
Hydrolysis	$\text{Am}^{3+} + \text{H}_2\text{O} = \text{Am}(\text{OH})^{2+} + \text{H}^+$	- 5.80	- 8.0	- 6.8
	$\text{Am}^{3+} + 2\text{H}_2\text{O} = \text{Am}(\text{OH})_2^+ + 2\text{H}^+$	-13.0	-16.9	-15.7
	$\text{Am}^{3+} + 3\text{H}_2\text{O} = \text{Am}(\text{OH})_3 + 3\text{H}^+$	-21.0	-26.5	-25.5
	$\text{Am}^{3+} + 4\text{H}_2\text{O} = \text{Am}(\text{OH})_4^- + 4\text{H}^+$	-30.0	-37.1	-36.9
	$\text{Am}^{3+} + 2\text{H}_2\text{O} = \text{Am}_2(\text{OH})_2^{4+} + 2\text{H}^+$	-11.0	-13.8	-12.6
Precipitation	$\text{Am}^{3+} + 3\text{H}_2\text{O} = \text{Am}(\text{OH})_3 + 3\text{H}^+$	-12.0	-18.7	-17.5

NaClO_4 were calculated as a function of pH using these estimates and are shown in Figure 1 as the curve labelled B. Clearly our experimental data favor the solubility limit line calculated from the Baes and Mesmer estimates (curve B) over the line calculated using Allard's estimates (curve A). In fact, if the solubility of $\text{Am}(\text{OH})_3$ estimated by Baes and Mesmer is increased about a factor of 10, i.e. changing $\log k = -18.7$ to $\log k = -17.5$, the calculated curve labelled C results.

It is impossible to estimate each solubility constant of Am by the measurement of gross Am radioactivity. However, we could estimate the solubility constant assuming $[\text{Am}]_{\text{exp}} = a[\text{Am}]_{\text{BM}}$, where $[\text{Am}]_{\text{exp}}$ and $[\text{Am}]_{\text{BM}}$ represent experimentally determined Am concentration and theoretically determined Am concentration by Baes and Mesmer respectively, and a is proportional constants.

Am concentration in solution can be shown as

$$\begin{aligned}
 [\text{Am}] &= [\text{Am}^{3+}] + [\text{Am}(\text{OH})^{2+}] \\
 &\quad + [\text{Am}(\text{OH})_2^+] + \dots \\
 &= [\text{Am}^{3+}] + \frac{[\text{Am}^{3+}]}{[\text{H}^+]} k_1 + \frac{[\text{Am}^{3+}]}{[\text{H}^+]^2} k_2 \\
 &\quad + \dots \quad (1)
 \end{aligned}$$

$$\begin{aligned}
 \text{where, } k_1 &= \frac{[\text{Am}(\text{OH})^{2+}][\text{H}^+]}{[\text{Am}^{3+}]} \\
 k_2 &= \frac{[\text{Am}(\text{OH})_2^+][\text{H}^+]^2}{[\text{Am}^{3+}]}
 \end{aligned}$$

Assuming $[\text{Am}]_{\text{exp}} = a[\text{Am}]_{\text{BM}}$, we obtain

$$[\text{Am}]_{\text{exp}} = a \left\{ [\text{Am}^{3+}] + \frac{[\text{Am}^{3+}]}{[\text{H}^+]} (k_1)_{\text{BM}} \right.$$

$$\left. + \frac{[\text{Am}^{3+}]}{[\text{H}^+]^2} (k_2)_{\text{BM}} + \dots \right\} \quad (2)$$

Where, $(k_1)_{\text{BM}}$ and $(k_2)_{\text{BM}}$ etc. show the hydrolysis constants determined by Baes and Mesmer calculation.

Comparing eq. (1) with eq. (2), it can be shown by

$$k_1 = a(k_1)_{\text{BM}}, \quad k_2 = a(k_2)_{\text{BM}}$$

If solubility constants of Am by Baes and Mesmer are increased about a factor of 10, we can estimate experimentally determined solubility constant of Am as shown in Table 2.

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