

INFO #: 18845680

LOS ALAMOS NATIONAL LABORATORY  
Jean-Francois Lucchini

Entered: 11/5/2008 1:50:00PM

NB 11/12/2008  
12:00 AM PT  
A

SHIP VIA: **Ariel**

*Ariel*

FILLED ON: 11/05/2008

**Infotrieve, Inc.**

1888 Century Park East, Ste 600

Los Angeles, CA 90067

Phone 800-422-4633 or 203-423-2175

Fax



# Holdings

Send article only if in the Library collection

NB 11/12/2008  
12:00 AM PT  
A

SHIP TO: 14288 / 2205718

LOS ALAMOS NATIONAL LABORATORY  
Jean-Francois Lucchini  
A141

Please contact us if you have questions or comments regarding this article.

Email: [service@infotrieve.com](mailto:service@infotrieve.com)

Phone: (800) 422-4633

CUSTOMER INFO  
PHONE: +1.575.234.5556  
FAX: +1.575.887.3051  
TEAM: T8-14288  
COURIER:

## ARTICLE INFORMATION

ARIEL:

0033-8230  
RADIOCHIMICA ACTA

NOTES:

44-5():39 44 1988

Main 1962-1993  
Publisher 2000-2002 Online

HYDROLYSIS REACTIONS OF AM(III) AND AM(V)  
Send article only if in the Library collection

CCD 0  
SHIP VIA Ariel  
ORDER #  
BILLING REF  
ORDERED ON 11/05/2008  
FILLED ON 11/05/2008  
NEED BY 11/12/2008  
ATTENTION Jean-Francois Lucchini  
INFO # 18845680

This document is protected by U.S. and International copyright laws. No additional reproduction is authorized. Complete credit should be given to the original source.

## Hydrolysis Reactions of Am(III) and Am(V)

By S. STADLER and J. I. KIM, Institut für Radiochemie, TU München, 8046 Garching, FRG

(Received October 9, 1987; revised December 17, 1987)

*Hydrolysis constants/Solubility product/Americium(III)/Americium(V)/Speciation*

### Abstract

Hydrolysis reactions of Am(III) have been investigated in non-complexing solution as well as saline solutions under CO<sub>2</sub>-free conditions. The solubility experiment in combination with radiometric pH-titration is carried out for the pH range from 6 to 13, at different ionic strengths. In non-complexing solution, the solubility product is found to be increasing along with an increase of the specific  $\alpha$ -activity in a given experimental solution. In concentrated NaCl solutions ( $I \geq 3M$ ,  $pH > 7$ ) with high specific  $\alpha$ -activities ( $> 1$  Ci/L), the  $\alpha$ -radiolysis starts generating substantial amounts of oxidized chlorine species, e. g. ClO<sup>-</sup>, which results in the oxidation of Am(III) to Am(V). The hydrolysis reaction of Am(V) in 3M NaCl is also investigated by radiometric pH-titration. Solubility products ( $K_{sp}$ ) of Am(OH)<sub>3</sub>(s) and AmO<sub>2</sub>(OH)(s) and hydrolysis constants of Am(III) and Am(V) are calculated from the solubility data. The speciation of different hydrolysis products, undertaken by laser-induced photoacoustic spectroscopy (LPAS), has verified probable species assessed theoretically on the basis of solubility experiments.

### 1. Introduction

The geochemical behaviour of Am(III) is controlled sensitively by its hydrolysis reactions that cause solubility constraints of Am compounds in natural water. The hydrolysis constants are therefore the first important chemical parameters for understanding the migration behaviour of americium in natural aquatic systems [1]. Various efforts have been devoted to the determination of individual hydrolysis constants of Am(III) by either experiment [2–13] or evaluation from systematics associated with hydrolysis reactions of trivalent metal ions, e. g. lanthanides [14, 15]. As far as hydrolysis reactions of trivalent actinide ions are concerned, the investigation has been concentrated much more on the Am<sup>3+</sup> ion than on other actinide ions [1], since Am(III) remains rather stable as a trivalent ion under various experimental conditions. Consequently more data are available in the literature for its solubility product as well as hydrolysis constants. However, there are large discrepancies among published data, even in several logarithmic units, which would eventually result in a considerable uncertainty in the source term evaluation for a given repository site. Further improvement of the constants is therefore of logical necessity.

The present work is intended to redetermine the solubility product and hydrolysis constants of Am(III) in non-complexing NaClO<sub>4</sub> solution in order to verify the previous results [12, 16] and further to determine the

same constants in saline solutions of different NaCl concentrations, which are requisite conditions for the near field chemistry of the German repository site at Gorleben. While carrying out experiment, it is found that  $\alpha$ -radiation induced radiolysis reactions in concentrated NaCl solutions become significant, resulting in the oxidation of Am(III) to Am(V) [17–19]. For this reason the hydrolysis reactions of Am(V) have been also investigated in a selected saline solution.

### 2. Experimental

Hydrolysis reactions are studied by solubility measurements in combination with radiometric pH titration. The <sup>241</sup>Am solution in 0.01M HClO<sub>4</sub> or HCl is introduced into a thermostated double-walled glass vessel with the inner volume of 200 ml through which pure Ar gas (99.998%) is passed continuously. The Am solution is diluted with NaClO<sub>4</sub> or NaCl to attain a desired ionic strength:  $\mu = 0.1$  mol/L for NaClO<sub>4</sub> and  $\mu = 0.1–5.0$  mol/L for NaCl. The Am concentration in each experiment is maintained at  $6 \times 10^{-3}$  mol/L or less. By addition of several drops of CO<sub>2</sub>-free 11M NaOH (Baker Co.) the solution is adjusted to pH = 12–13, allowing the Am ion to precipitate as hydroxide. After pH of the solution becomes stabilized, the solution is sampled to determine the Am concentration. While changing pH stepwise downwards, at each stabilized pH the solution is sampled for the concentration measurement of Am. The stabilization of each pH step takes 1 or 2 days. Ar gas is bubbled through during the whole experiment. The Am concentration is determined by liquid scintillation counting after the phase separation of colloids by ultrafiltration at different pore sizes: 220 nm, 30 nm, 20 kD (ca. 2 nm) and 5 kD (ca. 1.3 nm). The titration is carried out downwards as well as upwards of pH.

Am(V) is produced by allowing to stand the Am(III) hydroxide precipitate in 3M NaCl at pH > 8 for a week. The  $\alpha$ -induced radiolysis reactions increase the redox potential of the solution to over +1000 mV at about 1 Ci/L specific  $\alpha$ -activity of <sup>241</sup>Am in the solution. The hydrolysis experiment of Am(V) is carried out as described above in 3M NaCl.

The speciation of Am in solution is made by absorption spectroscopy for higher concentrations and by laser-induced photoacoustic spectroscopy (LPAS) for lower concentrations. The LPAS has a speciation sensitivity of Am<sup>3+</sup> at  $10^{-8}$  mol/L or a few ppb range [20, 21].

### 3. Results and discussion

#### 3.1. Am (III) hydrolysis in non-complexing solution

The study of hydrolysis reactions by solubility measurements as a function of pH requires first of all the solubility product of  $\text{Am}(\text{OH})_3(\text{s})$  for a given experimental condition. The solubility product  $K_{sp}$  is determined spectroscopically in non-complexing solution of  $0.1\text{ M NaClO}_4$  at  $\text{pH} = 6.34$ . The concentration of  $\text{Am}^{3+}$  under equilibrium with  $\text{Am}(\text{OH})_3(\text{s})$  is determined by comparing its spectrum with that from  $1\text{ M HClO}_4$ . No difference is observed in the two spectra as for absorption characteristics, e. g. peak position, shape and width. The spectroscopic concentration is found to be equal to the value obtained by liquid scintillation counting. The solubility product is then determined by the known relation:

$$\begin{aligned} \log K_{sp} &= \log [\text{Am}^{3+}] + 3 \log Q_w + 3 \text{pH} + 3 \log \gamma_{\text{H}^+} \\ &= -25.0 \pm 0.3 \end{aligned} \quad (1)$$

where  $[\text{Am}^{3+}]$  is the Am concentration determined by spectrophotometry,  $Q_w$  the ion product of  $\text{H}_2\text{O}$  in  $0.1\text{ M NaClO}_4$  ( $\log Q_w = -13.78$  [22]) and  $\gamma_{\text{H}^+}$  the activity coefficient of  $\text{H}^+$  at ionic strength of  $0.1\text{ mol/L}$ . The spectroscopic investigation has revealed that the  $\text{Am}^{3+}$  ion is the only species present in the solution at  $\text{pH} = 6.34$ , although the speciation by calculation (cf. section 3.2) indicates the presence of  $\text{Am}(\text{OH})^{2+}$  at about 5% under this condition. The reason may be the absorption coefficient of  $\text{Am}(\text{OH})^{2+}$ , which is presumably lower than that of  $\text{Am}^{3+}$ . The correction for the value of 5% gives rise to a decrease of the solubility product by 0.02 logarithmic unit, which is found to be negligible in comparison with the experimental error given above ( $\pm 0.3$ ).

Based on the solubility product thus determined, the stepwise hydrolysis reactions are evaluated from the solubility data as shown in Fig. 1, which follows a certain function of pH. As the ionic strength is maintained constant at  $0.1\text{ M NaClO}_4$  and the Am concentration remains far below the ionic strength for all equilibrium solutions, the evaluation is proceeded simply on the concentration basis. The total Am concentration observed in each equilibrium solution can be described by the relation:

$$[\text{Am}(\text{III})]_{\text{tot}} = \frac{K_{sp}}{[\text{OH}]^3} \sum \beta_i [\text{OH}]^i \quad (2)$$

with

$$\beta_i = \frac{[\text{Am}(\text{OH})_i^{3-i}]}{[\text{Am}^{3+}][\text{OH}]^i} \quad (3)$$

Eq. 2 is valid for the solution containing only monomeric species. The generation of polymers and colloids of Am(III) has been carefully examined firstly by ultrafiltration with the aid of activity measurement with decreasing the pore size from  $220\text{ nm}$  to about  $1.3\text{ nm}$  and secondly by spectroscopic investigation of filtrates. The

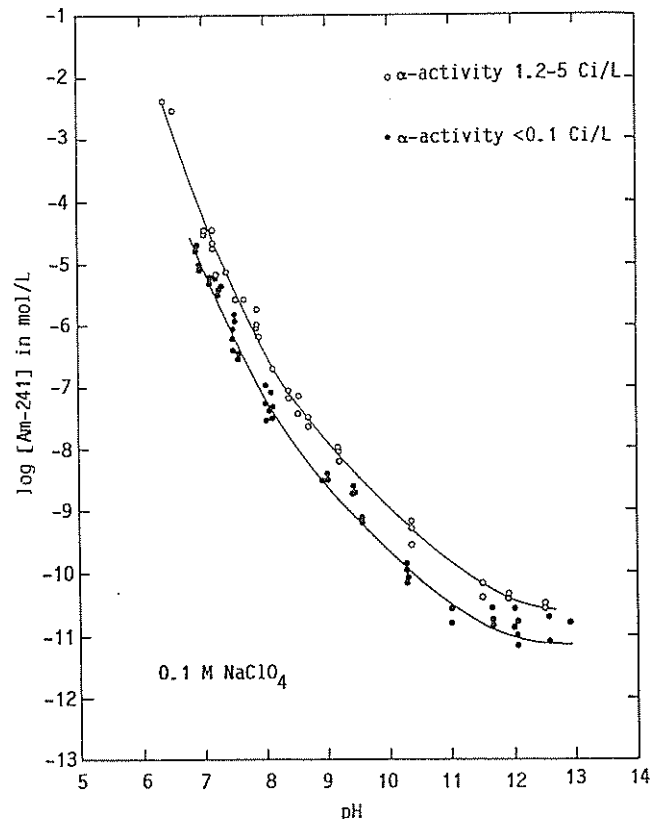


Fig. 1. Solubility of Am(III) hydroxide precipitate in  $0.1\text{ M NaClO}_4$  as a function of pH. The upper and lower results are from solutions containing the specific  $\alpha$ -activity of  $1.2-5\text{ Ci/L}$  and  $<0.1\text{ Ci/L}$ , respectively.

results from a combination of the two procedures does not disclose any inference to the presence of either polymers or colloids in solutions under investigation.

On the increase of the total specific activity of  $^{241}\text{Am}$  in a given experimental solution by augmenting the amount of  $\text{Am}(\text{OH})_3(\text{s})$  in a constant solution volume, it is observed that the solubility at each pH becomes also increased. Such an increase is noticed only for the specific activity changing from  $0.1\text{ Ci/L}$  to  $1.2\text{ Ci/L}$ , but further increase over  $1.2\text{ Ci/L}$  does not result in additional solubility change.

A solubility increase due to the higher specific activity of  $^{227}\text{Ac}(\text{OH})_3(\text{s})$  is mentioned already in the literature [23], which is noted from experiments with and without separation of  $\alpha$ -emitting daughter nuclides of  $^{227}\text{Ac}$ . Other experiments with non-radioactive metal hydroxides of different surface areas have demonstrated that a larger surface area leads to a relatively higher solubility [24]. These two phenomena provide some plausible explanations to the present experimental results. Increasing the amount of  $\text{Am}(\text{OH})_3(\text{s})$  in a given solution, the relatively larger intensity of  $\alpha$ -particles is created within the unit volume of solid which may cause in a larger solid surface due to  $\alpha$ -recoil splittings. On the other hand, the higher  $\alpha$ -specific activity in a given aqueous solution increases the concentration of radiolysis products, e. g.  $\text{H}_2\text{O}_2$ ,  $\text{H}_2$  etc. [25]. Chemical and physical reactions of these products, including gas bubbling in microscopic scale, may

**Table 1.** Solubility products of Am(OH)<sub>3</sub>(s) and hydrolysis constants of Am(III) in NaClO<sub>4</sub> and NaCl solutions

log <i>K</i> <sub>sp</sub>	log β <sub>1</sub>	log β <sub>2</sub>	log β <sub>3</sub>	Medium
-25.7 ± 0.3	6.3 ± 0.3	12.2 ± 0.4	14.4 ± 0.5	0.1 M NaClO <sub>4</sub> , 0.1 Ci/L
-25.0 ± 0.3	6.3 ± 0.2	12.2 ± 0.3	14.4 ± 0.2	0.1 M NaClO <sub>4</sub> , 1.2–5 Ci/L
-25.1 ± 0.5	6.0 ± 0.4	12.2 ± 0.5	14.8 ± 0.5	0.1 M NaCl, 2–5 Ci/L
-25.0 ± 0.1	5.6 ± 0.3	11.6 ± 0.4	14.1 ± 0.5	0.6 M NaCl, 2–5 Ci/L

lead to a change in hydroxide particles, presumably a surface increase. A combination of these effects can be the reason for the solubility increase of Am(OH)<sub>3</sub>(s) to a certain limited extent.

The solubility increase due to the specific activity of <sup>241</sup>Am in 0.1 M NaClO<sub>4</sub> is shown in Fig. 1. Since the solubility product is a parameter describing the primary dissolution process that releases the Am<sup>3+</sup> ion from its hydroxide ppt, while the subsequent hydrolysis reactions of the ion take place in the bulk solution, the solubility increase may be solely related to an increase made to the solubility product. Such an assumption is founded on the fact that the solubility curves from the two solutions of different specific activities (Fig. 1) run in parallel within the uncertainty of each experiment.

Taking into account the *K*<sub>sp</sub> value known by Eq. 1, the hydrolysis constants are calculated according to Eq. 2 at first for the upper solubility curve in Fig. 1 from the experiment with higher specific activity (> 1.2 Ci/L). Based on these hydrolysis constants, the solubility product for the lower solubility curve (< 0.1 Ci/L) is then evaluated. The results are given in Table 1. There is no indication of the presence of the anionic hydrolysis species, *i. e.* Am(OH)<sub>4</sub><sup>-</sup>, in different systems under investigation. The solubility product from the 0.1 Ci/L solution is somewhat lower by 0.7 logarithmic unit than the value from the solution with > 1.2 Ci/L.

The solubility products and hydrolysis constants are further determined in 0.1 M NaCl and 0.6 M NaCl and given also in Table 1. Since the chloride complexation will influence the hydrolysis reactions of Am<sup>3+</sup> to a negligible extent, there are almost no differences in β values between 0.1 M NaClO<sub>4</sub> and 0.1 M NaCl. However, the solubility products in these solutions seem to differ slightly from each other. In 0.6 M NaCl, because of the higher ionic strength the hydrolysis constants tend towards somewhat smaller values, whereas the solubility product is virtually not changed from the value in 0.1 NaCl.

Among different values attained for each reaction constants from the present experiment, the following values are considered to be recommendable for the solution with ionic strength, μ = 0.1 mol/L:

$$\log K_{sp} = -25.7 \pm 0.3$$

$$\log \beta_1 = 6.3 \pm 0.3$$

$$\log \beta_2 = 12.2 \pm 0.4$$

$$\log \beta_3 = 14.4 \pm 0.5$$

as these are determined in the non-complexing solu-

tion of low ionic strength with a minimal radiation effect (0.1 Ci/L). Although the values from other experimental conditions as shown in Table 1 do not vary significantly from the above data, they are somewhat impaired by radiation as well as chloride ion effects.

**Table 2.** Comparison of solubility products of Am(OH)<sub>3</sub>(s) and hydrolysis constants of Am(III)

log <i>K</i> <sub>sp</sub>	log β <sub>1</sub>	log β <sub>2</sub>	log β <sub>3</sub>	Medium	References
-25.7	6.3	12.2	14.4	0.1 M NaCl <sub>0</sub> (0.1 Ci/L)	this work
-	10.7	20.9	-	0.005 M NH <sub>4</sub> ClO <sub>4</sub>	[2]
-	11.3	-	-	0.005 M KCl	[3]
-	7.86	-	-	0.1 M LiClO <sub>4</sub>	[4]
-	8.48	-	-	0.1 M LiClO <sub>4</sub>	[5]
-	6.77	-	-	1.0 NaClO <sub>4</sub>	[6]
-	6.3	-	-	1.0 NaClO <sub>4</sub>	[7]
-	6.19	-	-	0.7 M NaCl	[8]
-24.2	<5.6	10.6	<14.7	0.003 M CaCl <sub>2</sub>	[9]
-24.8	6.1	11.0	16.5	0.1 NaClO <sub>4</sub>	[10, 11]
-27.49	5.85	12.79	16.63	0.1 NaClO <sub>4</sub>	[12]
-	-	12.8	-	0.2 NaClO <sub>4</sub>	[13]
-24.5	6.0	11.1	15.5	Calculation	[14]
-23.5	6.0	11.0	15.5	Calculation	[15]

The constants assessed from the present experiment are compared with the literature values in Table 2. The log *K*<sub>sp</sub> value of -25.7 from this experiment is distinctively lower than the literature values [9–11, 15] and larger than the previous experimental value from our laboratory [12]. The estimated data from ALLARD [15] is too large by almost two logarithmic units. Besides all earlier data for β<sub>1</sub> [2–5] which seem to be too large, the recent experimental values [6–8, 10, 11] are reasonably in good agreement with one another, with which our β<sub>1</sub> value is in better accord. The experimental β<sub>2</sub> values reported in the literature [9–13], besides the value of SHALINETS and STEPANOV [2] which is abnormally too large, show a maximal difference of almost two logarithmic units. They result in an average value of log β<sub>2</sub> = 11.8 which is still slightly lower than our value. The values for the third hydrolysis constant β<sub>3</sub> known in the literature [9–15] are all too large in comparison with the value from this work, even slightly over two logarithmic units. The β<sub>3</sub> value is determined from the higher pH region in which the Am solubility is no longer pH dependent and hence can be derived by the relation:

$$[\text{Am(III)}]_{\text{tot}} = K_{sp} \beta_3 \quad (4)$$

Eq. 4 describes that the accuracy of β<sub>3</sub> is directly related with that of *K*<sub>sp</sub> and as a whole with the accuracy of the concentration measurement of Am in a given experimental

solution. Since at  $\text{pH} > 12$  the Am concentration is found to be very low, *i. e.* in the region of  $10^{-11}$  mol/L, any error in sampling or/and contamination in the glove-box atmosphere will lead to a falsified equilibrium concentration at the end. The solubility of Am(III) determined in the pH independent region is given at  $3.2 \times 10^{-10}$  mol/L by RAI *et al.* [9],  $5.0 \times 10^{-9}$  mol/L by SILVA [11], and  $1.4 \times 10^{-11}$  mol/L by BERNKOPF and KIM [12]. The estimation made by ALLARD [15] shows a value of  $10^{-8}$  mol/L. The present experiment in 0.1 M NaClO<sub>4</sub> with a specific  $\alpha$ -activity of 0.1 Ci/L gives an average value of  $5.6 \times 10^{-12}$  mol/L, which is lower by 890 times than the value determined by SILVA [11], and by 1800 times than the estimated value [15]. In a separate experiment [26], it is observed that from unperturbed Am solution surfaces the Am aerosol is generated and transported into the atmosphere. For this reason the glove-box atmosphere is in general easily contaminated by treating Am solutions in open vials for a prolonged time. Experiment has demonstrated that such a contamination may lead to an addition of the Am concentration at least about  $2 \times 10^{-10}$  mol/L to each sampling and hence cause a limitation to the solubility measurement at the higher pH. Whether or not this kind of error is involved in the determination of  $\beta_3$  in the literature work is however unknown. In this work a great care is taken to avoid such an error for the determination of Am concentrations in equilibrium solution at  $\text{pH} > 10$ .

### 3.2. Speciation of Am(III) in hydrolysis experiment

The speciation of Am(III) ions is made at first by calculation based on the thermodynamic data from this experiment for the relative concentration of each species as a function of pH. The results are illustrated in Fig. 2. The calculated results are then verified for a number of experimental solutions by laser-induced photoacoustic spec-

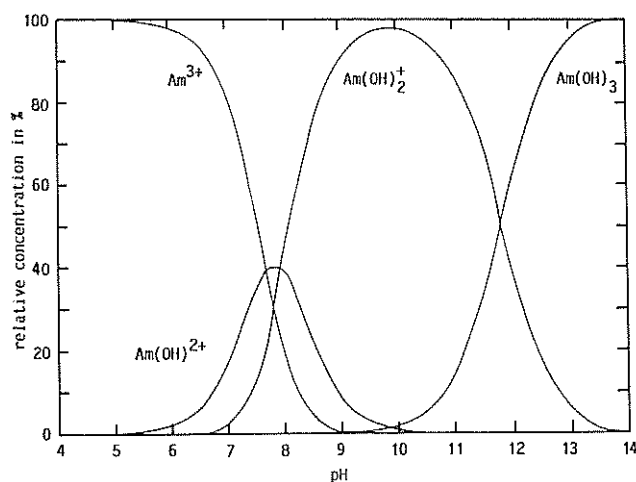


Fig. 2. Relative amounts of Am(III) species in 0.1 M NaClO<sub>4</sub> as a function of pH. Calculation is made by the solubility product and hydrolysis constants determined in 0.1 M NaClO<sub>4</sub> with the specific  $\alpha$ -activity of 0.1 Ci/L (cf. Table 1).

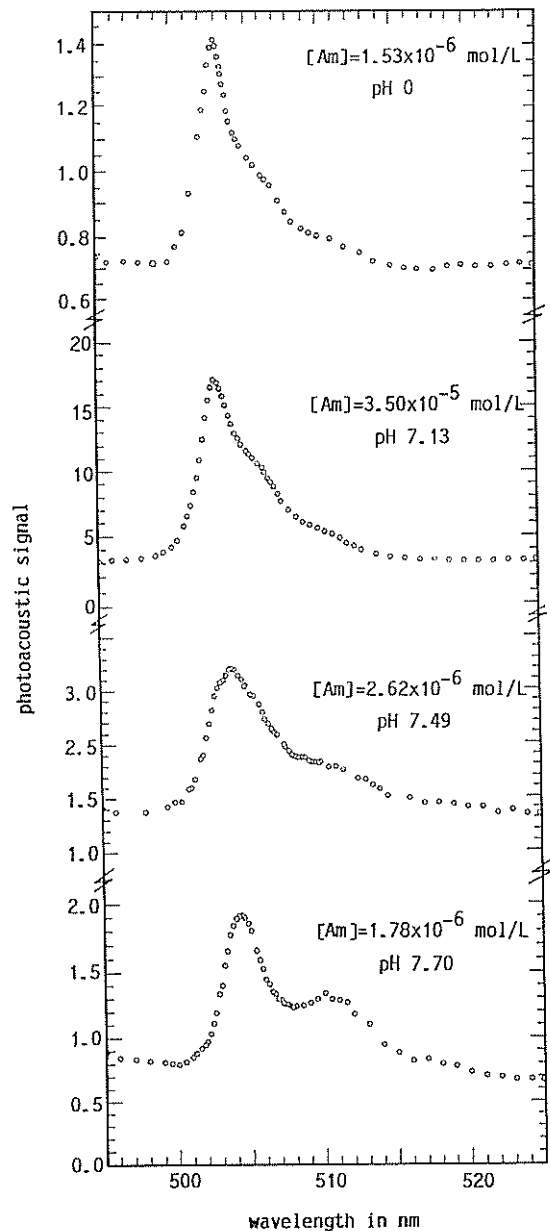


Fig. 3. Photoacoustic spectra (equivalent to absorption spectra) taken by the LPAS for the hydrolysis reactions of Am<sup>3+</sup> in 0.1 M NaClO<sub>4</sub> with varying pH. Speciation spectra shown here verifies the theoretical speciation given in Fig. 2.

troscopy (LPAS). The spectroscopic speciation results are illustrated in Fig. 3. The first spectrum (top) represents the absorption characteristics of the Am<sup>3+</sup> ion in 1 M HClO<sub>4</sub>, which is shown here as a reference spectrum for the comparison purpose. In this acid medium, the Am<sup>3+</sup> ion is the only species present and has the main absorption band at 503.2 nm accompanied by the one large shoulder at 506 nm and the other small one at 510 nm. These two shoulder peaks become overlapped on the increase of pH by absorption bands of Am hydroxide species. The second spectrum taken at pH = 7.13 shows a change in absorption feature, *i. e.* broadening of the absorption band through decreasing of the main peak at 503.2 nm. This change can be ascribed to the presence of species mixture, presumably Am<sup>3+</sup> and Am(OH)<sup>2+</sup>. For

the same pH, the speciation by calculation (Fig. 2) indicates the presence of the  $\text{Am}^{3+}$  ion about 75% and the  $\text{Am}(\text{OH})^{2+}$  ion about 25%. Since the molar absorption coefficient of  $\text{Am}^{3+}$  is expected to be larger than that of  $\text{Am}(\text{OH})^{2+}$  and the concentration of the former is greater as well, the latter species may not be easily distinguished in the spectrum. However, in comparison with the spectrum at pH 0, the ratio of 503.2 nm peak to 506 nm shoulder is clearly decreased. On increasing pH, as shown in the third spectrum, the main absorption peak at 503.2 nm for  $\text{Am}^{3+}$  is starting to shift to 504.5 nm which may be assigned to the absorption of  $\text{Am}(\text{OH})^{2+}$ . At the same time the absorption in the region of 510 nm becomes rather pronounced, probably due to the concentration increase of  $\text{Am}(\text{OH})^{2+}$ . By changing further to pH = 7.70, the total Am concentration is decreased to  $1.78 \times 10^{-6}$  mol/L and the spectrum (bottom) is changed as well, revealing the presence of  $\text{Am}(\text{OH})^{2+}$  at 504.5 nm as well as  $\text{Am}(\text{OH})^{2+}$  at 510.5 nm. According to calculation shown in Fig. 2, at pH = 7.70, the  $\text{Am}^{3+}$  ion is expected to be present in small amount, nevertheless its absorption cannot be distinguished well because this is overlapped by the  $\text{Am}(\text{OH})^{2+}$  absorption (504.5 nm). The build-up of  $\text{Am}(\text{OH})_3$ , which starts at pH > 10, cannot be speciated by spectroscopy, since at this pH region the Am concentration becomes beyond the spectroscopic detection limit ( $10^{-8}$  mol/L). However, the solubility data which become independent of pH at > 12 indicate clearly the presence of  $\text{Am}(\text{OH})_3$  in the solution. The spectroscopic speciation has so far verified the species predicted by calculation; the experimental results in Figs. 2 and 3 are in fact corroborating with each other for the important region of hydrolysis reactions. The further improvement of spectroscopic quantification of each species is in progress.

### 3.3. Am(V) hydrolysis in saline solution

As the Am(III) hydroxide is introduced in 3 M NaCl at the concentration of about  $10^{-3}$  mol/L, the auto-radiolytical oxidation produces the  $\text{AmO}_2^+$  ion in the solution. The oxidation becomes completed within a week [17–19]. Radiolysis reactions induced by  $\alpha$ -radiation transfer the NaCl solution to a strongly oxidizing medium. The process is depending on the specific  $\alpha$ -activity, NaCl concentration and pH [18, 19]. Experiment is conducted with 1 Ci/L  $^{241}\text{Am}(\text{III})$  in 3 M NaCl solution at pH = 8.3. The initial Am(III) hydroxide is dissolved as Am(V) in a week to a concentration of  $10^{-4}$  mol/L. Using the radiometric pH titration the solubility of Am(V) has been measured in the pH range from 8.3 to 13 forwards and backwards under Ar atmosphere. The results are given in Fig. 4. Since the chloride complexation of the pentavalent actinide ion is negligibly weak [14, 27, 28] in comparison with hydrolysis reactions in the pH range under investigation, the solubilities shown in Fig. 4 are assumed to be caused by hydrolysis reactions alone. The solubility product and first hydrolysis constant are calculated to be

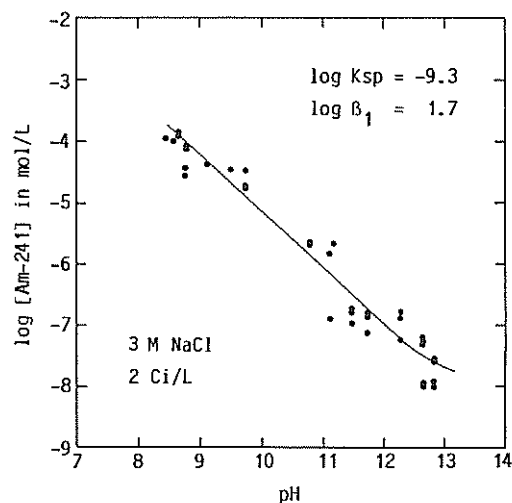


Fig. 4. Solubility of Am(V) hydroxide precipitate in 3 M NaCl (specific  $\alpha$ -activity of 2 Ci/L) as a function of pH.

$$\log K_{sp} = -9.3 \pm 0.5$$

$$\log \beta_1 = 1.7 \pm 0.6$$

for the  $\text{AmO}_2^+$  ion. Since the salt effects in NaCl solutions are not so large [29], an approximate correction of both constants to the zero ionic strength ( $\mu = 0$ ) gives the values:  $\log K_{sp} = -9.5 \pm 0.5$  and  $\log \beta_1 = 1.9 \pm 0.6$ . The present experimental results are compared with the literature data in Table 3 for different pentavalent actinide ions. In view of a mono-hydroxide, the reported values for the solubility product are varying considerably. Excluding two upper limit values [31], the rest data give rise to an average value of  $-9.24 \pm 0.4$ . The  $\beta_1$  value from the present experiment is too low in comparison with other data. Whether or not the effects of intensive  $\alpha$ -radiation or of chloride ion concentration play any significant role is uncertain. However, there is gas generation in the solution, e.g.  $\text{H}_2$ ,  $\text{H}_2\text{O}_2$  and  $\text{Cl}_2$ , which may partly impair the first hydrolysis reaction.

Table 3. Solubility products of  $\text{AmO}_2(\text{OH})(s)$  and hydrolysis constants of actinides(V)

	$\log K_{sp}$	$\log \beta_1$	$\log \beta_2$	$\mu$ [mol/L]	References
Am	-9.3	1.7	-	3.0	this work
Np	-9.8	5.13	-	0.0	[30]
	< -8.98	4.93	-	0.1	[31]
	-	4.68	-	1.0	[32]
	-9.73	5.1	-	0.02	[33]
	-	3.92	-	-	[34]
	-9.0	3.92	-	0.2	[35]
	-9.2	-	-	0.1	[36]
	-8.81	2.33	4.89	1.0	[37]
	-	4.16	-	1.0	[38]
	-	5.15	-	0.001	[42]
Pu	-	4.3	-	0.0	[14]
	< -8.6	-	-	0.0	[31]
	-8.8	4.6	-	0.0	[39]
	-9.3	-	-	0.0	[40]
	-	4.3	-	0.003	[41]

## Literature

1. KIM, J. I.: Chemical Behaviour of Transuranic Elements in Natural Aquatic Systems. In: *Handbook on the Physics and Chemistry of the Actinides* (A. J. FREEMAN, C. KELLER, ed.) Elsevier Science Publishers B. V., Amsterdam 1986, p. 413.
2. SHALINETS, A. B., STEPANOV, A. V.: Investigation of Complex Formation of the Trivalent Actinide and Lanthanide Elements by Method of Electromigration, XVII Hydrolysis. *Radiokhimiya* 14, 280 (1972).
3. MARIN, B., KINKINDAI, T.: Etude comparée de l'hydrolyse de l'euprotinium et de l'americiem en milieu chlorure par électrophorèse sur papier. *C. R. Acad. Sci. Ser. C* 268, 1 (1969).
4. DESIRE, B., HUSSONNOIS, M., GUILLAUMONT, R.: Détermination de la première constante d'hydrolyse de l'americiem, du curium, du berkelium et du californium. *C. R. Acad. Sci. Ser. C* 269, 448 (1969).
5. HUSSONNOIS, M., HUBERT, S., BRILLARD, L., GUILLAUMONT, R.: Détermination de la première constante d'hydrolyse de l'einsteinium. *Radiochem. Radioanal. Lett.* 15, 47 (1973).
6. NAIR, G. M., CHANDER, K., JOSHI, J. K.: Hydrolysis Constants of Plutonium(III) and Americium(III). *Radiochim. Acta* 30, 37 (1982).
7. LUNDQVIST, R.: Hydrophilic Complexes of the Actinides. I. Carbonates of Trivalent Americium and Europium. *Acta Chem. Scand. A* 36, 741 (1982).
8. CACECI, M. S., CHOPPIN, G. R.: Determination of the First Hydrolysis Constant of Eu(III) and Am(III). *Radiochim. Acta* 33, 101 (1983).
9. RAI, D., STRICKERT, R. G., MOORE, D. A., RYAN, J. L.: Am(III) Hydrolysis Constants and Solubility of Am(III)-Hydroxide. *Radiochim. Acta* 33, 201 (1983).
10. SILVA, R. J.: The Behaviour of Americium in Aqueous Carbonate Systems. Report LBL-16690, November (1983).
11. SILVA, R. J.: Thermodynamic Properties of Chemical Species in Nuclear Waste. The Solubilities of Crystalline Neodymium and Americium Trihydroxides. Report LBL-15055, December (1982).
12. BERNKOPF, M., KIM, J. I.: Hydrolysis Reactions and Carbonate Complexation of Americium(III) in Natural Aquatic Systems. Report RCM-02884, 1984.
13. BIDOGLIO, G.: Characterization of Am(III) Complexes with Bicarbonate and Carbonate Ions at Groundwater Concentration Levels. *Radiochem. Radioanal. Lett.* 53, 45 (1982).
14. PHILLIPS, S. L.: Hydrolysis and Formation Constants at 25°C. Report LBL-14313, May (1982).
15. ALLARD, B.: Solubilities of Actinides in Neutral or Basic Solutions. In: *Actinides in Perspective* (N. M. EDELSTEIN, ed.) Pergamon Press, New York 1982, p. 553.
16. KIM, J. I., BERNKOPF, M., LIERSE, CH., KOPPOLD, F.: Hydrolysis Reactions of Am(III) and Pu(VI) Ions in Near-Neutral Solutions. In: *Geochemical Behaviour of Disposed Radioactive Waste* (S. BARNEY, J. D. NAVRATIL, W. W. SCHULZ, ed.) ACS Symp. Ser. 246, American Chemical Society, Washington D.C. 1984, p. 115.
17. MAGIRIUS, S., CARNALL, W. T., KIM, J. I.: Radiolytic Oxidation of Am(III) to Am(V) in NaCl Solutions. *Radiochim. Acta* 38, 29 (1985).
18. BÜPPELMANN, K., MAGIRIUS, S., LIERSE, CH., KIM, J. I.: Radiolytic Oxidation of Americium(III) to Americium(V) and Plutonium(IV) to Plutonium(VI) in Saline Solution. *J. Less-Common Met.* 122, 329 (1986).
19. KIM, J. I., LIERSE, CH., BÜPPELMANN, K., MAGIRIUS, S.: Radiolytically Induced Oxidation Reactions of Actinide Ions in Concentrated Salt Solutions. *Mater. Res. Soc. Symp. Proc. Vol. 84*, 603 (1987).
20. SCHREPP, W., STUMPE, R., KIM, J. I., WALTHER, H.: Oxidation-State-Specific Detection of Uranium in Aqueous Solution by Photoacoustic Spectroscopy. *Appl. Phys.* B32, 207 (1983).
21. STUMPE, R., KIM, J. I., SCHREPP, W., WALTHER, H.: Speciation of Actinide Ions in Aqueous Solution by Laser-induced Photoacoustic Spectroscopy. *Appl. Phys.* B34, 203 (1984).
22. BAES, C. F., MESMER, R. E.: *The Hydrolysis of Cations*. John Wiley & Sons, Inc., New York 1976, p. 85.
23. ZIV, D. M., SHESTAKOVA, I. A.: Investigation of the Solubility of Certain Actinium Compounds. II. Determination of the Solubility and Estimation of the Relative Basicity of Actinium Hydroxide. *Radiokhimiya* 7, 175 (1965).
24. FEITKNECHT, W., SCHINDLER, P.: *Solubility Constants of Metal Oxides, Metal Hydroxides and Metal Hydroxide Salts in Aqueous Solution*. Butterworths, London 1963.
25. SWALLOW, A. J.: *Radiation Chemistry*. Longman, London 1973, p. 136.
26. MOON, H. C., BAUMGÄRTNER, F., KIM, J. I.: Generation of Am and Eu Aerosols from Unperturbed Solution Surfaces. *Radiochim. Acta* 35, 223 (1984).
27. GAINAR, I., SYKES, K. W.: *J. Chem. Soc.* 4452 (1964).
28. VASUDEVA RAO, P. R., GUDI, N. M., BAGAWDE, S. V., PATIL, S. K.: The Complexing of Np(V) by some Inorganic Ligands. *J. Inorg. Nucl. Chem.* 41, 235 (1979).
29. in Ref. 22, p. 75.
30. PHILLIPS, S. L., PHILLIPS, C. A., SKEEN, J.: Hydrolysis, Formation and Ionisation Constants at 25°C and at High Temperature-High Ionic Strength. Report LBL-14996, February (1985).
31. KRAUS, K. A., NELSON, F.: Report AECD-1864 (1948).
32. MAYA, L.: Hydrolysis and Carbonate Complexation of Dioxoneptunium(V) in 1.0M NaClO<sub>4</sub> at 25°C. *Inorg. Chem.* 22, 2093 (1983).
33. SEVOSTYANOVA, E. P., KHALTURIN, G. V.: Hydrolytic Behaviour of Dioxoneptunium(V). *Radiokhimiya* 18, 870 (1976).
34. VODOVATOV, V. A., KOLOKOLTSOV, V. B., KOVALEVA, T. V., MASHIROV, L. G., SUGLOBOV, D. N., SLES, V. G.: Coordination Properties of Actinide(V) Dioxocations. In: *Transplutonium Elements* (W. MÜLLER, R. LINDNER, ed.) North-Holland Publishing Company, Amsterdam 1976, p. 247.
35. MOSKVIN, A. I.: Hydrolytic Behaviour of Neptunium(IV, V, VI). *Radiokhimiya* 13, 681 (1971).
36. KRAUS, K. A.: Proc. Int. Conf. Peaceful Uses At. Energy, Geneva 1955, A/Conf. 8, 73 (1956).
37. LIERSE, CH., TREIBER, W., KIM, J. I.: Hydrolysis Reactions of Neptunium(V). *Radiochim. Acta* 38, 27 (1985).
38. BIDOGLIO, G., TANET, G., CHATT, A.: Studies on Neptunium(V) Carbonate Complexes under Geologic Repository Conditions. *Radiochim. Acta* 38, 21 (1985).
39. ALLARD, B., RYDBERG, J.: Behaviour of Plutonium in Natural Waters. In: *Plutonium Chemistry* (W. T. CARNALL, G. R. CHOPPIN, ed.) ACS Symp. Ser. 216, 275 (1983).
40. GEL'MAN, A. D., ZAITSEVA, V.-P.: Dokl. Akad. Nauk SSSR 157, 1403 (1964).
41. KRAUS, K. A., DAM, J. R.: Hydrolytic Behaviour of Plutonium(V), Acid Constant of Plutonyl Ion. In: *The Transuranium Elements* (G. T. SEABORG, J. J. KATZ, W. M. MANNINGS, ed.) McGraw-Hill, New York 1949, p. 478.
42. SCHMIDT, K. H., GORDON, S., THOMPSON, C., SULLIVAN, J. C.: A Pulse Radiolysis Study of the Reduction of Neptunium(V) by Hydrated Electron. *J. Inorg. Nucl. Chem.* 42, 611 (1980).