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Radiochimica Acta 38, 29 – 32 (1985)

Radiolytic Oxidation of Am(III) to Am(V) in NaCl Solutions

By S. MAGIRIUS, W. T. CARNALL* and J. I. KIM, Institut für Radiochemie, TU München, 8046 Garching

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Americium/Radiolytic oxidation of Am/*Laser photoacoustic spectroscopy*

Abstract

The autoradiolytic oxidation of ^{241}Am(III) to ^{241}Am(V) in 5 *M* NaCl solution has been investigated by pulsed laser-induced photoacoustic spectroscopy and spectrophotometry. In the presence of a moderate dose rate (1 Ci/L) of own α-radiation, the Am(III) ions are quantitatively oxidized to Am(V) within a week.

Introduction

Am(V) solutions are routinely prepared by the oxidation of Am(III) in the presence of alkali carbonates by electrolysis [1] or with powerful oxidants such as ozone, peroxydisulfate or hypochlorite [2]. The last oxidant was used with Am(III) in 40% K_2CO_3 solution at room temperature in experiments that initially established the pentavalent oxidation state of Am [3]. Further investigations showed the oxidation of $Am(OH)_3$ to $Am(OH)_4$ in 0.2 *M* NaOCl (pH > 7) at ~ 90 °C [4].

Subsequently, it was found that Am(III) could also be radiolytically oxidized to Am(V) in concentrated K_2CO_3 solutions without benefit of an extra oxidizing agent [5]. However, this experiment was carried out with mixtures of Am(III) and Cm(III) at a very high dose rate of α-radiation equal to 100 – 300 W/L ((3 – 8) × 10^3 Ci/L).

We report here a further contribution to the redox chemistry of Am(III) in basic solution related to but distinct from the work cited above. We have observed the formation of AmO_2^+ in weakly basic (pH = 8 – 9) carbonate-free NaCl solutions in contact with solid $^{241}Am(OH)_3$ in the presence of a moderate dose rate (~ 1 Ci/L) of α-radiation. In the absence of, or at low concentrations (< 1 *M*) of Cl^-, no oxidized species of Am are observed.

Experimental

In a typical experiment, to 150 ml ^{241}Am(III) solution of 0.01 *M* HCl, containing 1.3 × 10^{-3} mole/L Am, solid NaCl is added to make 5 *M* NaCl solution and the solution is then neutralized to pH = 8.3 by addition of several drops of CO_2-free 11 *M* NaOH. The activity of the solution is 1.07 Ci/L. The precipitated $Am(OH)_3$ is light pink in color and the solution is colorless. The experiment is carried out in a double-walled glass reaction cell which is temperature controlled (25 ± 0.2 °C) by water circulation from a thermostat. The solution is maintained CO_2-free and anoxic by passage of Ar through the reaction cell.

The measurement of Am concentration in the solution is begun two hours after preparation and is continued at regular time intervals during the approach to solubility equilibrium. Within 24 hours, the precipitate began to show discoloration and became progressively dark brown as being consistent with results observed in the literature [4]. The solution also developes a light-brownish appearance. After 24 hours, aliquots of the solution are taken for speciation. Since at this moment the solution contains a total of only 3.4 × 10^{-6} mole/L Am, it is too dilute for accurate determination of the different oxidation states of Am by conventional absorption spectroscopy. The speciation is, therefore, made by a pulsed laser-induced photoacoustic spectroscopic technique [6], which provides the detection sensitivity about three orders of magnitude greater than normal absorption spectroscopy. For a given experimental condition, the Am(III) species originally present in solution appears to be quantitatively converted to Am(V) species within a week.

After the equilibrium concentration of Am(V) in solution is established at pH = 8 – 9, the pH of the solution is adjusted to obtain solubility equilibria of the Am(V) in the pH range 7 – 13. From these data, the solubility product and primary hydrolysis constant are determined. Spectrophotometric measurements are also made with a Beckman UV spectrophotometer Model 5240 using standard 1 cm cells for the solutions of higher Am concentration.

Results and discussion

The time dependent solubility curve for Am in 5 *M* NaCl at pH = 8.3 is shown in Fig. 1. The solubility increase primarily reflects the oxidation process of the various Am(III)-species yielding the AmO_2^+ ion in the solution. In the absence of the oxidation process, the solubility of $Am(OH)_3$ would be < 10^{-9} mole/L in 0.1 *M* $NaClO_4$ [7], and ~ 10^{-8} mole/L in 1 *M* NaCl at the same pH [14]. The present results demonstrate a rapid time-dependent increase of the Am concentration in the solution with an approach to equilibrium after approximately one week of reaction time. The increase in solubility due to oxidation of Am(III) to AmO_2^+ is confirmed, as shown in Fig. 2, by a photoacoustic spectrum which is taken after a reac-

* on leave from Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439 USA.

tion time of 24 hours. The absorption bands at 503.3 nm and 513.6 nm are characteristic of the Am^{3+} and AmO_2^+ ions, respectively.

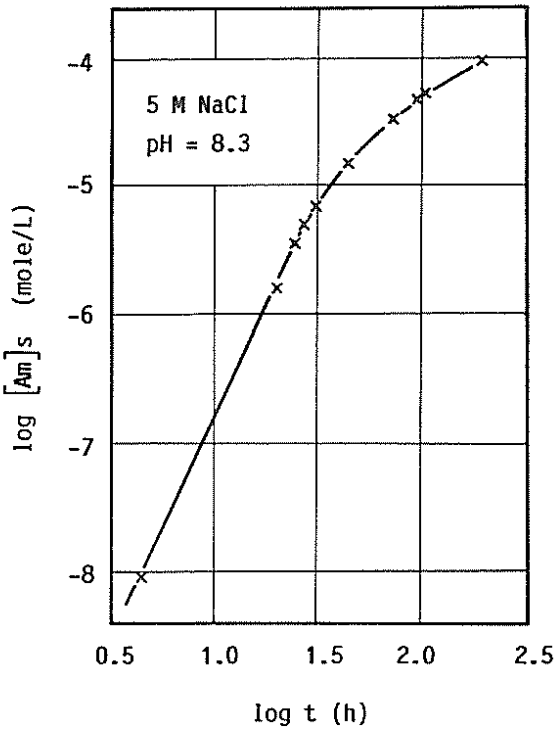

Fig. 1. The time dependent solubility of $Am(OH)_3$ in 5 *M* NaCl solution; the saturation concentration at pH = 8.3 remains approximately 10^{-4} mole/L (α-activity ~ 1 Ci/L).

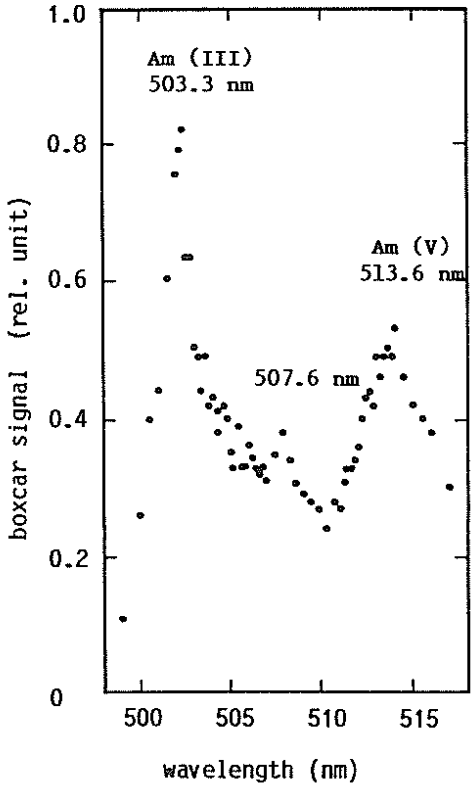

Fig. 2. The photoacoustic spectrum (equivalent to absorption spectrum) taken after 24 h of the $Am(OH)_3$ dissolution in 5 *M* NaCl solution (pH = 8.3) under ~ 1 Ci/L α-activity. The concentrations of Am(III) and Am(V) are determined to be 4.7×10^{-7} mole/L and 2.9×10^{-6} mole/L, respectively.

An evaluation of the spectra in Fig. 2 based on a total Am concentration of 3.4×10^{-6} mole/L in the solution, which is determined by liquid scintillation counting, is consistent with Am(III) and Am(V) concentrations of 4.7×10^{-7} mole/L and 2.9×10^{-6} mole/L, respectively. The indicated Am(V) concentration amounts to 86% of the total Am in solution based on molar absorptivities $\epsilon(503.3\,\text{nm}) = 390$ L/mole and $\epsilon(513.6\,\text{nm}) = 41$ L/mole, which are also characteristic of Am^{3+} and AmO_2^+ in acid solutions [8, 9]. It is possible that the weak absorption indicated at 507.6 nm is due to a small amount of Am carbonate complex ions [6], which may have been produced by the sorption of CO_2 from the air during the sampling of the solution for spectroscopy. Although the air contact time is short, i. e. several minutes, a solution of pH = 8.3 may sorb CO_2 rather rapidly. However, in acid solution there is also evidence of a shoulder on the Am(III) band near 506 nm [6]. The Am(III) concentration of ~ 5×10^{-7} mole/L in 5 *M* NaCl may actually be near to the equilibrium solubility in this solution. However, this value is found to be greater than the values observed in 0.1 *M* $NaClO_4$ [7] and 1 *M* NaCl [14].

A solution absorption spectrum of Am(V) at pH = 8.3 in 5 *M* NaCl obtained using the Beckman UV Spectrometer, as shown in Fig. 3, clearly illustrates characteristic absorption bands at 514, 648 and 716 nm [8, 9]. Their molar absorption coefficients are determined to be $\epsilon = 41$, $\epsilon = 5$ and $\epsilon = 58$, respectively. A sharp increase in absorption at < 400 nm appears to be similar to that observed in acid solutions [9] but can reasonably be attributed to radiolysis products. This spectrum, taken after one week's reaction time, reveals only Am(V) present in solution with no detectable Am(III). Measurements are extended to 995 nm where a principal absorption band in Am(VI) is known to occur [10], but no absorption feature is found.

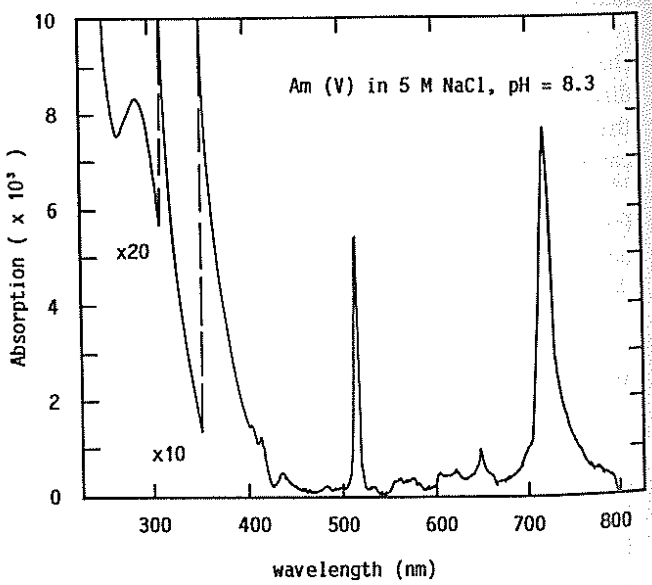

Fig. 3. The absorption spectrum of the AmO_2^+ ion in 5 *M* NaCl (pH = 8.3); the concentration equals to a saturation value, 1.3×10^{-4} mole/L.

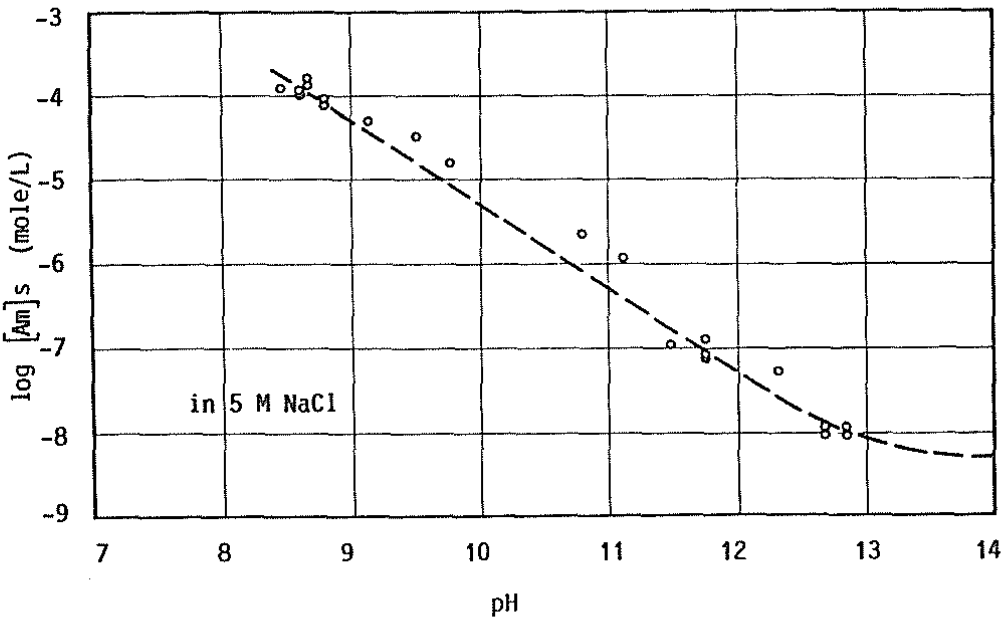

Fig. 4. The solubility of the AmO_2^+ ion in 5 *M* NaCl as a function of pH; the dotted line corresponds to a least square fitting of Eq. 9.

Radiolysis of the aqueous NaCl solutions with the 5.49 and 5.44 MeV α-particles of ^{241}Am, is expected to involve, among others, important reactions of the type [11, 12, 18]:

$$OH^\cdot + Cl^- \rightleftharpoons Cl^\cdot + OH^- \quad (1)$$

$$Cl^\cdot + Cl^- \rightleftharpoons Cl_2^- \quad (2)$$

$$2\,Cl^\cdot + H_2O \rightarrow H^+ + Cl^- + HClO \quad (3)$$

and at the relatively high pH of 8–9 [19],

$$HClO \rightleftharpoons H^+ + ClO^- \quad (4)$$

The *in situ* formation of ClO^- presumably leads to oxidation of the Am(III) species. Such a presumption is based on experimental facts and the knowledge available in the literature [19]. The Eh value of the experimental solution is measured to be slightly over 1000 mV and for a less pure salt solution (natural rock salt) the value exceeds to 1250 mV. In water with a similar amount of the Am precipitate, the Eh value is found to remain under 550 mV. According to the Eh-pH relationship for the chlorine species [19] in an oxidizing alkaline solution (pH > 8), the reaction of Eq. 4 favors the formation of ClO^-. As is expected [19], upon acidifying the solution, the generation of Cl_2 gas is detected. The absorption spectrum of the solution, being in contact with the Am ppt, shows a distinctive but somewhat broad peak at 286 nm (cf. Fig. 3). This peak disappears, once the Am ppt is separated from the solution or the pH of the solution is decreased (pH < 7). This phenomenon is in accordance with the fact that the concentration of ClO^- decreases with lowering Eh as well as pH [19]. The presence of ClO^- is thus indirectly verified. The known absorption maximum of Cl_2^- at 340 nm [11] would be lost in the rather intense and generally increasing ultraviolet absorption shown in Fig. 3. The absorption bands for ClO^- and $ClO^\cdot$ are known to be at 292 nm [15] and 280 nm [16], respectively. The peak observed in this experiment at 286 nm (Fig. 3) is located between the two bands in question. It is probable that the species ClO^- and $ClO^\cdot$ are in an equilibrium state under the present experimental condition, such that [16]

$$ClO^- + OH^\cdot \rightleftharpoons ClO^\cdot + OH^- \quad (5)$$

The $ClO^\cdot$ radical is also a strong oxidant. The reaction of Eq. 5 may give rise to the present spectroscopic observation of the absorption band at 286 nm. This postulation is, however, subject to sound verification by further experiment.

The quick dissolution of the Am ppt in the solution by acidification increases the absorption bands of Am(III) and Am(V). The result suggests the presence of the two oxidation states in the Am ppt, while Am(V) being predominant. The absorption spectrum of Am(V) shown in Fig. 3 does not provide difinitive information as to the presence of other oxidation states in the solution. Whether the solution contains only the Am(V) ion cannot be established based on the spectroscopic study alone, because the spectroscopic characteristics of Am(IV) and Am(VI) under the condition of present investigation are not clearly known. An indirect experiment is, therefore, conducted to verify this fact, namely the solubility measurement as a function of pH. The results are given in Fig. 4, which shows the equilibrium concentration of Am in solution as a function of pH. Interpretation of the experimental points is made as follows: the soluble species are assumed to be pentavalent ions such as:

$$[Am]s = [AmO_2^+] + [AmO_2(OH)] + [AmO_2(OH)_2^-] \quad (6)$$

with the solubility product Ksp and hydrolysis constant β_i ($i = 1, 2$):

$$Ksp = [AmO_2^+][OH^-] \quad (7)$$

$$\beta_i = \frac{[AmO_2(OH)_i^{i-1}]}{[AmO_2^+][OH^-]^i} \quad (8)$$

Combination of Eqs. 6–8 becomes

$$[Am]s = \frac{Ksp}{[OH^-]} + Ksp\beta_1 + Ksp\beta_2[OH^-] \quad (9)$$

Evaluation by a least squares fitting of Eq. 9 gives rise to the following constants:

$$\log Ksp = -9.3 \pm 0.5$$
$$\log \beta_1 = 1.5 \pm 0.5$$

The value for β_2 is too small and uncertain to consider as significant. The solubility product is comparable with the value for the NpO_2^+ ion in 0.1 *M* NaCl ($\log Ksp = -9.2$) [17], although the experiments are carried out in solutions of different ionic strength. The reliable β_1 value for Np(V) in 1 *M* $NaClO_4$ is 2.3 ± 0.6 [20], which can be taken for comparison. The solubility product and primary hydrolysis constant suggest that the predominant species is the AmO_2^+ ion. The presence of other oxidation states in the solution cannot be verified. In complexing solutions, the Am ions of various oxidation states are observed in the neutral as well as higher pH range [1].

The generation of the ClO^- ion appears to take place primarily at the surface of the $Am(OH)_3$ precipitate where the radiation dosage is at a maximum. When a portion of the solution is filtered and thus separated from the bulk source of activity, there is a slow decrease of the Am(V) concentration with time. In their analysis of the production of Cl_2^- in basic solutions by pulse radiolysis, ANBAR and THOMAS [11] found evidence for the origin of Cl_2^- in the "spur" regions where the initial concentrations of the products of radiolysis are greatest. In the present experiment, we are not able to verify the generation of Cl_2^-, which is supposed to show absorption at 340 nm (cf. Fig. 3).

The disproportionation reaction of Am(V) in acid solution to form Am(III) and Am(VI) has been investigated [13] as has the reverse reaction. However, the corresponding reaction mechanisms in basic solution, if the analogue processes do occur, do not appear to have been examined. COLEMAN *et al.* [10] suggest that Am(VI) may be reduced to Am(V) at pH > 4 even in the absence of Am(III), possibly by the reaction of Am(VI) with H_2O. Detailed investigations of the rate of ClO^- generation as a function of NaCl concentration, the α-radiation dose, and the pH of solution are in progress in this laboratory.

The present experiment demonstrates a simple method to prepare Am(V) in aqueous solution without using external oxidizing agents or electrochemical elaborations. The results identify an important chemical process that must be taken into account in the chemical assessment of nuclear waste repositories in salt deposits.

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