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Preparation and Properties of Aqueous Tetravalent Americium[1]

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Stable aqueous solutions of tetravalent americium are prepared readily by reaction of $Am(OH)_4$ with saturated ammonium fluoride. Heating to 90° does not cause disproportionation of Am(IV) nor its chemical reduction by water. Slow reduction of Am(IV) to Am(III) occurs due to Am^{241} alpha radiation. At 25°, the solubility of Am(IV) in 13 *M* NH_4F is 0.02 *M* and the solid phase in equilibrium is $(NH_4)_4AmF_8$. Concentrated solutions of KF, RbF, and CsF also react with $Am(OH)_4$ yielding sparingly soluble Am(IV)–fluoride complexes. In 13 *M* NH_4F, 0.02 *M* Am(IV) has a rose color and a characteristic absorption spectrum which is different from those of Am(III), Am(V), and Am(VI). The narrow Am(IV) peak at 4560 Å. ($\epsilon = 30$) is separated from peaks of other americium valence states and can be used to determine Am(IV) quantitatively. Iodide ion reduces Am(IV) to Am(III). Ozone oxidizes Am(IV) in 13 *M* NH_4F to Am(VI).

Introduction

The chemistry of americium has been studied by workers in many laboratories (U. S., U. K., and U.S.S.R.) for more than ten years. The absorption spectra and other characteristics of Am(III), Am(V), and Am(VI) as pure aqueous species now are well established. Tetravalent americium, which is missing from the series of aqueous ions, has been looked for without success in reactions which should have produced it in solution,[2a–j] *e.g.:* reduction of Am(V) and Am(VI); disproportionation of Am(V); and dissolution of AmO_2 in acid. No aqueous species of Am(IV) was found during this time, and tetravalent americium was known only in AmO_2, AmF_4, and $KAmF_5$, all prepared by anhydrous methods.[2d]

During the recent work on the preparation of $Am(OH)_4$, attempts were made to observe Am(IV) spectrophotometrically on dissolution of $Am(OH)_4$ in various reagents.[3] In alkaline solution, $Am(OH)_4$ is very insoluble. It dissolves readily in dilute acid with conservation of oxidation number. However, the resulting Am(IV) is rapidly and completely consumed by the reactions: 2Am(IV) = Am(III) + Am(V) and Am(IV) + Am(V) = Am(VI) + Am(III).

In summary, then, there is considerable evidence for reactions *involving* Am(IV) as a kinetic intermediate but all workers agree that concentrations of Am(IV) directly observable as a solution species were not obtained. In aqueous acid solution the formal potential of $Am^{+3} = Am^{+4} + e^-$ was reported to be -2.44 v.,[2c] but indications are that this value is actually more negative (-2.6 to -2.9 v.).[4a] This change in the Am^{+3}, Am^{+4} potential would serve to reduce the value of the Am^{+4}, AmO_2^+ potential to less than -1.0 v., and increase the free energy available to Am^{+4} disproportionation. Thus the failure to observe Am(IV) in aqueous solution seemed quite consistent with the data indicating that Am^{+4} is thermodynamically unstable.

Here the matter rested until conditions for stabilizing pure tetravalent americium in solution were discovered in a simple and unexpected manner. Work had been in progress on a crystalline rubidium fluoride–americium complex, thought to contain Am(IV), which had been made by allowing Am^{241} alpha radiation to reduce pentavalent americium in rubidium fluoride solution.[4b] A metathetical reaction was attempted treating $Am(OH)_4$ with saturated NH_4F. It was reasoned that the ammonium ion would tie up the hydroxide displaced from $Am(OH)_4$ by fluoride, permitting the reaction to go to completion to form a crystalline ammonium–Am(IV)–fluoride complex. However, it was found that saturated ammonium

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) L. B. Asprey and S. E. Stephanou, AECU-924 (1950); (b) S. E. Stephanou, L. B. Asprey, and R. A. Penneman, AECU-925 (1950); (c) L. Eyring, H. R. Lohr, and B. B. Cunningham, *J. Am. Chem. Soc.*, **74**, 1186 (1952); (d) L. B. Asprey, *ibid.*, **76**, 2019 (1954); (e) S. R. Gunn and B. B. Cunningham, *ibid.*, **79**, 1563 (1957); (f) G. R. Hall and P. D. Herniman, *J. Chem. Soc.*, 2214 (1954); (g) G. N. Yakovlev and V. N. Kosyakov, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, **7**, 363 (1956); **28**, 373 (1958); (h) R. A. Penneman and L. B. Asprey, *ibid.*, **7**, 355 (1956); (i) G. R. Hall and T. L. Markin, *J. Inorg. & Nuclear Chem.*, **4**, 296 (1957); (j) R. A. Penneman and T. K. Keenan, National Academy of Sciences NS-3006 (1960).

(3) R. A. Penneman, J. S. Coleman, and T. K. Keenan, *J. Inorg. & Nuclear Chem.*, **17**, 138 (1961).

(4) (a) B. B. Cunningham, private communication, 1961, reported in ref. 3; (b) F. H. Kruse and L. B. Asprey, *Inorg. Chem.*, **1**, 137 (1962).

fluoride dissolves americium tetrahydroxide in significant quantities.[5] The resulting clear, rose-colored solution shows absorption peaks which cannot be attributed to any soluble americium species previously known. From this and other evidence presented in the Experimental section, we conclude that tetravalent americium has been stabilized as a soluble aqueous species. Properties of this new aqueous species are described.

Experimental

Reagents.—Stock solutions of reagent grade NH_4F, KF, RbF, and CsF were prepared in polyethylene containers. Reagent NaOCl was kept refrigerated until used. Americium of >99% purity was used.

Preparation of $Am(OH)_4$.—Americium trihydroxide (on a 10–50 mg. scale) was precipitated from dilute nitric acid solution using a minimum of NH_3(g) and thoroughly washed with water. The pink precipitate was stirred and heated at 90° with 0.2 *M* NaOCl–0.2 *M* NaOH. Immediate darkening of the $Am(OH)_3$ precipitate followed addition of hypochlorite-base. In some preparations oxidation was complete in 5 min.; however, heating usually was continued for 30 min. The resulting black precipitate was washed free of base and hypochlorite. This procedure forms $Am(OH)_4$ as described previously.[3]

Preparation of Am(IV) in Ammonium Fluoride Solutions.—In a preliminary communication[5] the concentration of saturated NH_4F was given as 15 *M*. At 25°, we determined the concentration to be 13.7 *M*. Dilution of the saturated NH_4F solution by the $Am(OH)_4$ slurry gave a final NH_4F solution of 13 *M*. Freshly prepared $Am(OH)_4$ dissolves cleanly in 13 *M* NH_4F solution up to an Am(IV) concentration of 5 g./l. When this solubility is exceeded *at room temperature*, red crystals having the composition $(NH_4)_4AmF_8$ precipitate.[6] However, a light tan solid having a different X-ray powder pattern is formed when the solubility is exceeded at 90°. When measured at room temperature the americium solubility of the red complex is 0.020 *M*; the solubility of the light tan salt is 0.024 *M*. No work was done on the conversion of one form to the other.

Treatment of $Am(OH)_4$ with 7 *M* NH_4F gives an Am(IV) solution of lower concentration than is obtained using 13 *M* NH_4F. The solubility of americium decreases from 0.02 *M* in 13 *M* NH_4F to 0.0002 *M* in 1 *M* NH_4F.

Absorption Spectra.—The absorption spectra of Am(IV) solutions were taken at 25° using a Cary recording spectrophotometer. Double-stoppered quartz cells of 1, 2.5, and 5-cm. length were used *vs.* reference solutions having the same fluoride concentration as the sample.

The absorption spectrum of Am(IV) in 13 *M* NH_4F is shown in Fig. 1.

Preparation of Am(IV) in Alkali Fluoride Solution.—On treatment of $Am(OH)_4$ with 12 *M* KF, dissolution occurs more slowly than in the case of saturated NH_4F, and the solubility is lower, 0.01 *M*. In 10 *M* CsF the solubility of Am(IV) is 0.003 *M*. In 10 *M* RbF the solubility is 0.02 *M*, and a precipitate of Rb_2AmF_6 was obtained (for X-ray structure see ref. 4b).

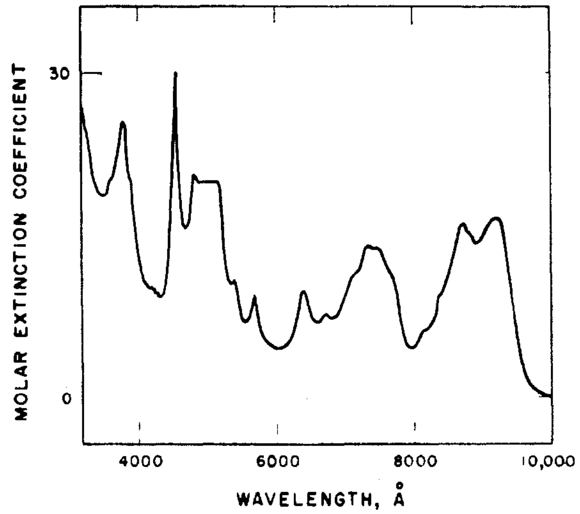

Fig. 1.—Absorption spectra of aqueous Am(IV) in 13 *M* NH_4F.

Reduction of Am(IV) to Am(III) in 13 *M* NH_4F Solution.—Reduction of Am(IV) to insoluble AmF_3 is observed due to effects of Am^{241} alpha radiation at a rate of *ca.* 4% per hr., similar to the Am(VI)–Am(V) self-reduction rate also caused by Am^{241} alpha radiation.[2a,g,i] Addition of a KI crystal caused immediate reduction of Am(IV) in 13 *M* NH_4F solution. However, 0.04 *M* NaCl caused only slow reduction of a 0.009 *M* Am(IV) solution.

Effect of Temperature on Stability of Am(IV) in 13 *M* NH_4F Solution.—The concentration of Am(IV) was found to be unchanged (aside from slight reduction by alpha radiation) after heating to 90° for 60 min., then cooling to 25°. No absorption from other americium species was observed, thus indicating that no disproportionation of Am(IV) had occurred.

Oxidation of Am(IV) to Am(VI) with Ozone.—When a solution of Am(IV) in 13 *M* NH_4F is treated with ozone ($O_2 + 5\% O_3$) at 25°, the pink color begins to lighten within a few minutes. After an hour the color is light yellow and the absorption spectrum shows the characteristic peaks of Am(VI). On standing, the concentration of Am(VI) was observed to decrease while that of Am(IV) increased until all of the Am(VI) was gone.

Attempted Oxidation of Am(III) in Saturated NH_4F with Ozone.—Freshly precipitated $Am(OH)_3$ was slurried with saturated NH_4F in a stream of ozone. After 4 hr. only the characteristic peaks of Am(III) were present, and no oxidation had occurred.

Dissolution of $Am(OH)_4$ in Saturated $(NH_4)_2C_2O_4$.—One anion other than fluoride was found to stabilize Am(IV) partially. Treatment of $Am(OH)_4$ with saturated ammonium oxalate gives a solution in which the 4560 Å. peak of Am(IV) is clearly detectable even though the major part of $Am(OH)_4$ disproportionates into Am(III) and Am(V) on dissolution. The oxalate complex of Am(IV), once formed, is apparently stable to disproportionation. On standing, radiation-induced reduction of Am(V) was ob-

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[5] A preliminary report appeared as a Communication to the Editor, *J. Am. Chem. Soc.*, **83**, 2200 (1961).

[6] This formula was established by preparation and analysis of the isostructural tetravalent uranium compound, $(NH_4)_4UF_8$. The $NH_4F–UF_4–H_2O$ system is being investigated currently by R. A. Penneman and F. H. Kruse, who will report their results of that study in a later publication.

served to occur preferentially, forming some additional Am(IV).

Dissolution of $Am(OH)_4$ in Saturated $(NH_4)_2SO_4$.—When $Am(OH)_4$ was stirred with a saturated solution of $(NH_4)_2SO_4$ a clear solution was obtained. The absorption spectrum showed only Am(III) and Am(V) resulting from the disproportionation of Am(IV).

Results and Discussion

Previous work[8] has shown that, on dissolution of $Am(OH)_4$ in dilute acid, the resulting Am(IV) disproportionates very rapidly giving Am(III) and Am(V). This reaction has prevented previous observation of tetravalent americium in solution. Dissolution of $Am(OH)_4$ in concentrated ammonium or alkali fluoride, however, gives stable solutions of tetravalent americium in which disproportionation of Am(IV) does not occur. The resulting solution is stable on heating to 90°. Thus, Am(IV) in 13 *M* NH_4F does not disproportionate even at 90°, nor is Am(IV) reduced to Am(III) by water. Both of these reactions might have been expected. The fluoride complex of Am(IV) undergoes oxidation to Am(VI) on treatment with ozone; it is reduced to Am(III) by iodide and by effects of its own alpha radiation.

Actinide tetrafluorides are quite insoluble in water. Furthermore, AmF_4 is *reduced* by water unless additional fluoride is present.[2d] The striking increase in Am(IV) solubility with increasing fluoride concentration and, indeed, the *stability* of the soluble Am(IV) shows clearly that we are dealing with fluoride complexes. In solid AmF_4, americium is coördinated by eight fluoride ions at the corner of an Archimedian antiprism.[7] The absorption spectrum of Am(IV) in concentrated fluoride solution bears a striking resemblance to the absorption spectrum of solid AmF_4.[8] (See Table I.)

Table I

Principal Am(IV) Peaks, Å.

Am(IV) in 13 *M* NH_4F	AmF_4 (solid)	Am(IV) in 13 *M* NH_4F	AmF_4 (solid)
9230 ± 20[a]	9180	5678 ± 3	5680
8730 ± 10	8620	5393 ± 5	5360
7310 ± 5[a]	7440	5150 ± 25[a]	4860
7450 ± 10		4818 ± 5	
...	7030	4558 ± 2[b]	4530
6705 ± 5	...	3777 ± 3	3760
6387 ± 5	6390		

[a] Broad and asymmetric. [b] $\epsilon = 30$ measured at a slit width of 0.02 mm. on the Cary Model 14 spectrophotometer.

In a study[9] of the different double fluorides of Pu(IV), it was shown that the electronic absorption spectrum of Pu(IV) changes drastically in different fluoride environments. That the spectrum of Am(IV) in concentrated fluoride solution resembles so strongly the absorption spectrum of solid AmF_4 suggests that Am(IV) in 13 *M* NH_4F has a similar environment.

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(7) R. D. Burbank and F. N. Bensey, Jr., USAEC K-1280 (1956); *Chem. Abstr.*, **51**, 4090 (1957).

(8) L. B. Asprey and T. K. Keenan, *J. Inorg. & Nuclear Chem.*, **7**, 27 (1958).

(9) I. F. Alenchikova, L. L. Zaitseva, L. V. Lipis, V. V. Fomin, and N. T. Chebotarev, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, **28**, 309 (1958).