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Spectroelectrochemical Studies of the Actinides: Stabilization of Americium (IV) in Aqueous Carbonate Solution*

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Americium(III, IV, V, VI) Redox potentials/Absorption spectra - Carbonate solutions/Complexes

Abstract

The application of spectroelectrochemical techniques to the study of the actinide elements is described. Reticulated vitreous carbon, porous metal foam, and platinum screen optically transparent electrodes have been used for simultaneous generation and characterization of some less-stable oxidation states of americium.

Stable 2^{+3} Am(IV) has been prepared by electrolytic oxidation of 243 Am(III) in various carbonate solutions including $(\text{NH}_4)_2\text{CO}_3$, Na_2CO_3 , K_2CO_3 , and Cs_2CO_3 . Quantitative spectrophotometric and potentiometric redox titrations were performed on Am(IV) solutions to confirm the identity of the oxidation state. Cyclic voltammetric studies showed a quasi-reversible Am(IV)/Am(III) couple in $2M$ Na_2CO_3 - NaHCO_3 at pH 9.7. The corresponding formal redox potential in this medium was estimated to be 0.92 ± 0.01 V vs NHE. This value was used to estimate the standard potential for the Am(IV)/Am(III) couple as 2.6 ± 0.1 V.

Application of 1.1 V to a stable Am(IV)- K_2CO_3 solution provided for quantitative oxidation to Am(V), resulting in the formation of an Am(V) double-carbonate precipitate. Am(V) and Am(VI) were generated electrochemically at 1.1 V and 1.3 V, respectively, in $2M$ Na_2CO_3 solution.

The absorption spectra and redox behavior of Am(III), Am(IV), and Am(V) in carbonate solution are reported.

Introduction

Spectroelectrochemistry, a unique combination of spectroscopic and electrochemical techniques, has proven to be an effective approach to the study of oxidation-reduction reactions. Oxidation states of electro-active species are changed electrochemically by the addition or removal of electrons at an electrode surface. Spectroscopic measurements of the solution near the electrode surface are made simultaneously with the electrochemical generation process [1]. Spectroelectrochemical techniques provide a convenient method for obtaining spectra and reduction potentials of actinide species in solution.

The most applicable and simple form of spectroelectrochemistry involves the coupling of transmission spectroscopy to the electrode process by passing an optical beam directly through an optically transparent electrode (OTE) and the solution adjacent to it. The use of an OTE for *in situ* spectral observation of an electrogenerated product was first demonstrated in 1964 by KUWANA *et al.* [2]. The gold "minigrad" OTE in a thin-layer configuration was introduced in 1967 by MURRAY *et al.* [3]. These electrodes were used to study redox couples of highly absorbing species; however, the relatively short

effective pathlengths of these cells preclude their use for study of many actinide species which exhibit relatively low molar absorptivities or are only available in limited quantities. The recent development of an OTE made from reticulated vitreous carbon (RVC)¹ [4] provided for longer pathlengths while still maintaining the rapid electrolysis characteristics of a thin-layer cell. Similar in structure and behavior to the RVC-OTE is a new OTE made of porous metal foam (PMF)², introduced here for the first time. The general usefulness of spectroelectrochemistry as applied to the actinide elements was investigated by studying some less-stable oxidation states of americium in aqueous solution.

Am(IV) is rather unstable with respect to disproportionation in most mineral acid solutions because of the high value of the Am(IV)/Am(III) potential. This potential value has been reported to be in the range from 2.0 to 2.9 V [5]. The variation in the reported potentials is a result of the instability of Am(IV) which precluded direct potentiometric determination. Stable Am(IV) can be prepared, however, in strongly complexing aqueous solution. The first observation of stable aqueous Am(IV) was by ASPREY and PENNEMAN who dissolved Am(OH)₃ in saturated ammonium fluoride solution [6]. Concentrated KF, RbF, and CsF solutions were also found to increase the stability of Am(IV) [7]. YANIR *et al.* prepared stable Am(IV) by electrolytic oxidation of Am(III) in concentrated phosphoric acid and reported a formal potential of 1.75 V for the Am(IV)/Am(III) couple in this medium [8]. This work has been confirmed and extended by MYASOEDOV *et al.* [9, 10]. STOKELY prepared Am(IV) by electrolytic oxidation of Am(III) in concentrated H₃PO₄ and determined a value for the formal reduction potential of 1.77 V for the Am(IV)/Am(III) couple [11]. Am(IV) can also be stabilized by diluting an alkali fluoride solution of Am(IV) with concentrated acidic potassium pyrophosphate [8] and by oxidation of Am(III) in phos-

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¹ RVC is a registered trademark of Normar Industries, Anaheim, CA.

² PMF obtained from Astro Met Associates, Inc., Cincinnati, OH.

photungstate solutions [12]. A formal potential value of 1.52 ± 0.01 V for the Am(IV)/Am(III) couple in phosphotungstate media has been reported [13].

The stabilization of Pr(IV) and Tb(IV) in concentrated aqueous carbonate solution suggested the possibility of stabilizing Am(IV) in this same medium [14]. The carbonate ion preferentially complexes M(IV) lanthanide and actinide ions, significantly affecting the value of the $M(IV)/M(III)$ reduction potentials. A favorable change in the Am(IV)/Am(III) reduction potential provides stability for Am(IV) in concentrated aqueous carbonate solution.

be placed in the beam of a spectrophotometer for spectrochemical studies.

A more elaborate OTE cell was constructed especially for studies of actinides inside a glove box. A Teflon cell holder was made which positions a quartz spectroscopy cell in the sample beam of the spectrophotometer. The cell holder is fitted with a sliding lid in which an OTE, reference and counter electrodes are mounted. When the lid is lowered, the electrodes are immersed in the actinide solution. This cell arrangement requires only 0.75 mL of bulk actinide solution, and the device is easily manipulated in a glove box.

Instrumentation

Electrochemical measurements were performed with an EG & G PARC Model 173D/179D/175 potentiostat/coulometer/universal programmer interfaced to a cell in a glove box. The glove box was modified with an appendage, equipped with quartz windows, which fits into the sample compartment of a Cary Model 14-H spectrophotometer. A Corning Model 130 pH meter was used with a Fisher Scientific Model E-5A combination glass electrode with a silver/silver chloride reference for pH measurements.

Chemicals

The common chemicals used in this work were of standard ACS-certified reagent grade and were used without further purification. The K_2CO_3 and KOH were of ultra-pure (99.99%) quality and were obtained from Thikol-Ventron, Alfa Products, Danvers, MA.

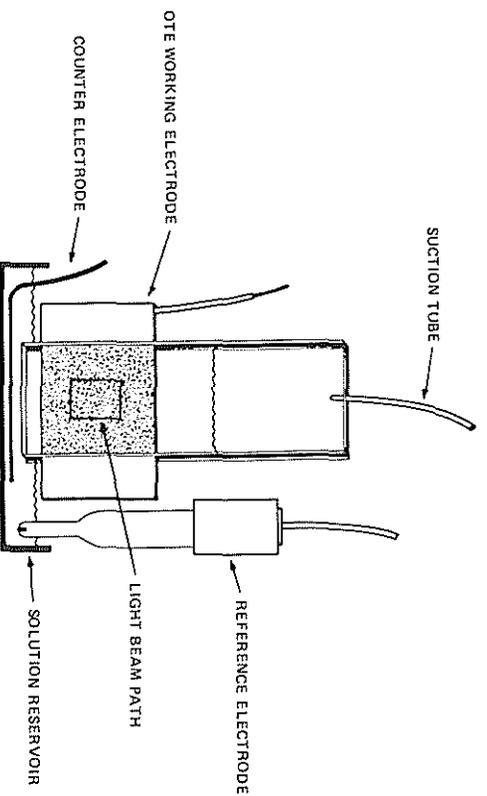
Multimilligram quantities of americium-243 were purified by chromatographic separations. The ^{243}Am was

Experimental

Optically transparent electrodes

Optically transparent electrodes were constructed by sand-wiching slices of RCV or PMF, or a trimmed section of platinum screen, between two quartz plates as described elsewhere [4, 14, 15]. The RVC-OTE's were made from 100 "pores-per-inch" RVC sectioned with a diamond saw to thicknesses of 0.62 or 1.0 mm. The PMF-OTE's were made from nickel PMF (series 280-5) cut to 3.0 or 5.0 mm thick sections which were plated with platinum. The platinum screen OTE was fashioned from sections of 40-mesh screen, 0.46 mm thick.

A simple OTE cell arrangement is shown in Fig. 1. The OTE "working" electrode cell is dipped into a solution reservoir (≥ 3 mL), and a portion of the solution is drawn up into the cell by suction. Reference and counter electrodes are placed in the bulk solution, completing the three electrode system. Using this arrangement conventional voltammetry can be performed, or the entire assembly can



ORNL-DWG 81-19001

Fig. 1. A simple optically transparent electrode (OTE) cell assembly

received as an air-dried chloride salt, $\text{AmCl}_3 \cdot n\text{H}_2\text{O}$, which resulted from evaporation of the eluent from the final ion-exchange column.

Procedures

The common inorganic chemicals were dissolved in distilled deionized water to prepare stock solutions. $\text{AmCl}_3 \cdot n\text{H}_2\text{O}$ was dissolved directly in the various carbonate solutions ($2M(\text{NH}_4)_2\text{CO}_3$, $2M\text{Na}_2\text{CO}_3$, $5.5M\text{K}_2\text{CO}_3$, and $5M\text{Cs}_2\text{CO}_3$) resulting in solutions 10^{-3} to $10^{-1}M$ in Am(III) . In order to eliminate chloride ion, some Am(III) -carbonate solutions were made by first preparing Am(OH)_3 which was then dissolved in the various carbonate solutions. The pH of the various Am(III) carbonate solutions was measured with a low-sodium-error glass electrode calibrated with known concentrations of NaOH and buffer solutions. First-scan cyclic voltammograms of the various solutions were obtained at platinum and RVC microelectrodes. Voltammograms of the Am(III) - Na_2CO_3 solutions were recorded as a function of pH. The pH was adjusted by bubbling CO_2 gas through the solutions.

Aliquots of from 0.75 to 1.0 mL of the Am(III) carbonate solutions were placed in quartz cuvetts in the Teflon cell holder assembly, and the cell holder was placed in the beam of the spectrophotometer for recording initial absorption spectra. 10 to 20 μL of the solutions were removed and diluted for alpha counting analysis. The electrodes were lowered into the solutions and the initial potentials were applied. Then the potential was made more positive until a change in the spectrum was noted or until visual observation confirmed a change in the color of the solution. Depending upon the pH of the solutions and the types of OTE used, some spectra were recorded after the potential was no longer imposed or after the electrodes were completely removed from the solutions.

Bulk solution electrolyses were performed at constant potential using platinum screen working electrodes in 2 to 4 mL of solution. Stirring was provided by a small magnetic stirrer or by bubbling N_2 gas through the solution.

Solid oxidation products formed at the OTE were collected, dried, and dissolved in $1M\text{HClO}_4$. The absorption spectra of the resultant solutions were recorded.

Spectrophotometric and potentiometric titrations were performed with standardized $\text{K}_4\text{Fe(CN)}_6$ in pH-adjusted Na_2CO_3 solutions.

Results and discussion

Potassium carbonate solutions

Americium(IV) was initially studied in the RVC-OTE under the same conditions as those for the stabilization of Pr(IV) and Tb(IV) , i. e., $5.5M\text{K}_2\text{CO}_3$ - $1M\text{KOH}$ [14]. The Am(V) , produced under these conditions at 0.94V^3 exhibited limited stability. The golden-yellow Am(IV) produced at

the anode surface was somewhat unstable and dissipated into the pink Am(III) bulk solution within a few minutes after stoppage of the applied potential.

At an applied potential of 1.1 V, a light brown Am precipitate formed at the electrode. The precipitate was collected, washed, and dissolved in $1M\text{HClO}_4$. Upon dissolution of the solid, gas bubbles evolved, a heavy white precipitate of KClO_4 formed, and a colorless supernatant solution resulted. The spectrum of the acidic supernatant solution exhibited only absorption peaks characteristic of Am(V) . The precipitate, concluded to be a potassium Am(V) double-carbonate [16], formed only at an applied potential $\geq 1.1\text{V}$. No Am(V) precipitate formed at potentials lower than 1.1 V during electrolytic oxidation of Am(III) to Am(IV) in potassium carbonate solution. Thus Am(V) was generated electrolytically and not as a result of the disproportionation of Am(IV) . In this manner it was determined that Am(IV) was the species exhibiting the golden-yellow color, and that it was slowly reduced to Am(III) , but was stable to disproportionation in potassium carbonate solution [17].

Sodium carbonate solutions

The oxidation of Am(III) was studied in $2M\text{Na}_2\text{CO}_3$ in order to generate a soluble Am(V) species [16] and to investigate the stability of Am(IV) as a function of pH. Cyclic voltammograms of the Am(IV)/Am(III) couple at various pH values are shown in Fig. 2. At pH 12.5 an oxida-

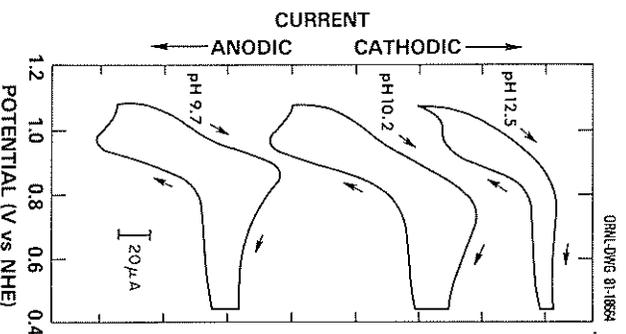


Fig. 2. First-scan cyclic voltammograms of the Am(IV)/Am(III) couple in $2M\text{Na}_2\text{CO}_3$ solution at various pH values. $[\text{Am(III)}] = 2.0 \times 10^{-5}M$, scan rate: 20mV/s , platinum wire microelectrode

³ All potential values in this work are reported in volts versus the Normal Hydrogen Electrode (NHE).

tion wave for the reaction $\text{Am(III)} \rightarrow \text{Am(IV)} + e^-$ was partially obscured by the oxygen evolution wave, and no evidence for a corresponding reduction wave was observed. Therefore, the electrode reaction was irreversible under these conditions. At pH 10.2 the wave for oxygen evolution appeared at a more positive potential where it did not interfere with the Am(III) oxidation wave; a reduction wave for Am(IV) was also observed at this pH. At pH 9.7 the optimum conditions were obtained for the $\text{Am(IV)}/\text{Am(III)}$ couple in this medium. The separation between the anodic and cathodic peak potentials of the cyclic voltammograms exceeded the 59 mV value characteristic of a completely reversible system. The peak potential separation for the Am couple in this medium ranged between 210 mV, at a potential sweep rate of 200 mV/s, to 95 mV, at 20 mV/s. The anodic and cathodic peak current values were nearly equal for all the various sweep rates. Thus the $\text{Am(IV)}/\text{Am(III)}$ couple is "quasi-reversible" in $2M \text{Na}_2\text{CO}_3\text{-NaHCO}_3^4$ at pH 9.7. Precipitation of americium resulted below pH 8 (presumably Am(OH)_3). The fact that the $\text{Am(IV)}/\text{Am(III)}$ couple is quasi-reversible under certain conditions indicates that it is the $\text{Am(IV)}/\text{Am(III)}$ couple, since higher oxidation states would involve oxyanions (i. e., for $\text{Am(V)} : \text{AmO}_2^+$) and such an oxygen-transfer process should be electrochemically irreversible.

The formal reduction potential for the $\text{Am(IV)}/\text{Am(III)}$ couple in $2M \text{Na}_2\text{CO}_3\text{-NaHCO}_3$ at pH 9.7 was estimated from the quasi-reversible, cyclic voltammogram (by determining the mid-potential between the cathodic and anodic peak potentials) to be 0.92 ± 0.01 V. Assuming the shift in the $\text{Am(IV)}/\text{Am(III)}$ potential provided by carbonate complexation is the same as that observed for the $\text{Ce(IV)}/\text{Ce(III)}$ couple in this medium (1.7 V less positive than that in noncomplexing solution [14]), the standard potential for the $\text{Am(IV)}/\text{Am(III)}$ couple was estimated to be 2.6 ± 0.1 V. This value is in agreement with the $\text{Am(IV)}/\text{Am(III)}$ standard potential value of 2.62 ± 0.09 V recently reported by MORSS and FUGER [5].

The solution absorption spectrum of Am(III) in $2M \text{Na}_2\text{CO}_3\text{-NaHCO}_3$ at pH 9.7 is shown in Fig. 3 and is similar to that in $6.0M \text{K}_2\text{CO}_3$ reported by SHILOH *et al.* [18]. The most intense band ($\epsilon = 240 M^{-1} \text{cm}^{-1}$), which is attributed to an f-f transition, is at 507 nm. This band is observed at 503 nm ($\epsilon = 380 M^{-1} \text{cm}^{-1}$) in noncomplexing perchloric acid solution [19]. The shift in the wavelength at which this maximum absorption occurs, the change of its molar absorptivity, and the broadening of this absorption band are all evidence for complexation of Am(III) by carbonate ions.

The spectrum of electrolytically generated Am(IV) in $2M \text{Na}_2\text{CO}_3\text{-NaHCO}_3$ at pH 9.7 is also shown in Fig. 3. This spectrum is characterized by a broad-band absorption centered at about 360 nm ($\epsilon = 2900 M^{-1} \text{cm}^{-1}$) which is probably due to a charge-transfer mechanism. The appearance of this Am(IV) absorbance and the concomitant disappearance of the Am(III) f-f bands, during spectroelectrochemical oxidation, indicated that an Am(IV) species was being generated. Application of a reducing

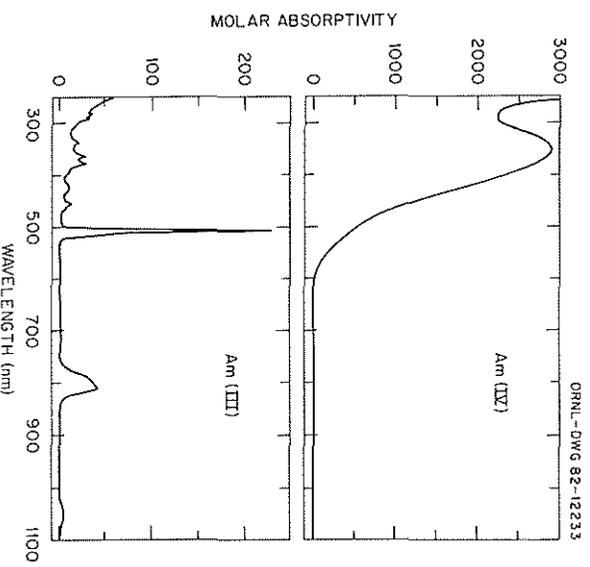


Fig. 3. Absorption spectra of Am(III) and Am(IV) in $2M \text{Na}_2\text{CO}_3\text{-NaHCO}_3$ solution at pH 9.7

potential caused the disappearance of the Am(IV) spectrum and the simultaneous reappearance of the Am(III) spectrum. Since a spectrum of Am(IV) in aqueous carbonate solution had not been reported and the observed americium spectrum did not resemble that of Am(IV) in concentrated fluoride solutions [6] nor that of Am(IV) in concentrated phosphoric acid solutions [8], further verification was required to confirm that Am(IV) was the species produced in carbonate media.

Quantitative spectrophotometric and potentiometric redox titrations were performed on Am(IV) carbonate solutions to confirm the identity of the oxidation state. Results of a typical titration are shown in Figs. 4 and 5. Solution absorption spectra of Am(III) and Am(IV) , in $2M \text{Na}_2\text{CO}_3\text{-NaHCO}_3$ at pH 9.7, as a function of $\text{K}_4\text{Fe(CN)}_6$ titrant added in the spectrophotometric redox titration of Am(IV) are shown in Fig. 4. The broad shoulder of the absorption band of Am(IV) (spectrum A) decreases with the concomitant increase of the Am(III) band (spectra B through F) as the redox titration proceeds. The shoulders below 470 nm in spectra E and F are the result of absorption by excess titrant. A plot of Am(III) absorbance as a function of the volume of titrant added is displayed in Fig. 5. The Am(III) absorption at 507 nm was corrected for both dilution effects and the background absorption of Am(IV) and the redox titrant. In this and other titrations, it was found that one equivalent of titrant was required to reduce one equivalent of Am(IV) , confirming a one-electron process. The oxidation of Am(III) to Am(IV) in $2M \text{Na}_2\text{CO}_3\text{-NaHCO}_3$ at pH 9.7 was found to be nearly 100% complete, as determined by the results of the redox titrations, producing a red-brown solution.

⁴ This formula is used to identify a carbonate-bicarbonate solution which results from the pH adjustment of an initial $2M \text{Na}_2\text{CO}_3$ solution.

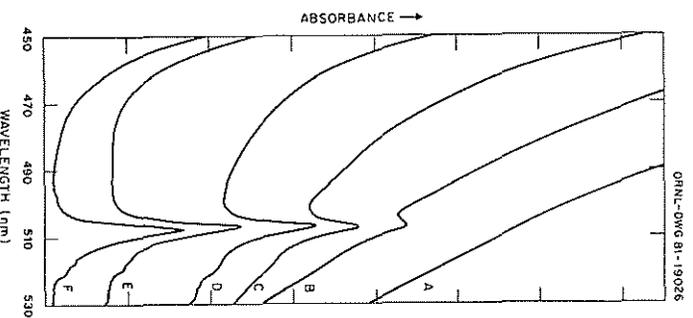


Fig. 4. Absorption spectra of Am(III) and Am(IV) in $2M$ Na_2CO_3 - NaHCO_3 solution at pH 9.7 as a function of the volume of $\text{K}_4\text{Fe}(\text{CN})_6$ titrant added. (A) $0 \mu\text{L}$, (B) $50 \mu\text{L}$, (C) $100 \mu\text{L}$, (D) $150 \mu\text{L}$, (E) $175 \mu\text{L}$, and (F) $200 \mu\text{L}$. Initial conditions: Volume = $500 \mu\text{L}$; $[\text{Am}(\text{IV})] = 2.65 \times 10^{-3} M$ (via alpha counting); $[\text{K}_4\text{Fe}(\text{CN})_6] = 5.39 \times 10^{-3} M$

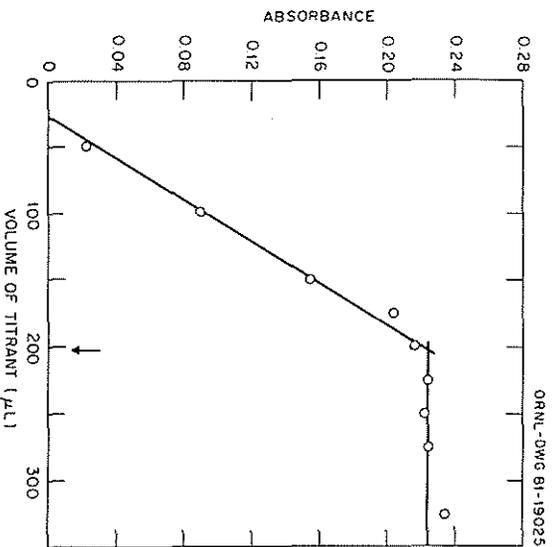


Fig. 5. Plot of absorbance at 507 nm versus volume of $\text{K}_4\text{Fe}(\text{CN})_6$ titrant added in the spectrophotometric titration of Am(IV) in $2M$ Na_2CO_3 - NaHCO_3 solution at pH 9.7. $203 \mu\text{L}$ of $5.39 \times 10^{-3} M$ $\text{K}_4\text{Fe}(\text{CN})_6$ required to reduce $500 \mu\text{L}$ of $2.65 \times 10^{-3} M$ Am(IV). Moles of $\text{K}_4\text{Fe}(\text{CN})_6$ /moles of Am(IV) = 0.83

To confirm in yet another way that the oxidized Am species was Am(IV), known concentrations of Am(IV) in $2M$ Na_2CO_3 - NaHCO_3 at pH 9.7 were acidified with HClO_4 . The spectra of the resultant solutions corresponded to that of an equal mixture of Am(III) and Am(V) which could have only resulted from disproportionation of Am(IV). Additionally, application of 1.1 V to the working electrode in a stable Am(IV)-sodium carbonate solution

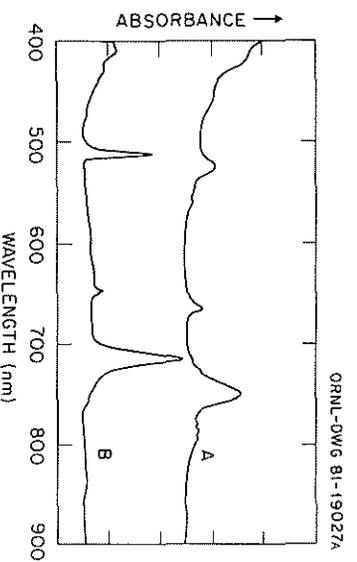


Fig. 6. Absorption spectra of Am(V) in (A) $2M$ Na_2CO_3 - NaOH and (B) $1M$ HClO_4 solutions

resulted in the generation of a soluble Am(V) species.

This was noted by the appearance of new absorption bands of low molar absorptivity at 525 and 663 nm and a main peak at 751 nm . COLEMAN *et al.* [16] reported a value of 730 nm for the main peak of Am(V) in dilute sodium carbonate-bicarbonate solution.

When 1.3 V was applied to the working electrode in a stable Am(IV)-sodium carbonate solution, oxygen gas was evolved and soluble Am(VI) was generated. The presence of Am(VI) was confirmed by the addition of concentrated NaOH to the solution, which resulted in the rapid reduction of the dark red-brown Am(VI) solution to a faint yellow solution [16] exhibiting the spectrum of Am(V) in basic solution shown in Fig. 6. Acidification of this basic Am(V) solution with HClO_4 resulted in the characteristic spectrum of Am(V) in acid solution also shown in Fig. 6 [20]. The addition of NaOH to an Am(IV)- Na_2CO_3 solution does not result in the discoloration of the solution. Although the red-brown carbonate complexes of Am(IV) and Am(VI) in solution are nearly identical in appearance, differentiation of the two species can be made by chemical, electrochemical, and spectrophotometric means.

Ammonium and cesium carbonate solutions

Am(IV) was also generated in $2M$ $(\text{NH}_4)_2\text{CO}_3$ and $5M$ Cs_2CO_3 solutions. The $(\text{NH}_4)_2\text{CO}_3$ solvent medium allowed nearly complete oxidation of Am(III) to Am(IV), since the solvent is self-buffered at pH 9.5, which is near the optimum pH for stability of Am(IV) in carbonate solutions. However, the limited solubility of Am(OH)₃ in this medium precluded extensive studies in this solvent. Qualitatively, Am(OH)₃ was more soluble in Cs_2CO_3 solution than in ammonium and sodium carbonate solutions but less soluble than in the potassium carbonate medium. A cesium Am(V) double-carbonate salt was obtained as a precipitate in Cs_2CO_3 solution at potentials equal to or exceeding 1.1 V .

Nature of the complex ions

The carbonate complexes of selected trivalent lanthanides

have been studied by SHERRY and MARINSKY [21] and those of trivalent americium by KELLER and FANG [22]. These workers determined that at carbonate concentrations greater than 2 M the identity of the complex is $[\text{Am}^{\text{III}}(\text{OH})(\text{CO}_3)_4]^{6-}$. DUMONCEAU [23] also reports a tetracarboxylate-complex of the form $[\text{M}^{\text{III}}(\text{CO}_3)_4]^{5-}$ for lanthanides in carbonate-bicarbonate solutions. LUNDQVIST [24] indicates, however, that in concentrated Na_2CO_3 solutions, the tricarboxylate-complex $[\text{Am}(\text{CO}_3)_3]^{3-}$ is the most likely species present and not a tetracarboxylate-complex. SHILOH *et al.* [18] reported the existence of the complex $[\text{Am}(\text{OH})(\text{CO}_3)_3]^{4-}$ in solutions of 0.1–0.6 M potassium carbonate.

The quasi-reversible nature of the cyclic voltammogram for the $\text{Am}(\text{IV})/\text{Am}(\text{III})$ couple in sodium carbonate-bicarbonate solution suggests that, whatever the form of the trivalent americium carbonate complex, the tetravalent americium complex should be quite similar.

The nature of the $\text{Am}(\text{V})$ -carbonate and $\text{Am}(\text{VI})$ -carbonate complexes should be different from that of the $\text{Am}(\text{IV})$ complex since the former species are expected to involve the AmO_2^+ and AmO_2^{2+} oxyanions, respectively. The differences in the peak positions and intensities (Fig. 6) observed between the $\text{Am}(\text{V})$ spectrum in carbonate medium and that in perchloric acid medium indicate complexation of $\text{Am}(\text{V})$ in carbonate solutions. The compositions of the $\text{Am}(\text{V})$ - and $\text{Am}(\text{VI})$ -carbonate complexes are unknown.

Conclusions

Spectroelectrochemical study of the oxidation of $\text{Am}(\text{III})$ in concentrated aqueous carbonate solution provided the first observation of $\text{Am}(\text{IV})$ in this medium. Although the electrolytically generated $\text{Am}(\text{IV})$ was not completely stable in the solution in which it was initially observed (5.5 M K_2CO_3 -1 M KOH), the use of an optically transparent electrode allowed for complete spectral characterization of the $\text{Am}(\text{IV})$ species produced. Conventional cyclic voltammetric analysis permitted a determination of the proper conditions for a quasi-reversible $\text{Am}(\text{IV})/\text{Am}(\text{III})$ couple, and thus the optimum conditions for the stabilization of $\text{Am}(\text{IV})$. The formal reduction potential for the $\text{Am}(\text{IV})/\text{Am}(\text{III})$ couple in 2 M Na_2CO_3 - NaHCO_3 at pH 9.7 was found to be 0.92 ± 0.01 V. From the known shift in potential (≈ 1.7 V) of similar lanthanide $\text{M}(\text{IV})/\text{M}(\text{III})$ couples in carbonate media versus non-complexing media, assuming complexation constants of similar magnitude, the standard reduction potential for the $\text{Am}(\text{IV})/\text{Am}(\text{III})$ couple was calculated to be 2.6 ± 0.1 V.

The assignment of oxidation state IV to the oxidized americium species in carbonate solution was based on:

- (a) the characteristic solution absorption spectrum (which is quite similar to the reported spectrum of pulse-radiolytically-produced $\text{Am}(\text{IV})$ in perchlorate medium [25]);
- (b) correlation of the standard $\text{Am}(\text{IV})/\text{Am}(\text{III})$ potential

with the known shift in reduction potentials previously measured for lanthanide $\text{M}(\text{IV})/\text{M}(\text{III})$ couples in carbonate media; (c) the quasi-reversible nature of the $\text{Am}(\text{IV})/\text{Am}(\text{III})$ couple in pH-adjusted sodium carbonate solution; (d) disproportionation of stable $\text{Am}(\text{IV})$ carbonate solutions in perchloric acid media; (e) quantitative oxidation of stable $\text{Am}(\text{IV})$ to $\text{Am}(\text{V})$ to $\text{Am}(\text{VI})$ in carbonate media; and (f) quantitative spectrophotometric and potentiometric redox titrimetry.

$\text{Am}(\text{V})$ was generated electrolytically as a soluble species in sodium and ammonium carbonate solutions and as an $\text{Am}(\text{V})$ double-carbonate precipitate in potassium and cesium carbonate media. $\text{Am}(\text{VI})$ was generated electrolytically in sodium carbonate solution; the dark red-brown $\text{Am}(\text{VI})$ carbonate complex is well known [16, 26, 27], but the species composition is unknown.

The results of further studies of americium redox couples in concentrated aqueous carbonate media will be presented in a forthcoming publication [28].

It is anticipated that the continued development of improved cell designs and new electrode materials, which provide longer pathlengths and larger electrode surface areas, while maintaining a minimal sample volume, will enhance the applications of spectroelectrochemistry to studies of actinide redox couples. The use of complexing aqueous solutions in conjunction with spectroelectrochemical techniques as a means of generating and stabilizing less-stable oxidation states of the actinides will be exploited further. It is expected that concentrated aqueous carbonate solutions can provide stability for other unusual actinide oxidation states such as $\text{Cm}(\text{IV})$ and $\text{Cf}(\text{IV})$. Such investigations are planned or are currently in progress, and the results of these studies will be published separately.

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