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Coexistence of Americium in Four Oxidation States in Sodium Carbonate-Sodium Bicarbonate Medium

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The values of the apparent normal potentials of the couples Am(VI)/Am(V) and Am(IV)/Am(III) in sodium bicarbonate-sodium carbonate media 1.2 M < $[HCO_3^- + CO_3^{2-}]$ < 2.3 M were obtained by ferrocyanide potentiometric titration combined with spectrophotometric measurements. While the Am(VI)/Am(V) couple ($E^{\circ\prime} \approx 0.975 \pm 0.01$ V vs. NHE) is independent of carbonate concentration, the potential of the Am(IV)/Am(III) couple decreases monotonically as CO_3^{2-} concentration increases ($E^{\circ\prime} = 0.924 \pm 0.01$ V vs. NHE to $[CO_3^{2-}] = 1$ M). The variation of 127 mV in the normal potential of the couple Am(IV)/Am(III) as a function of log $[CO_3^{2-}]$ suggests the exchange of two carbonate molecules during passage from the carbonate form of Am(III) to that of Am(IV). The coexistence of four species at equilibrium, Am(III), Am(IV), Am(V), and Am(VI), is demonstrated by preparing mixtures of pure species Am(VI) and Am(III) that react with the formation of Am(IV) and Am(V). The absorption spectra of the species and their electrochemical behavior are analyzed.

Introduction

The investigations of transuranium elements in carbonate medium answer two major concerns: (1) a better knowledge of the behavior of transuranium elements in media routinely used for their purification, where they may exist in oxidation states normally unstable in acidic medium (it should be noted that the selective precipitation of pentavalent americium in K_2CO_3[1,2] medium is the standard process used to separate americium from curium and from fission products) and (2) the compilation of a thermodynamic and chemical data bank to predict the behavior of transuranium elements in the ecosystem, in which the work of certain authors[3-5] has demonstrated the importance of carbonate complexes in surface runoff.

Until recently, three oxidation states of americium were known in carbonate medium: Am(III),[6,7] Am(V),[6-8] and Am(VI).[9-11] Quite recently, Hobart et al.[12] pointed out the existence of americium with oxidation state IV in this medium. This study was undertaken to examine the electrochemical and chemical behavior of the couples Am(IV)/Am(III) and Am(VI)/Am(V) in sodium bicarbonate-sodium carbonate medium.

The sodium medium was selected to minimize pentavalent americium precipitation.

Experimental Section

1. Preparation and Determinations of the Solutions. The chemicals used, Na_2CO_3, $Na_2S_2O_8$, NH_3, N_2H_4, $K_4Fe(CN)_6{\cdot}3H_2O$, and NaOH (Prolabo), of analytical grade were employed without additional purification. The americium oxide with the isotopic composition ^{243}Am 96%, ^{241}Am 4%, containing less than 100 ppm of ^{244}Cm and 0.2% of inactive impurities was supplied by the Transuranium Production Section of CEN-FAR.[13] The bicarbonate-carbonate solutions used were prepared by dissolving anhydrous Na_2CO_3 in double-distilled water and bubbling CO_2 gas to adjust the pH to the desired value in the range from 9.5 to 12. The CO_3^{2-} and HCO_3^- ion concentrations of these solutions were determined by volumetry. The ferrocyanide solutions used to determine the oxidized solutions of Am(III) were prepared by dissolving $K_4Fe(CN)_6{\cdot}3H_2O$ in suitable $NaHCO_3$-Na_2CO_3 solutions. After acidification by H_2SO_4, the $Fe(CN)_6^{4-}$ ion concentrations in these solutions were determined by potentiometry with a standard solution of Ce(IV).

The mother solutions of 10^{-1} M Am(III) were prepared by dissolving AmO_2 in 4 M HNO_3-10^{-5} M HF.

The Am(III) solutions in $NaHCO_3$-Na_2CO_3 media were prepared by the following procedure: precipitation of Am(III) hydroxide from an aliquot of the mother solution (4-8 mg of ^{243}Am) by NH_3 in the presence of hydrazine, centrifugation of the precipitate and repeated washings with distilled water until practically neutral wash waters were obtained (pH 7-8), and redissolution of freshly prepared hydroxide gel in the $NaHCO_3$-Na_2CO_3 solution of the desired concentration.

This procedure avoids the precipitation of Am(III) peroxide or Am(IV) hydroxide described by Buijs and Louwrier.[14] The americium concentration in the solutions was determined by α-particle radiometry.

2. Preparation of Americium Solutions with Oxidation States IV, VI, and V in $NaHCO_3$-Na_2CO_3 Medium. Am(IV) was prepared electrochemically by anodic oxidation at potentials of 0.900 V vs. NHE for the medium $[HCO_3^- + CO_3^{2-}] = 2.3$ M, pH 10.2, and 0.950 V vs. NHE for the medium $[HCO_3^- + CO_3^{2-}] = 1.5$ M, pH 9.5. The oxidation interrupted after 2-3 h was not quantitative. The yields measured by coulometry fluctuated between 0.60 and 0.86. The Am(IV) solutions, stable for ~12 h in the best conditions, were golden yellow for concentrations around 5×10^{-4} M and orange-red for americium concentrations equal to or greater than 10^{-3} M.

The Am(VI) solutions were prepared either by electrochemical oxidation at the potential of 1.2 V vs. NHE or by chemical oxidation with sodium persulfate. In the latter procedure, oxidation was performed on a water bath at a temperature of 60-80 °C starting with solutions of Am(IV) or Am(III). At this temperature, the excess oxidant was destroyed in about 2 h. The color of the Am(VI) solutions changed from orange-red to reddish brown when the americium concentration rose from 5×10^{-4} M to 10^{-3} M.

The Am(V) solutions were prepared by electrochemical reduction of Am(VI) solutions at a potential of 0.450 V vs. NHE. The Am(V) solutions were colorless but on aging assumed a yellow color, probably due to the dismutation of Am(V).

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Table I. Molar Extinction Coefficients of Am(III), Am(IV), Am(V), and Am(VI) in the Medium [$NaHCO_3$ + Na_2CO_3] = 2 M, pH 10[a]

species	λ, nm	ε, M^{-1} cm^{-1}	species	λ, nm	ε, M^{-1} cm^{-1}
Am(III)	285	88	Am(V)	520	15
	337	56		654	15
	365	53		662	12
	380	52		736	23
	424	26		752	16
	456	26	Am(VI)	369	2714
	506	257		383	2657
	658	42		606	1074
Am(IV)	369	2812		682	73
	383	2711			
	506	683			
	660	9			

[a] Measured on a Hewlett-Packard HP 8450A spectrophotometer.

3. Electrochemical Measurements. The electrochemistry cell was equipped with four electrodes: a mercuric sulfate reference electrode of Hg/Hg_2SO_4 in saturated K_2SO_4 ($E° = 0.656$ V vs. NHE), an auxiliary electrode consisting of a platinum strip isolated from the solution by a frit, and two working electrodes used alternately. The macroelectrode (platinum grid) served for species oxidations and reductions; the microelectrode (Platinum wire) served for the voltammogram plots.

The electrochemical cell was thermostated at 25 °C with use of a Haake circulation unit. The cyclic voltammograms were obtained by a potentiostat unit (PRT 20-2) with a Tacussel pilot (GSTP-3). Recordings were made on a Hewlett-Packard 7040 A X-Y recorder. The current yields were read on a Tacussel digital coulometer (1G 6N). Before a series of voltammograms was plotted, the platinum microelectrode was washed with concentrated HNO_3, rinsed with water, and wiped. To obtain the steady-state voltammogram, two to four scanning cycles were generally adequate.

During the determinations of the oxidized americium solutions by ferrocyanide with spectrophotometric observation, the equilibrium potentials were measured, after each addition, directly in the spectrophotometric cell with a Pt-SCE microelectrode (Metrohm EA 259). The value found for the apparent normal potential of the couple $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ was 0.520 ± 0.01 V vs. NHE in the medium [Na_2CO_3] + [$NaHCO_3$] = 2 M, pH 10.

To minimize the effects due to catalytic reduction by platinum,[15] the equilibrium potentials must be read with agitation. An interval of 30 s to $1^1/_2$ min was required to obtain a stable potential, depending on the operating conditions.

4. Spectrophotometric Measurements. The measurements were taken by using Helma QS cells with 10-mm optical paths. The Hewlett-Packard 8450 A spectrophotometer used allowed measurements of absorption spectra in the wavelength range from 200 to 800 nm. This instrument allows very rapid measurements (0.1 s for the entire spectrum) and their simultaneous storage in internal memory and on magnetic tape, thus facilitating subsequent mathematical processing. In addition, certain measurements were taken from 800 to 1300 nm on a Beckman 5280 spectrophotometer.

The spectrophotometric determinations of the solutions of Am(IV) and Am(VI), or their mixtures, were carried out directly in the spectrophotometric cells by the addition of precise and successive volumes of a ferrocyanide solution, until the extinction of the absorption band of Am(IV) or Am(VI) or of their mixture. To prevent the interference of absorption bands of the couple $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, the optical density of Am(VI) or Am(IV) was measured not at the top of the peak at 369 nm but usually at 506 nm. The performance of a ferrocyanide determination (the couple $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ is very rapid in the medium) required 10–15 min and 20–25 minutes with spectrophotometric observation for the measurement of the equilibrium potential of the solution.

All the determinations were terminated by the addition of hydrazine, a powerful reducing agent (−1.15 V vs. NHE at pH 14), in order to restore all the americium solution to the form of Am(III), which is easy to measure by spectrophotometry.

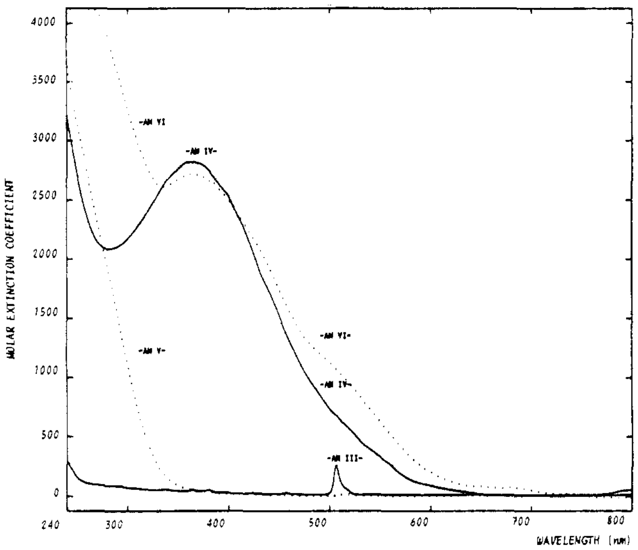

Figure 1. Solution absorption spectra of Am(VI), Am(V), Am(IV), and Am(III) in the medium [$NaHCO_3$ + $NaCO_3$] = 2 M at pH 10.

Results

1. Absorption Spectra of the Am(III), Am(IV), Am(V), and Am(VI) Species. The absorption spectra of the americium species at the four oxidation states in $NaHCO_3$–Na_2CO_3 medium are shown in Figure 1. The main values given in Table I are concerned with the molecular extinction coefficients in the medium [HCO_3^- + CO_3^{2-}] = 2 M at pH 10. The preparation of an absolutely pure solution of Am(IV) was not possible in our operating conditions, and the Am(IV) spectrum was obtained by deducting the low contribution of Am(III). The Am(IV) concentration was obtained by ferrocyanide determination. The observation of the different spectra in Figure 1 calls for the following remarks:

(1) Spectrophotometry allows Am(III) determination with good accuracy at 506 nm (at 506 nm, ε(Am(III)) = 257). The presence of Am(V), of which the absorption spectrum above 350 nm displays a peak at 520 nm with a very low molar extinction coefficient (ε = 15), does not produce any interference with the Am(III) peak.

(2) The Am(IV) and Am(VI) spectra are closely comparable, with the same charge-transfer band with a maximum at 369 nm and very similar molar extinction coefficients, 2812 and 2714, respectively, for Am(IV) and Am(VI). A more pronounced spectral differentiation appears between 480 and 650 nm, where Am(VI) is more absorbent than Am(IV). For example, at 506 nm, ε(Am(VI)) = 1074 and ε(Am(IV)) = 683.

Consequently, spectrophotometry alone does not allow one to distinguish between Am(IV) and Am(VI), in the event that both species coexist in solution.

2. Voltammetric Analyses. The behavior of the species Am(III), Am(IV), and Am(VI) in solution was investigated by cyclic voltammetry with a polished platinum electrode, at different scanning rates (500–20 mV s^{-1}). Only the solutions relatively concentrated in carbonate, [$NaHCO_3$ + Na_2CO_3] = 2 M allowed the solubilization of Am(III) at sufficient concentrations ($C = 10^{-3}$–(4×10^{-3}) M) for an electrochemical investigation. The very low solubility of Am(III) in saturated sodium bicarbonate solutions (~1.2 M, pH <8.5), limits the experimental approach in these media. Only the voltammograms plotted at slow speed (20 mV s^{-1}) and for solutions with pH ≤10 approach reversibility.

The shapes of these plots are practically identical whatever the species present in solution: Am(III), Am(IV), or Am(VI). Figure 2 shows the voltammogram of a 2×10^{-3} M solution of Am(III) in the medium [HCO_3^- + CO_3^{2-}] = 2 M at pH

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(15) C. Musikas, Thesis, Paris XI University, June 1977, p 66.

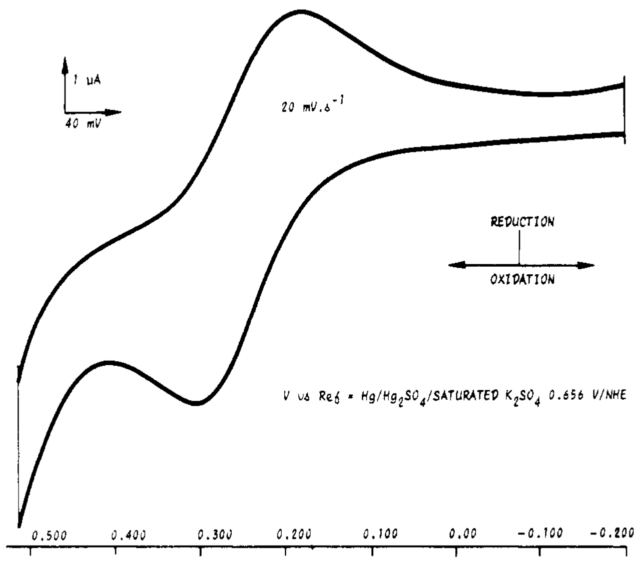

Figure 2. Cyclic voltammogram of 2×10^{-3} M Am(III) in $[CO_3^{2-}] = [HCO_3^-] = 1$ M medium.

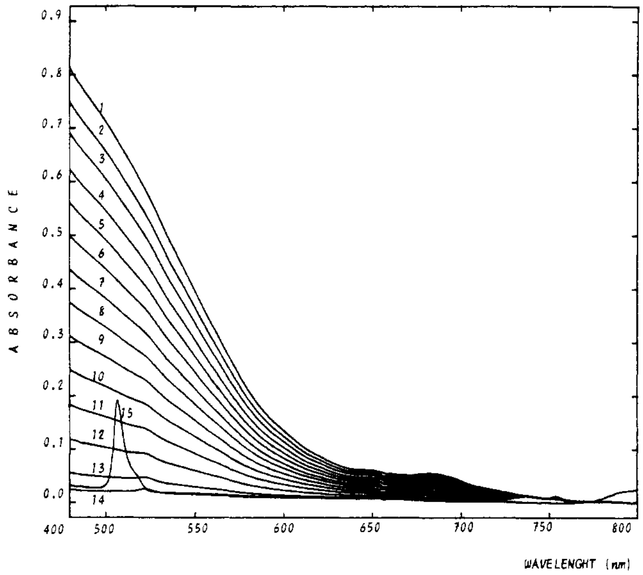

Figure 3. Spectrophotometric titration of Am(VI) with 5.12×10^{-3} M ferrocyanide solution in the medium $[NaHCO_3 + Na_2CO_3] = 2$ M at pH 10: (1) initial solution; (2–14) reduced solutions with ferrocyanide; (15) final solution after hydrazine addition.

9.8 for the potential scanning range 0.450–1.150 V vs. NHE at a rate of 20 mV s^{-1}.

Two peaks separated by about 100 mV are observable. The anode peak appears at 0.940 V vs. NHE before the oxygen wave (0.980 V vs. NHE), while the cathode peak is located at around 0.840 V vs. NHE.

However, voltammetric analysis is faced with two difficulties: (1) the voltammogram results in steady-state diffusion with agitation are difficult to reproduce for study, and (2) the shift of the oxygen wave to lower anodic potentials when the pH increases (60 mV/pH unit) obscures progressively the americium oxidation wave at pH >11.5 and so there is no evidence for a corresponding reduction of americium.

Thus cyclic voltammetry does not furnish precise data concerning the apparent normal potentials of the couples Am(VI)/Am(V) and Am(IV)/Am(III). Consequently, only potentiometric titration with a fast couple such as ferrocyanide/ferricyanide, combined with spectrophotometric observation, can reveal the differences between the two oxidized species Am(IV) and Am(VI).

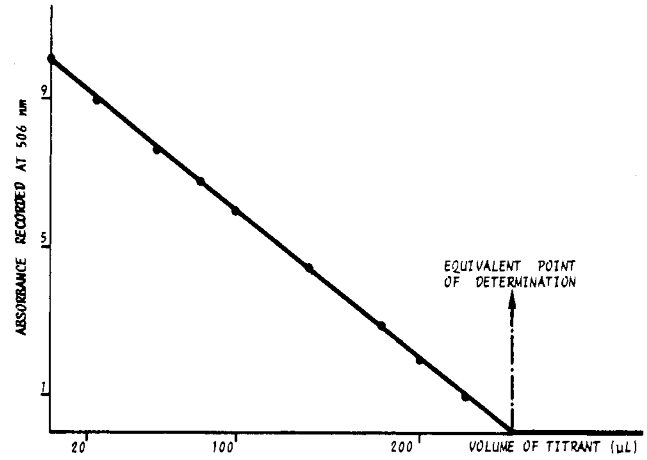

Figure 4. Absorbance portrayed in centimeters vs. volume of titrant added in the spectrophotometric titration of Am(VI) with $Fe(CN)_6^{4-}$.

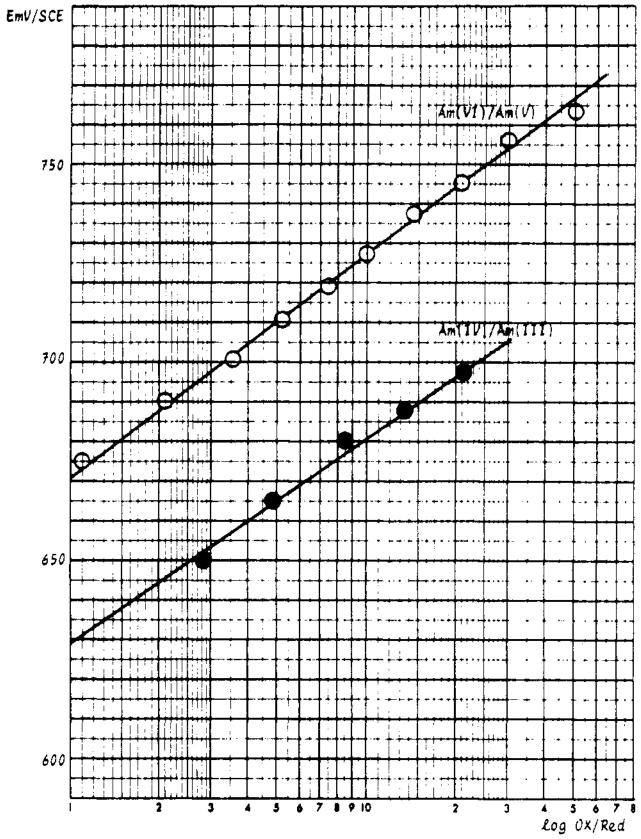

Figure 5. Determination of apparent normal potentials of Am(VI)/Am(V) and Am(IV)/Am(III) redox couples in $[HCO_3^-] = 1.15$ M, $[CO_3^{2-}] = 0.85$ M medium (pH 10) by Nernstian plot.

3. Apparent Normal Potential of Couples Am(VI)/Am(V) and Am(IV)/Am(III). (a) Am(VI)/Am(V). The determination of Am(VI) by ferrocyanide is reflected in spectrophotometry by a collapse of the Am(VI) absorption band in the region from 460 to 800 nm (Figure 3) without the appearance of americium in oxidation state III, of which the characteristic band is expected at 506 nm. Reduction by $Fe(CN)_6^{4-}$ stops at the Am(V) state and thus only involves one electron. Equimolar correspondence exists between the quantity of ferrocyanide added and the quantity of americium(VI) reduced. The final addition of hydrazine serves to measure the total concentration of americium by quantitative reduction to Am(III). The curve obtained by plotting the optical density at 506 nm as a function of titrant volume displays an equivalent point that gives the initial Am(VI) content (Figure 4). Figure 5 shows a plot of the equilibrium potential values

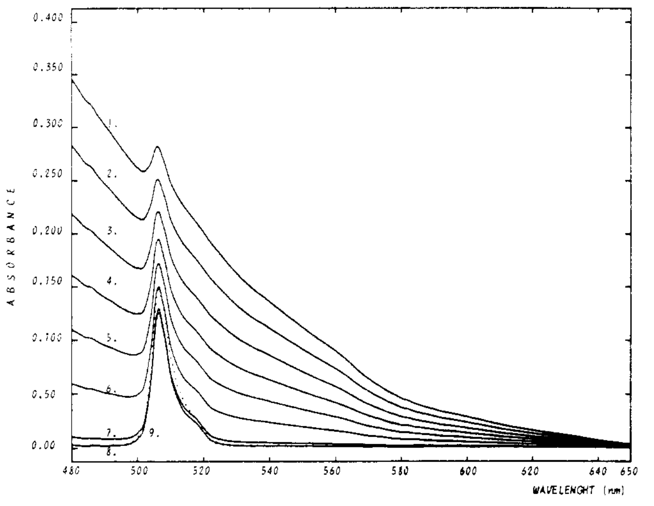

Figure 6. Spectrophotometric titration of Am(IV) with 5.12 × 10^{-3} M ferrocyanide solution in the medium [$NaHCO_3$ + Na_2CO_3] = 2 M, pH 10: (1) initial solution; (2–8) reduced solutions as a function of titrant added; (9) final solution after hydrazine addition.

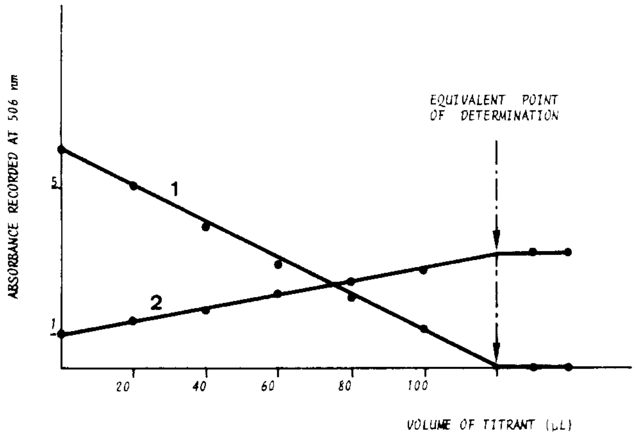

Figure 7. Absorbance portrayed in centimeters vs. volume of titrant added in the spectrophotometric titration of Am(IV) with $Fe(CN)_6^{4-}$: (1) Am(IV); (2) Am(III).

measured at each determination step as a function of log (Am(VI)/Am(V)). With the experiment described in Figure 3, Nernst's law is confirmed: the slope is 55 mV, and the apparent normal potential is found equal to $E°'$ = 0.726 vs. SCE (*R* correlation coefficient 0.998) for the medium examined ([$NaHCO_3$] = 1.15 M, [Na_2CO_3] = 0.85 M, pH 10 ± 0.1).

(b) Am(IV)/Am(III). The action of ferrocyanide on Am(IV) (Figure 6) is reflected simultaneously by (1) a decrease of the Am(IV) absorption band and (2) an increase in the Am(III) absorption band at 506 nm.

The following observations are plotted in Figure 7: (curve 1) optical density values of the oxidized species in solution, Am(IV), as a function of titrant volume; (curve 2) optical density values of Am(III) as a function of $Fe(CN)_6^{4-}$ solution volume.

Curve 1 serves to determine the concentration of oxidized americium. Since curves 1 and 2 have the same equivalent point, it may be concluded that the initial oxidized species was Am(IV) and that each addition of $Fe(CN)_6^{4-}$ produced an equimolar quantity of Am(III).

However, as may be seen from Figure 6, after the addition of hydrazine, while the solution investigated essentially contained Am(IV) and Am(III), it nevertheless contained a small quantity of Am(V). In Figure 5, the equilibrium potential values measured at each determination step are plotted as a function of log Am(IV)/Am(III). The application of Nernst's law for the experiment in Figure 6 serves to determine, for the medium concerned ([HCO_3^-] = 1.15 M, [CO_3^{2-}] = 0.85 M at pH 10), the apparent normal potential of 0.680 V vs. SCE (*R* correlation 0.995). The slope of the line representing *E* (mV) = log (Am(IV)/Am(III)) is found equal to 51.7.

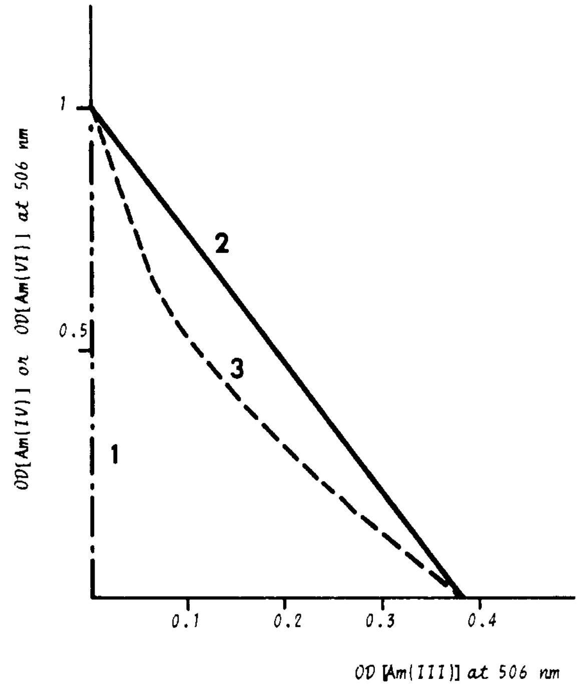

Figure 8. Reduction of oxidized species of americium with ferrocyanide: (1) Am(VI) → Am(V); (2) Am(IV) → Am(III); (3) Am(VI) + Am(IV) → Am(V) + Am(III).

In short, the reduction by ferrocyanide of americium with oxidation state IV or VI or their mixture only involves a single electron and produces Am(III) and Am(V), respectively. The curve representing the variation in optical density of the oxidized forms of americium as a function of peak height at 506 nm that is characteristic of Am(III), is portrayed in Figure 8. The reducing action of ferrocyanide can be summarized by the following: (1) if the oxidized species is Am(VI) (curve 1), the plot of OD(Am(VI)) = *f*[OD(Am(III))] is a line parallel to the *y* axis; (2) if the solution only contains Am(IV), the curve OD(Am(IV)) = *f*[OD(Am(III))] (curve 2) is a line with a slope approaching 0.38, the ratio of the molar extinction coefficients of Am(III) and Am(IV) at 506 nm; (3) for a mixture containing both species Am(IV) and Am(VI), the curve OD(Am(IV) + Am(VI)) = *f*[OD(Am(III))] exhibits a concavity facing the *x* axis (curve 3).

4. Variation in Apparent Normal Potentials as a Function of Carbonate Concentration. The formal potentials of the couples Am(VI)/Am(V) and Am(IV)/Am(III) were determined for different $NaHCO_3$–$NaCO_3$ mixtures, of which the sum of the HCO_3^- and CO_3^{2-} ion concentrations was kept constant around 2 M, with use of the procedures described above.

The experimental values are shown in Figure 9, with the potential measured in mV with reference to the saturated calomel electrode (SCE) on the ordinate and the logarithm of the carbonate concentration on the abscissa. An examination of the experimental results shows the following.

(1) The apparent normal potential of the couple Am(VI)/Am(V) is practically independent of the CO_3^{2-} concentration: $E°'$(Am(VI)/Am(V)) = 0.720 ± 0.01 V vs. SCE; $\partial E/\partial \log [CO_3^{2-}] \approx 0$.

(2) The apparent normal potential of the couple Am(IV)/Am(III) decreases in a monotonic manner when [CO_3^{2-}]

Table II. Determination of the Equilibrium Constant *K* for the Reaction Am(VI) + Am(III) $\leftrightarrows$ Am(IV) + Am(V)

vol proportion mixture Am(VI)/Am(III), mL/mL	$10^4 \times$ $[\mathrm{Am(VI)}]_0$, M	$10^4 \times$ $[\mathrm{Am(III)}]_0$, M	$10^4 \times$ [Am(III)], M	$10^4\Delta$, M	$10^4 \times$ $\{[\mathrm{Am(VI)}]_0 - \Delta\}$, M	*K*
1/1	3.100	3.100	0.672	2.427	0.673	13.0
1.2/1	3.381	2.818	0.511	2.307	1.074	9.7
1.2/1.5	2.755	3.444	1.086	2.357	0.397	12.8
1.2/1.6	2.657	3.542	1.278	2.264	0.392	10.2
1.2/1.8	2.480	3.720	1.534	2.186	0.294	10.6

$K = 11.2 \pm 1.5$

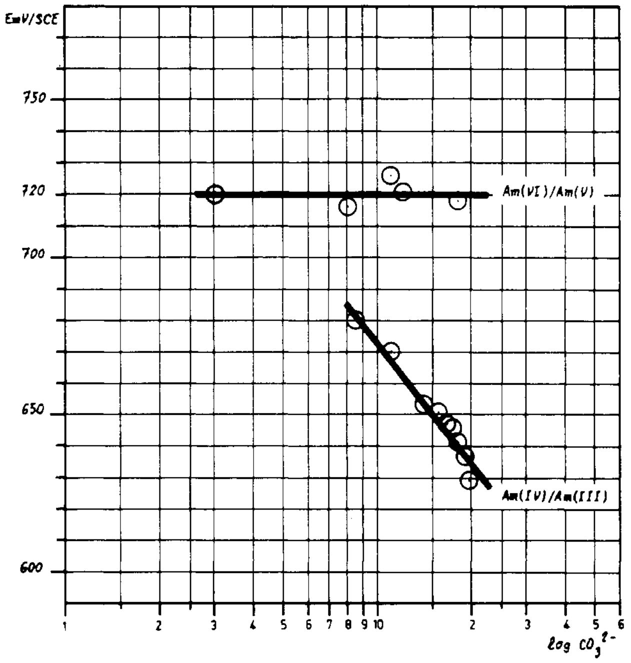

Figure 9. Variation of normal apparent potentials of the Am(VI)/Am(V) and Am(IV)/Am(III) couples vs. carbonate concentration.

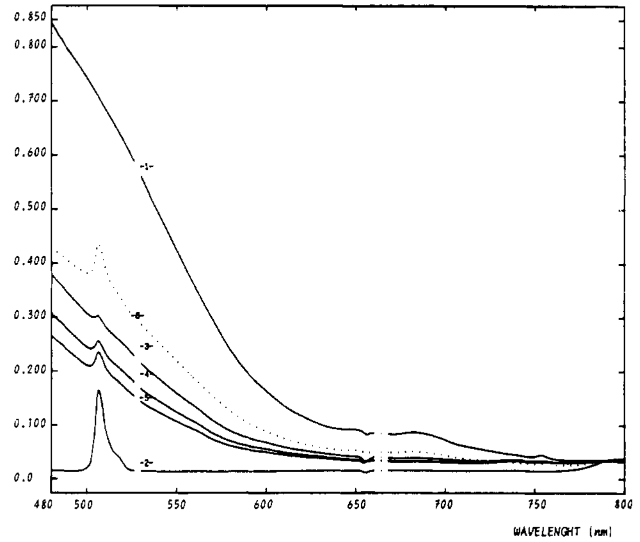

Figure 10. Study of the reaction Am(VI) + Am(III) $\rightleftarrows$ Am(IV) + Am(V): (1) pure Am(VI); (2) pure Am(III); (3) 1 mL of Am(VI) + 1 mL of Am(III); (4) 1.2 mL of Am(VI) + 1.5 mL of Am(III); (5) 1.2 mL of Am(VI) + 1.8 mL of Am(III); (6) theoretical Am(VI) + Am(III).

increases from 0.85 to 2 M, by 127 mV/unit of log $[\mathrm{CO_3}^{2-}]$: $E^{\circ\prime}(\mathrm{Am(IV)/Am(III)}) = 0.672 \pm 0.01$ V vs. SCE at $[\mathrm{CO_3}^{2-}] = 1$ M; $\partial E/\partial \log [\mathrm{CO_3}^{2-}] = 127$ mV with $R = 0.90$ (correlation coefficient).

This value postulates two carbonate molecules for the exchange when going from the carbonate form of Am(III) to that of Am(IV). But it is not possible to distinguish ligand effects from either carbonate or hydroxyl due to the pH variations.

The foregoing results agree with the work of Simakin:[11] (1) invariance of the potential of the couple Am(VI)/Am(V) as a function of sodium carbonate concentration and (2) monotonic decrease in the potential of the couple Pu(IV)/Pu(III) with carbonate concentration.

Furthermore, the value found for the potential of the couple $E^{\circ\prime}(\mathrm{Am(IV)/Am(III)}) = 0.887 \pm 0.01$ V vs. NHE for $[\mathrm{CO_3}^{2-}] = 2$ M is in good agreement with the value estimated by Fedoseev et al.[16] (0.890 V vs. NHE).

5. Coexistence of the Am(III), Am(IV), Am(V), and Am(VI) Species in Sodium Bicarbonate–Carbonate Medium. The deviation observed between the normal potentials of Am(VI)/Am(V) and Am(IV)/Am(III)

$$\Delta E = E(\mathrm{Am(VI)/Am(V)}) - E(\mathrm{Am(IV)/Am(III)}) > 0$$

for example, 60 mV for $[\mathrm{CO_3}^{2-}] = 1$ M, allows us to predict that the mixture of the two pure species Am(VI) and Am(III) will yield to the equilibrium reaction

$$\mathrm{Am(VI)} + \mathrm{Am(III)} \rightleftarrows \mathrm{Am(IV)} + \mathrm{Am(V)} \qquad (1)$$

This reaction expressed by the law of mass action is written

$$K = \frac{[\mathrm{Am(IV)}][(\mathrm{Am(V)}]}{[\mathrm{Am(III)}][(\mathrm{Am(VI)}]} \qquad (2)$$

where *K* represents the equilibrium constant and the values in brackets the concentrations of the species at equilibrium. By substituting in eq 2 the values of the ratios Am(IV)/Am(III) and Am(V)/Am(VI) determined from Nernst's law, we obtain

$$K = 10\ \exp\left\{\frac{E^{\circ\prime}(\mathrm{Am(VI)/Am(V)}) - E^{\circ\prime}(\mathrm{Am(IV)/Am(III)})}{0.058}\right\}$$

The experiment confirming this hypothesis is shown in Figure 10. Equimolar solutions (6.2×10^{-4} M) of Am(VI) and Am(III) are mixed in different proportions, and the absorption spectra of the mixed solutions are analyzed at 506 nm to measure the height of the characterized peak of Am(III).

The concentration of Am(III) at equilibrium is thus calculated for each mixture. This leads to the concentration of Am(III) that has reacted, and this is followed step by step by the concentration of each species at equilibrium.

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(16) A. M. Fedoseev, V. F. Peretruklin and N. W. Krot, *Dokl. Phys. Chem. (Engl. Transl.)*, **244** (1979).

Hence for the initial concentrations $[\mathrm{Am(III)}]_0$ and $[\mathrm{Am(VI)}]_0$ in the mixtures, the equilibrium concentrations of americium species may be calculated:

$$[\mathrm{Am(IV)}] = [\mathrm{Am(V)}] = [\mathrm{Am(III)}]_0 - [\mathrm{Am(III)}] = \Delta$$
$$[\mathrm{Am(VI)}] = [\mathrm{Am(VI)}]_0 - [\mathrm{Am(IV)}] = [\mathrm{Am(VI)}]_0 - \Delta$$

This serves to express K in the form

$$K = \frac{\Delta^2}{[\mathrm{Am(III)}]\{[\mathrm{Am(VI)}]_0 - \Delta\}}$$

The values of K for the different mixtures investigated is given in Table II. The mean constant obtained, $K = 11.20 \pm 1.5$, is consistent with the results summarized in Figure 9, and the anticipated value of K for a potential difference of 60 mV is equal to 10.

Conclusions

The possible coexistence of americium in four oxidation states in sodium bicarbonate–carbonate medium 1.2 M < $[\mathrm{HCO_3^-} + \mathrm{CO_3^{2-}}]$ < 2.3 M in the pH range from 9.5 to 10.5 is a particularly remarkable occurrence. Hitherto this property was only known for plutonium in dilute acidic medium.[17]

The difficulty of obtaining pure americium(IV) in carbonate media with the pH above 11 is not explained by the nearness of the apparent normal potentials of the two couples Am(IV)/Am(III) and Am(VI)/Am(V) but by the tendency of Am(IV) to disproportionate, experimentally observed at pH >11.5.

In fact, according to the measurements summarized in Figure 9, the difference between the potentials of the two systems increases with $\mathrm{CO_3^{2-}}$ concentration, i.e. with the pH. Contrary to what could be concluded from this reading alone, the stability of Am(VI) is greater in media with higher pH than that of Am(IV). This positively implies the involvement of a data element supplementary to that of the redox potentials of the couples investigated: the variation in potential of the couple Am(IV)/Am(V), whose dependence on pH is foreseeable, because it is related to the possibility of ionic Am(V) in the americyl form. The study of this important reaction, which has simply been touched on here, is a subject for investigation in its own right.

Registry No. Americium, 7440-35-9; disodium carbonate, 497-19-8; sodium bicarbonate, 144-55-8.

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(17) J. M. Cleveland, "Plutonium Handbook", O. J. Wick, Ed., 1961, Chapter 13.

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Coordination of Copper(II) in Aqueous $\mathrm{CuSO_4}$ Solution

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An aqueous copper(II) sulfate solution has been examined by X-ray diffraction. The existence of a distorted arrangement of six water molecules around $\mathrm{Cu^{2+}}$ ions has been established by distribution curve inspection and direct fitting of the structure function. The structural parameters of the aquocopper(II) ion have also been determined.

Introduction

It is well-known that the d^9 electronic configuration is expected to be subjected to Jahn–Teller distortions; Cu(II) is the species for which the greatest number of distorted coordinations have been found in solid crystalline compounds. Different kinds of distortions have also been identified in $\mathrm{CuL_6}$ complexes; they can be partly ascribed to crystal-packing requirements. In the liquid phase and in solution these constraints fail, and it is therefore interesting to investigate the variety of geometries observed under these conditions.

A good example of tetragonally distorted sixfold coordination has recently been given in an X-ray diffraction study of $\mathrm{Cu(ClO_4)_2}$ aqueous solutions.[1] Four water molecules, w_{eq} (equatorial position), lie in a square-planar configuration at a distance of 1.97–1.98 Å from the central ion, and two others, w_{ax} (axial position), are placed above and below the plane at 2.34–2.39 Å.

In $\mathrm{CuCl_2}$ solutions[2] the same technique has successfully described the occupancy of equatorial sites according to the mean configuration $\mathrm{Cu(H_2O)_{2.8}Cl_{1.2}}$, although the axial positions were not unambiguously determined. This result suggests that some solvent effect may exist so that more weakly bonded ligands may prefer the stabilization due to the solvent rather than occupy the axial sites.

Difficulties in describing unequivocally the environment of Cu(II) in $\mathrm{CuCl_2}$ solutions have been confirmed by Neilson[3] in a neutron diffraction investigation carried out with the isotopic substitution technique. The existence of two different coordination distances for Cu(II)–water pairs was not evident in a neutron diffraction study[4] of copper(II) perchlorate solutions.

In order to have more data on the coordination of aqueous Cu(II), we examined by X-ray diffraction a solution of $\mathrm{CuSO_4}$. Because of the solubility limit of this salt, just one solution has been investigated, with a concentration (1.37 mol/L at 20 ± 1 °C) smaller that that used in the study[1] of $\mathrm{Cu(ClO_4)_2}$ samples.

Experimental Details, Data Treatment, and Results

The saturated solutions was prepared by dissolving crystalline $\mathrm{CuSO_4{\cdot}5H_2O}$ in doubly distilled water at 20 ± 1 °C. The copper content was determined by direct titration with standard EDTA and after cation exchange on a cationic resin (Dowex 50W-X8). The molarity turned out to be 1.375 M, and the density was 1.207 g/mL, so that the stoichiometric coefficient x in the unit $(\mathrm{CuSO_4})_x(\mathrm{H_2O})_{1-x}$ had the value 0.0245.

The ϑ–ϑ X-ray diffractometer and the procedure of data collection and reduction have been previously described.[5,6]

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(5) G. Licheri, G. Piccaluga, and G. Pinna, *J. Chem. Phys.*, **64**, 2437 (1976).

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