

## Redox chemistry of americium in nitric acid media

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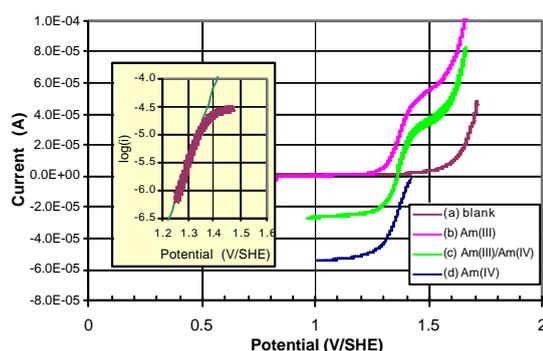
**Abstract**– The redox properties of the actinides are very important parameters for speciation studies and spent nuclear fuel reprocessing based on liquid-liquid extraction of actinides at different oxidation states (as in the PUREX or SESAME process [1]). They are also very useful for developing analytical tools including coulometry and redox titration [2–4]. This study addressed the americium(IV)/americium(III) and americium(VI)/americium(V) redox couples, focusing on exhaustive acquisition of the thermodynamic and kinetic parameters of americium oxidation at an electrode in a complexing nitric acid medium [5–8].

### INTRODUCTION

Data acquisition was undertaken on the thermodynamic and kinetic parameters of americium redox couples in aqueous media as part of the development work for the SESAME (SElective Separation of AMericium by Electrochemical means) process. The Am(IV)/Am(III) and Am(VI)/Am(V) redox couples were studied by voltammetry in an aqueous nitric acid medium with a complexing agent. The thermodynamic potentials and electron transfer rate constants were measured. The results were used to simulate experimental anodic conversion of americium(III) to americium(IV).

### Am(IV)/Am(III) REDOX COUPLE

The study was carried out in 0.1 mol/L nitric acid at room temperature ( $295 \text{ K} \pm 2 \text{ K}$ ). A ligand was used to stabilize americium at oxidation state (IV), as free



**Figure 1.** Current versus potential curves for a 1.1 mmol/L americium solution in 0.1 mol/L nitric acid with 40 mmol/L SiW: (b) reduced solution; (c) semi-oxidized solution; (d) fully oxidized solution. Rotating Pt disk electrode: surface area  $0.196 \text{ cm}^2$ , rotation speed 1000 rpm. Scan rate 10 mV/s.  $T = 295 \text{ K}$  (Inset: Tafel plot for the anodic part).

Am(IV) is unstable in aqueous solutions. Monovacant  $\text{K}_8\text{-}\alpha\text{-SiW}_{11}\text{O}_{39}$  (SiW) was selected as the complexant because it forms strong complexes with Am(IV) in acidic aqueous media (a complex with 1:2 stoichiometry with excess ligand) [9]. Americium was added to solution in its stable oxidation state (III) with 40-fold excess ligand with respect to americium. The latter can be partially or fully oxidized by controlled potential coulometry. The complexed metal cation was characterized electrochemically by voltammetry on a stationary or rotating platinum electrode.

### Thermodynamic data acquisition

*Number of electrons transferred:  $n$*

The number of electrons transferred estimated from the coulometry balance or by analysis of the current logarithmic transform (rotating electrode experiment) was  $0.95 \pm 0.07$ ;  $n$  was thus considered equal to 1.

*Standard conditional potential:  $E^{\circ'}$*

The standard conditional potential of the Am(IV)/Am(III) couple in aqueous 0.1 mol/L nitric acid and 0.04 mol/L SiW was estimated by three different methods:

- measurement of the equilibrium potential of the semi-oxidized solution (55.7% Am(III) and 44.3% Am(IV) based on visible spectrum analysis) and application of the Nernst equation;
- measurement of the half-wave potential on a rotating electrode during reduction of the fully oxidized solution;
- estimation of the half-wave potential of the convoluted current obtained on a stationary electrode for the fully oxidized solution.

The mean value of the three results gives:

$$E^{\circ'} = 1.360 \text{ V/SHE} \pm 0.005$$

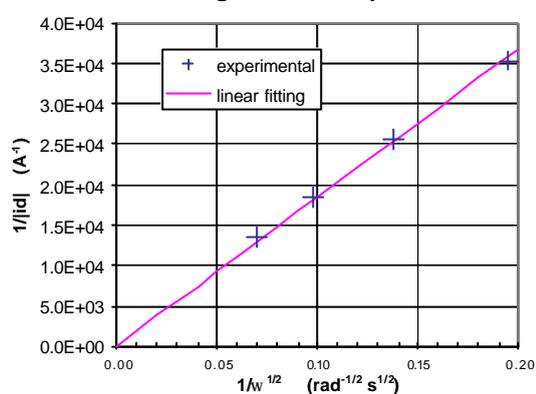
This is still a highly oxidizing potential, although the shift of about 1 V due to the effect of complexation

considerably lowers the potential of the Am(IV)/Am(III) couple ( $E^\circ = 2.34$  V [10]).

### Kinetic data acquisition

#### Mass transfer characterization

Mass transfer of the electroactive species is considered purely diffusional in the presence of an electrolyte (nitric acid medium). Complexed americium transport near the electrode can thus be described if its diffusion coefficient is known. It is measured from the current/potential curves obtained from a rotating electrode at different rotation speeds in a reduced or oxidized solution using the Levich equation.



**Figure 2.** Levich curve for reduction of 1.1 mmol/L americium(IV) solution in 0.1 mol/L nitric acid with 40 mmol/L SiW at 295 K. Rotating Pt disk electrode: surface area 0.196 cm<sup>2</sup>, scan rate 10 mV/s, T = 295 K.

The diffusion coefficients of complexed Am(III) and Am(IV) are identical in 0.1 mol/L nitric acid:

$$D = (0.28 \pm 0.02) \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$$

This is close to the value obtained for the Ce(IV)- $\alpha$  2-P<sub>2</sub>W<sub>17</sub>O<sub>61</sub> complex [11] and is characteristic of the polyoxometalates [12]. It is low compared with the diffusion coefficients of cerium(III) or ferrocyanide ions ( $0.62$  and  $0.90 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ , respectively [13]) as the complex is very large: the ionic radius of the ligand is about 0.5 nm [12].

#### Electron transfer characterization

The electron transfer kinetics are characterized in terms of transition state theory by two parameters: the standard rate constant  $ks$ , which expresses the ease of electron transfer, and the transfer coefficient  $\alpha$ , representing the symmetry of the energy barrier.

The transfer coefficient was measured from Tafel curves and application of the Butler-Volmer relation (linearizing the log current versus potential curve for small positive and negative overpotentials). It was estimated at:

$$\alpha = 0.39 \pm 0.06$$

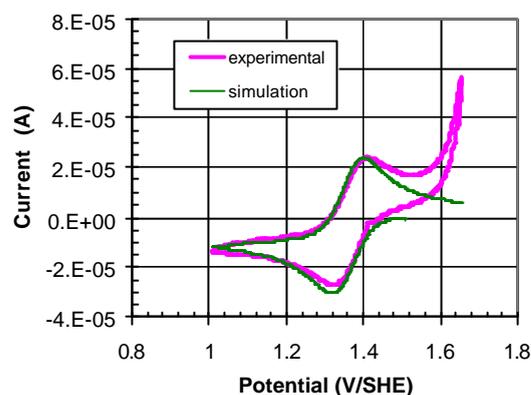
The electron transfer rate constant  $ks$  was measured by numeric simulation of cyclic voltammetry determinations of the americium(IV) solution [14]. The system was considered to be quasi-reversible for the sweep rates applied (25 to 200 mV·s<sup>-1</sup>).

Plotting the normalized kinetic constant  $ks_{norm}$ , as expressed below, versus the reciprocal of the sweep rate  $V$  provides an estimate of  $ks$ :

$$ks_{norm} = \frac{ks}{(Da)^{1/2}} \quad \text{avec} \quad a = \frac{nFV}{RT}$$

$$ks = (6 \pm 2) \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$$

This value can be compared with the standard rate constants of cerium(IV)/cerium(III) (slow transfer) or ferricyanide/ferrocyanide (fast transfer) on a platinum electrode in aqueous solution at 293 K ( $2 \times 10^{-4}$  and  $0.12 \text{ cm} \cdot \text{s}^{-1}$ , respectively [13]).



**Figure 3.** Cyclic voltammetry of a 1.1 mmol/L americium(IV) solution in 0.1 mol/L nitric acid with 40 mmol/L SiW at 295 K. Scan rate: 100 mV/s, stationary Pt disk electrode (surface area 0.196 cm<sup>2</sup>).

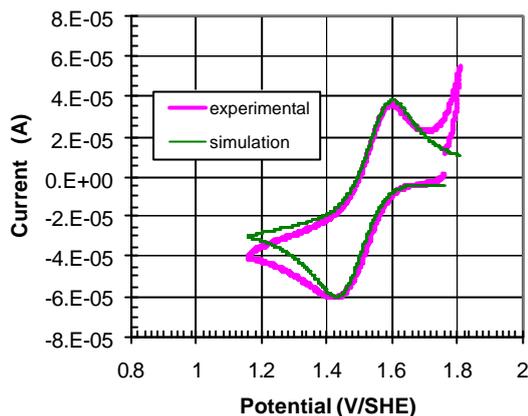
The result is characteristic of a quasi-reversible system for which the reaction corresponds to a slow charge transfer but for which the reverse reaction cannot be disregarded. The characteristics of this reaction are indicated in **Table I**.

**Table I.** Thermodynamic and kinetic parameters for Am(IV)/Am(III) redox couple in 0.1 mol/L nitric acid with 40 mmol/L SiW at 295 K

$\frac{\text{Am(IV)}}{\text{Am(III)}}$	$E^\circ$ mV/SHE	$D_{\text{Am(IV)}}$ cm <sup>2</sup> ·s <sup>-1</sup>	$D_{\text{Am(III)}}$ cm <sup>2</sup> ·s <sup>-1</sup>	$\alpha$	$ks$ cm·s <sup>-1</sup>
Value	1360	0.28	0.28	0.39	0.006
Uncertainty	5	0.02	0.02	0.06	0.002

## Am(VI)/Am(V) REDOX COUPLE

The Am(VI)/Am(V) couple was studied in an electrogenerated americium(VI) solution in 5 mol/L nitric acid in the presence of a phosphotungstate ligand  $K_{10}\alpha_2-P_2W_{17}O_{61}$  (PW) and silver nitrate (redox mediator) [15]. **Figure 4** shows a cyclic voltammometry plot obtained in reduction for this Am(VI) solution.



**Figure 4.** Cyclic voltammometry of a 3.67 mmol/L americium(VI) solution in 5 mol/L nitric acid with 1 mmol/L PW and 5 mmol/L  $AgNO_3$  at 295 K. Scan rate: 25 mV/s; stationary Pt disk electrode (surface area 0.196  $cm^2$ )

The thermodynamic and kinetic parameter values of the redox process can be obtained from the numeric simulation of this response versus the sweep rate (**Table II**).

**Table II.** Thermodynamic and kinetic parameters for Am(IV)/Am(III) redox pair in 0.1 mol/L nitric acid with 40 mmol/L SiW at 295 K

Am(VI) Am(V)	$E^{\circ'}$ mV/SHE	$D_{Am(VI)}$ $10^{-5} cm^2 \cdot s^{-1}$	$\alpha$	$ks$ $cm \cdot s^{-1}$
Value	1520	0.44	0.45	0.6
Uncertainty	20	0.05	0.05	0.2

The results confirm that americium(V) oxidizes at a high potential: 1.52 V/SHE, compared with 1.6 V/SHE in 1 mol/L  $HClO_4$  [16]. It is more difficult to oxidize than americium(IV) complexed by monovacant silicotungstate (1.52 V/SHE vs. 1.36 V/SHE). The oxidation kinetics of the Am(VI)/Am(V) couple on platinum are quasi-reversible, but slower than for the Am(IV)/Am(III) couple (the electron transfer constant is only one-tenth as high).

The presence of silver(II) oxidant in solution (standard potential 1.98 V/SHE [17]) thus guarantees the stability of americium(VI) in concentrated nitric acid.

## SIMULATION OF Am(IV) ELECTROGENERATION

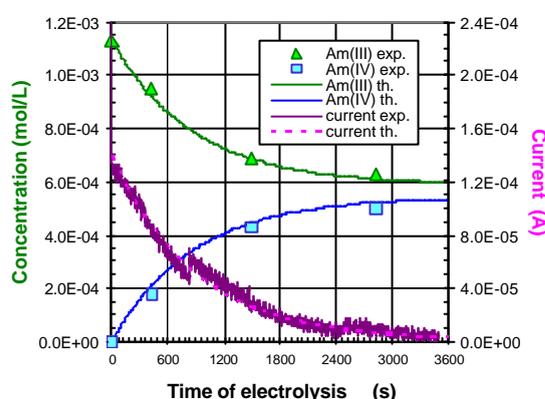
Having determined the thermodynamic and kinetic parameters of the redox reaction for the Am(IV)/Am(III) couple, it became possible to simulate the electrolysis kinetics of complexed americium(III). In the event of controlled-potential oxidation of a complexed Am(III) solution, the reaction is considered quasi-reversible and the current is expressed as follows [14]:

$$i = nFAks \frac{C_{Am(III)}b^{1-\alpha} - C_{Am(IV)}b^{-\alpha}}{1 + \frac{ks}{k_d}b^{1-\alpha} + \frac{ks}{k_d}b^{-\alpha}}$$

$$\text{where } k_d = \frac{D}{\delta}, \quad b = \exp\left(\frac{nF}{RT}(E-E^{\circ'})\right),$$

$\delta$  is the thickness of the steady-state diffusion boundary layer and the mass transfer coefficient  $k_d$  is assumed approximately equal to  $0.0015 cm \cdot s^{-1}$ .

**Figure 5** shows the simulated Am(III) and Am(IV) concentration variations and current variations during semi-quantitative electrolysis. The model provides a satisfactory fit between the theoretical curves and experimental values.



**Figure 5.** Kinetics of the anodic conversion of Am(III) into Am(IV): semi-quantitative electrolysis, simulation of the evolution of Am ion concentrations and current; 2  $cm^2$  platinum plate electrode; fixed potential of 1.358 V/SHE; volume 2.34 mL, T = 295 K.

## CONCLUSION

The thermodynamic and kinetic redox parameter values of the Am(IV)/Am(III) and Am(VI)/Am(V) couples necessary to understand americium oxidation at an electrode were determined. The findings are applicable not only for process studies to simulate the anodic conversion kinetics of Am(III) to Am(IV) or

Am(VI), but also for analytical work to develop coulometric determination methods for americium.

The next step in this research program will be to understand the mechanisms involved in the Am(IV)–Am(V) oxidation reaction, and in particular to investigate the coupled chemical reactions by which the aquo(IV) species is converted to actinyl(V).

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