Electrochemical Oxidation of Am(III) Ions in HNO₃ Solutions


Research Institute of Nuclear Reactors, State Scientific Center of the Russian Federation, Dimitrovgrad, Russia

Received July 20, 2000; in final form, November 28, 2000

Abstract—Formal oxidation potentials ($E^\circ_0$) of the Am(IV)/Am(III) couple were measured and the kinetics of electrochemical oxidation of Am(III) on platinum electrode in concentrated solutions of nitric acid (1–6 M) containing potassium phosphotungstate $K_{10}P_2W_{17}O_{61}$ (KPW) was studied. The formal potential $E^\circ_0$ only slightly depends on the concentration of HNO₃ and is shifted toward the negative region by $\approx 1.0$ V as compared with the standard values. The extent of Am(III) oxidation increases with increasing KPW concentration and decreasing concentration of nitric acid. Electrochemical oxidation of Am(III) is accompanied by radiochemical reduction of Am(IV) and is described by the equation $-\mathrm{d}C_\text{Am(III)}/\mathrm{d}t = (k + k_1)C_\text{Am(III)} - k_1C_0 - k_0$, where $k$ is the apparent rate constant of electrochemical oxidation of Am(III), $k_1$ is the apparent rate constant of Am(IV) reduction, and $k_0$ is the constant of radiation-chemical reduction of Am(IV).

Amercium(IV) in nitric acid solutions (pH 4.0–5.0) was first prepared by oxidation of Am(III) with potassium peroxydisulfate using salts of unsaturated phosphotungstic acids (KPW) [1]. Electrochemical oxidation of Am(III) to Am(IV) in these solutions was studied in [2, 3].

At present, utilization of potassium phosphotungstate (KPW) for stabilization of Am(IV) in concentrated solutions of mineral acids (1–8 M) is of particular importance [4–9]. It was found that fairly strong complexes $\text{M(PW)}_2$ with the stability constants varying within $10^5$–$10^{14}$ depending on the actinide nature are formed in nitric acid solutions at HNO₃ concentration >1 M and the KPW:Am ratio >2. Under these conditions the thermodynamic stability of Am(IV) ions increases.

This phenomenon is promising for the development of new processes for recovery and purification of actinides, regeneration of fission materials, and treatment of radioactive wastes. In particular, Donnet et al. [10] developed a procedure for processing radioactive wastes based on selective recovery of americium electrochemically oxidized on platinum electrode in concentrated nitric acid solutions containing KPW (SESAME process).

In this work we measured the formal oxidation potentials of the Am(IV)/Am(III) couple ($E^\circ_0$) and studied the kinetics of electrochemical oxidation of Am(III) on a platinum electrode in concentrated solutions of nitric acid in the presence of potassium phosphotungstate $K_{10}P_2W_{17}O_{61}$ (KPW).

EXPERIMENTAL

In our work we used a monoisotopic sample of $^{241}$Am and a sample of $^{243}$Am containing 0.6 wt % $^{241}$Am. At first, these preparations were treated to remove neighboring actinides and nonradioactive impurities by extraction-chromatographic procedures using DEHP [11] and TOPO [12].

The formal potentials $E^\circ_0$ of the Am(IV)/Am(III) couple were measured by the potentiometric procedure; the concentrations of Am(III) and Am(IV) were monitored spectrophotometrically. The electrochemical oxidation was performed on a smooth platinum electrode at 1.9 V with respect to NHE, which is 250–300 mV higher than $E^\circ_0$ in 0.1 M HNO₃ [3], using an electrochemical cell described previously in [13]. The absorption spectra were registered on a Beckman DU-640 spectrophotometer. Potassium phosphotungstate $K_{10}P_2W_{17}O_{61}$ was prepared by the procedure given elsewhere [14].

RESULTS AND DISCUSSION

The experimental formal potentials $E^\circ_0$ of the Am(IV)/Am(III) couple and the extent of Am(III) oxidation $\alpha$ as influenced by the concentrations of HNO₃ and KPW are listed in the table.

As seen, the observed shift of $E^\circ_0$ even in concentrated nitric acid solutions toward the negative range comprises nearly 1.0 V with respect to the standard potential calculated for the Am(IV)/Am(III) couple in aqueous solution (2.44 V). This decrease in $E^\circ_0$
suggests higher stability of the Am(IV)–KPW complexes as compared with the Am(III) complexes. Variations in the HNO₃ concentration do not noticeably affect the oxidation potential, whereas with increasing KPW concentration $E_0^p$ slightly decreases. Thus, our experimental results show that in the system studied it is possible to obtain fairly stable Am(IV) ion.

Moreover, at concentration of nitric acid up to 3 M at $C_{\text{KPW}}/C_{\text{Am(III)}} \geq 6$ Am(III) is oxidized almost quantitatively. With increasing concentration of nitric acid the extent of oxidation decreases, and in 5.7 M HNO₃ at 15-fold excess of KWP it reaches nearly 80% in 5.7 M HNO₃ and dose rates increasing KPW concentration, and it reaches nearly 80% in 5.7 M HNO₃ at 15-fold excess of KWP with respect to americium concentration.

The curves of electrochemical oxidation of Am(III) as influenced by nitric acid concentration are shown in Fig. 1. The mathematical treatment of the kinetic curves showed that at HNO₃ concentration <4 M they can be transformed into straight lines in the log $C_{\text{Am(III)}}$–time coordinates. This suggests that the rate of electrochemical oxidation of Am(III) under these conditions can be described by the following expression:

$$\frac{dC_{\text{Am(III)}}}{dt} = kC_{\text{Am(III)}}^r$$

where $k$ is the apparent rate constant of electrochemical oxidation of Am(III).

With increasing concentration of nitric acid to 5.7 M the shape of the kinetic curves of Am(III) oxidation changes (Fig. 1, curve 4). In the latter case the process attains the equilibrium; it cannot be described by Eq. (1). Under these conditions oxidation of Am(III) is probably accompanied by reduction of Am(IV).

To confirm this assumption, we studied the reduction of Am(IV) at various concentrations of KPW and HNO₃ and dose rates $J$. The KPW : Am ratio in these tests was $\geq 6$. The spectrophotometric data showed that in all cases Am(IV) is reduced to Am(III). For example, the kinetic curves of reduction of Am(IV) as influenced by the concentration of HNO₃ are shown in Fig. 2. The kinetic curves registered under the other experimental conditions are similar. The mathematical treatment of the kinetic curves showed that they can be transformed into the straight lines in the $\Delta C_{\text{Am(IV)}}/\Delta t$–$C_{\text{Am(IV)}}$ coordinates, and the equation of the rate of Am(IV) reduction can be given as follows:

$$-\frac{dC_{\text{Am(IV)}}}{dt} = k_0 + k_1C_{\text{Am(IV)}}$$

Oxidation potentials $E_0^p$ of Am(IV)/Am(III), extent of oxidation $\alpha$, and the rate constant of Am(III) $\rightarrow$ Am(IV) $+ \varepsilon$ oxidation ($k$) at various concentrations of HNO₃ and KPW: $C_0 = 0.92 \times 10^{-3}$ M. $S/V^* = 1.87$ cm² ml⁻¹. $T = 298$ K.

<table>
<thead>
<tr>
<th>$C_{\text{HNO}_3}$ M</th>
<th>$C_{\text{KPW}} \times 10^3$ M</th>
<th>$E_0^p$, V</th>
<th>$\alpha$, %</th>
<th>$k \times 10^4$, s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>5.5</td>
<td>1.54</td>
<td>100</td>
<td>33</td>
</tr>
<tr>
<td>1.9</td>
<td>5.5</td>
<td>1.56</td>
<td>100</td>
<td>14</td>
</tr>
<tr>
<td>2.9</td>
<td>5.5</td>
<td>1.55</td>
<td>98</td>
<td>7.9</td>
</tr>
<tr>
<td>3.9</td>
<td>5.5</td>
<td>1.57</td>
<td>94</td>
<td>6.3</td>
</tr>
<tr>
<td>5.7</td>
<td>5.5</td>
<td>1.54</td>
<td>34</td>
<td>5.2</td>
</tr>
<tr>
<td>5.7</td>
<td>7.9</td>
<td>1.44</td>
<td>78</td>
<td>4.7</td>
</tr>
<tr>
<td>5.7</td>
<td>10.6</td>
<td>1.45</td>
<td>85</td>
<td>4.4</td>
</tr>
<tr>
<td>5.7</td>
<td>13.6</td>
<td>1.42</td>
<td>81</td>
<td>4.0</td>
</tr>
</tbody>
</table>