The composition and stability of complex ions of tri- and tetravalent plutonium in oxalate solutions were investigated polarographically.

The complexes Pu(C₂O₄)₁⁻⁴ (preponderant amount) and Pu(C₂O₄)₄⁻⁵ were formed in solutions of potassium oxalate with pH 3.5-6. Under these conditions, Pu⁺⁴ gave a well expressed reverse reaction wave, suitable for the quantitative polarographic determination of plutonium. The oxidation-reduction potential of this reaction in 1 M potassium oxalate was equal to 0.205 V (relative to a saturated calomel electrode at a temperature of 25°C). Two Pu⁺⁴ complexes were simultaneously present in solutions at pH 6-8.

From data on the solubility of Pu(C₂O₄)₂, we determined the instability constants of the complex oxalate ions Pu(C₂O₄)⁻₃ and Pu(C₂O₄)₄⁻, and from the polarographic data those for Pu(C₂O₄)₂⁻⁴ ions:

$$K_{Pu(C_2O_4)_{2-3}} = 2.4 \times 10^{-12}, \quad K_{Pu(C_2O_4)_{4-5}} = 2.2 \times 10^{-11}, \quad K_{Pu(C_2O_4)_{2-4}} = 3.3 \times 10^{-38}.$$ 

The reports on the existence of oxalate complexes of trivalent plutonium are contradictory [1]. By spectrophotometry and solubility determination, W. Reas [2] established the existence of the Pu⁺⁴ ions PuC₂O₄⁺, Pu(C₂O₄)₂⁺, Pu(C₂O₄)₃⁻ and found the corresponding stability constants; he also showed the existence of Pu(C₂O₄)₄⁺ ions. There are references [1] to unpublished polarographic investigations of oxalate complexes of Pu⁺⁴, but the results are not given.

The authors of this article investigated polarographically the complex ion formation of tri- and tetravalent plutonium with oxalate ion at concentrations of the latter from 10⁻³ to 1.2 M. The work was carried out on a V-301 polarograph, which automatically recorded the curves of current strength against voltage. A dropping mercury electrode acted as the cathode; the anode was a saturated calomel electrode (sce). 0.01% of gelatin was added to the solution to suppress the maxima. The experiments were carried out at 25 ± 0.1°C. Purified argon was passed for 20 minutes through the solution in the electrolyzer to remove dissolved oxygen. The argon was freed from oxygen by passing through a tube containing copper filings heated to 700°C, two bottles with a solution of divalent chromium, a bottle with water and an empty flask to trap splash. The polarogram of the background (potassium oxalate), after the passage of argon, contained no waves up to the liberation of hydrogen. The correction for the resistance of the system (electrolyzer, intermediate bridge, calomel electrode and leads) was found, as usual, by determining the value of the half-wave potential under the same conditions, but with a different plutonium concentration in the solution, using a ratio of 1: 16.

Potassium oxalate was used as the complex forming salt as its solubility is considerably greater than that of the sodium or ammonium salts; this made it possible to investigate the complex plutonium oxalates over a wider range of oxalate ion concentrations.

Solutions of potassium oxalate and oxalic acid were mixed together to investigate the effect of pH of the medium on complex formation. Before taking quantitative measurements, we proved the reversibility of the electrode reaction Pu⁺⁴ ↔ Pu⁺³ in an oxalic acid solution. In addition, we compared the half-wave potentials
for continuous recording of curves and for plotting separate points (the electrode was maintained for 3 minutes at each value of the applied emf for plotting the curves by points). Waves from the same solutions continuously recorded and plotted as separate points, did not differ greatly in half-wave potentials or in wave height. The half-wave potential obtained by plotting points was 0.004–0.005 v more negative than the half-wave potential from continuous recording, with a measurement error of ± 0.002 v. This, apparently, is explained by the fact that the equilibrium at the electrode surface is not established immediately between the oxidized and reduced forms of plutonium ions. The concentration of the oxalate ions was calculated by the equation

\[ \Sigma \text{C}_2\text{O}_4 = [\text{C}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4^-] + [\text{H}_3\text{C}_2\text{O}_4] \]  

(1)

where \( \Sigma \text{C}_2\text{O}_4 \) is the analytical oxalate concentration, using the known concentration of hydrogen ions and the ionization constant of oxalic acid (\( K_1 = 5.9 \times 10^{-2}; \ K_2 = 6.4 \times 10^{-5} \)) [3]. The relation of the ionization constant of oxalic acid and the constant of the complex ions to the ionic strength of the solution was not considered. The usual methods for the polarographic investigation of complex formation were used [4]-[7].

**Experimental Results and Discussion**

We first plotted polarograms of the solutions, containing tetravalent plutonium and oxalate ions at different concentrations and with various solution pHs. The values of the half-wave potentials and wave heights are given in Table 1 and one of the polarograms is shown in Figure 1.

**Table 1**

The Effect of Concentration of \( \text{C}_2\text{O}_4^- \) Ions and pH of the Medium on the Complex Formation of Pu \( ^{4+} \) and Pu \( ^{5+} \)

<table>
<thead>
<tr>
<th>Conc. ( \text{[C}_2\text{O}_4^-] ) g-equiv/liter</th>
<th>Wave height ( \mu )amp</th>
<th>Half-wave potential, v</th>
<th>pH of solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>1.60</td>
<td>-0.193</td>
<td>7.89</td>
</tr>
<tr>
<td>1.000</td>
<td>1.53</td>
<td>-0.192</td>
<td>7.04</td>
</tr>
<tr>
<td>0.997</td>
<td>1.94</td>
<td>-0.194</td>
<td>6.70</td>
</tr>
<tr>
<td>0.985</td>
<td>2.25</td>
<td>-0.193</td>
<td>6.03</td>
</tr>
<tr>
<td>0.918</td>
<td>2.29</td>
<td>-0.196</td>
<td>5.25</td>
</tr>
<tr>
<td>0.423</td>
<td>2.23</td>
<td>-0.195</td>
<td>4.08</td>
</tr>
<tr>
<td>0.098</td>
<td>2.26</td>
<td>-0.194</td>
<td>3.58</td>
</tr>
<tr>
<td>0.028</td>
<td>2.31</td>
<td>-0.178</td>
<td>2.97*</td>
</tr>
<tr>
<td>--</td>
<td>2.11</td>
<td>-0.144</td>
<td>2.25</td>
</tr>
</tbody>
</table>

-- The wave was displaced considerably towards positive potentials.

| Concentration of Pu \( ^{4+} \) -- 6.5 \( \times 10^{-8} \) M |

A considerable displacement of the half-wave potential towards more negative values in comparison with the oxidation-reduction potential of Pu \( ^{4+} \) and Pu \( ^{5+} \) in a noncomplex-forming medium [3] indicated the presence of stable plutonium complexes in the solution. It was established that only one clearly expressed wave appeared on the polarogram at solution pHs of 3.5–6. Regardless of the sharp change in the concentration of oxalate ions in this pH range, the half-wave potential remained the same (Table 1). This indicates that the coordination numbers of Pu \( ^{4+} \) and Pu \( ^{5+} \) are equal. Two waves appear at pH 7.69.

According to our hypothesis, two complexes exist in oxalic acid solutions at pH 6–8 and an equilibrium is slowly established between them, as with other elements [9]. The experiments carried out showed that at a pH close to

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*Precipitation of oxalic acid was observed in the last samples.