CHAPTER 6

POLAROGRAPHIC BEHAVIOUR OF URANIUM(VI)-IODATE SYSTEM
As a result of the rapidly expanding nuclear energy effort, the literature concerning uranium chemistry has increased by orders of magnitude in the last two decades. In general, the composition of uranium bearing samples is complex. The co-ordination number of uranium is 8. The uranyl entity may be considered as having six unfilled co-ordination positions, one each being used for the two uranyl oxygens. A degree of uniqueness can be ascribed to the uranyl group itself which is present in all aqueous solutions as uranium(VI) species. The position of the uranyl ion in ion exchange displacement series indicates that this species is of normal size.

Uranium(VI) is the only stable state in solutions containing air. Pentavalent uranium disproportionates in solution to uranium(IV) and (VI). The solutions of uranium(V) are most stable in the pH range of 2 - 4 with a disproportionation half-life of at least two hours at room temperature in the absence of complicating factors\(^1\).

**Polarographic behaviour of uranium**

Herasymenko\(^2\) was the first to carry out a polarographic study of uranium. He observed that in neutral or weakly acid medium uranyl ion undergoes stepwise
reduction to produce a polarogram comprising three waves. He attributed these waves to the successive reduction of $^6$ to $^5$, to $^4$ and to $^3$ states. He also demonstrated that the polarogram of a uranyl solution which had been photochemically reduced to the $^4$ state shows only the third wave. Later, Harris and Kolthoff$^3$ verified the Herasymenko's interpretations.

In moderately acid solutions (0.01 to 0.02 M HCl) uranium exhibits two waves. The first wave corresponds to a one electron reduction of uranium(VI) to uranium(V). The second wave which is twice the first wave corresponds to a two electron reduction of U(V) to U(III). The double wave was found to be acid independent. The studies made with $^4$ uranium under the same experimental conditions and the value of $i_d/C m^{2/3} t^{1/6}$ provide a conclusive proof that the first wave is due to the reduction of $^6$ to the $^5$ state. On the other hand, in strongly acid medium the first uranyl wave increases with increasing acidity. This observation is explained in terms of the increasing instability of $^5$ uranium with respect to disproportionation into $\text{UO}^{++}$ and $\text{UO}_2^{++}$. However, the total height of the doublet wave remains constant. As the rate constant of the disproportionation of $^5$ uranium increases with increasing uranyl concentration the limiting current of the first wave in solutions of high acidity is not
proportional to the uranyl ion concentration. Carruthers\textsuperscript{4} developed a micro method for the determination of small quantities of sodium based on precipitation as sodium zinc uranyl acetate and later measuring the uranyl diffusion current. Harris and Kolthoff recommended the first uranyl wave in 0.1 M potassium chloride, 0.01 M HCl and $2 \times 10^{-4}\%$ thymol for the determination of uranium. The interference of iron could be avoided using hydroxylamine hydrochloride.

The fact that the reduction of either uranyl ion or uranous ion catalyses the reduction of nitrate ion was utilised by Harris and Kolthoff for the determination of traces of uranium. Kern and Orlemann\textsuperscript{5} prepared solutions of +5 uranium in sodium perchlorate and perchloric acid solutions by controlled potential reduction of uranyl ion at $-0.55\, V$ vs SCE at a mercury cathode. According to them, a mixture of +5 and +6 uranium produces a reversible anodic-cathodic wave. The well defined anodic diffusion current of +5 uranium was utilised to study the kinetics of its disproportionation into UO$_2^{++}$ and UO$_4^{++}$.

The polarography of +5 uranium has also been studied by Kraus, Nelson and Johnson\textsuperscript{6} whose results confirm the reversibility of the +6 to +5 couple at the dropping electrode. These authors also confirmed that the optimum stability of
+5 uranium is in the pH range 2 - 4. Kritchevsky and Hindjman reported an excellent study of the polarography of uranium. In addition to supplying the confirmation of the reversibility of $\text{UO}_2^{++} + e \rightleftharpoons \text{UO}_2^+$ couple, they demonstrated that $\text{U(IV)} = \text{U(III)}$ couple also behaves reversibly. In a very weakly acid medium containing +4 uranium, Kritchevsky and Hindman observed an incompletely developed anodic wave at -0.19 V vs SCE which probably results from the oxidation of $\text{UOH}^{+++}$ to $\text{UO}_2^+$. In an unbuffered very weakly acid medium (pH 2.7 - 3.2) Harris and Kolthoff noticed that the second reduction wave of uranyl ion divides into two waves. At pH values between about 3.3 and 4.0 the third wave is no longer observed and the height of the remaining second wave is the same as that of the first wave. In neutral solutions two waves are obtained, but the second at -0.6 V vs SCE. Harris and Kolthoff attributed these phenomena to the hydrolysis of the uranyl ion. Strubl observed that +6 uranium in an ammonium carbonate supporting electrolyte undergoes stepwise reduction to produce a doublet wave which he ascribed to reduction of the uranyl carbonate complex to the +4 and +2 complexes. However, Harris and Kolthoff showed conclusively from the magnitudes of the
diffusion current that the doublet wave corresponds to successive one electron reductions to the +5 and +4 states rather than to the +4 and +2 states. In 0.1 M sodium carbonate +6 uranium produces only a single reduction wave which is well formed but the limiting current is not proportional to the uranium concentration.

From the above discussion it may be concluded that uranium(VI) undergoes reduction in as many as four steps depending upon the experimental conditions such as pH, concentration of the acid, anions, etc. In moderately acid solutions, however, the metal ion produces only two waves corresponding to the reduction to pentavalent and tetravalent uranium species.

**Catalysing properties of uranium:**

Very few instances are reported in literature on uranium catalysed reduction of oxidants. Harris, Kolthoff and Matsuyama\(^\text{10}\) reported that either the uranyl or uranous uranium catalyses the reduction of nitrate at the dropping mercury electrode. Nitrate was determined by them polarographically in the presence of small amounts of uranium. However, use was made of this catalytic effect of uranium to determine the metal ion in the concentration range 2 x 10\(^{-7}\) M to 3 x 10\(^{-5}\) M.
According to Sinyakova and Karanovich\textsuperscript{11} the uranyl ion which is reduced at the electrode into $U^{3+}$ causes a catalytic current in nitrate solutions.

Grabowski and Grabowska\textsuperscript{12} reported a catalytic wave of oxalic acid in presence of uranyl ion. This wave appearing at a potential of $-1.3$ V vs SCE at low concentrations of oxalic acid increases linearly with the acid concentration. The wave corresponds to a transfer of two electrons. A complex in which two molecules of oxalic acid are bound on a uranium ion takes part in the electrode reaction. On the basis of the linear relationship between the height of the catalytic wave and the oxalic acid concentration, a method for the determination of calcium\textsuperscript{13} was reported.

\textbf{PRESENT INVESTIGATIONS}

\textbf{Experimental}

Uranyl acetate solution (0.001 M) prepared in conductivity water is used in these studies. To different aliquots of uranyl solution taken in a 25 ml standard flask, 3 ml of iodate solution (0.1 M) and conductivity water are added so that the total volume of the contents is always constant. The contents of the flask are made upto the mark with the acetate buffer of required pH. The solution
is shaken thoroughly to make it homogeneous and transferred to the polarographic cell. Pure hydrogen gas is bubbled through the experimental solution to remove dissolved oxygen and the polarogram recorded.

Results

Typical polarograms of uranium(VI) solution (A), iodate solution (B) and uranium(VI) - iodate mixture (C), recorded in an acetate - acetic acid buffer solution of pH 5.0 are presented in Fig. III.6.1. An analysis of the figure reveals that uranium(VI) does not produce any reduction wave under the experimental conditions. On the other hand, iodate exhibited a well defined cathodic reduction wave at about -0.6 V vs SCE. However, a mixture of uranium(VI) and iodate exhibited two well defined reduction waves. The first wave has a defined plateau and has the characteristics of the simple iodate wave. Further, the second wave consists of a very sharp peak at about -1.28 V vs SCE. In view of the difference in the polarographic behaviour of uranium(VI) and uranium(VI) - iodate mixture, further studies are made on the effect of pH so as to establish the optimum conditions for the appearance of this type of polarographic wave. The data relating to the effect of pH on the characteristics of the wave is shown in Table III.6.1. An examination of the data
Fig. III.6.1s Typical polarograms of

(A) Uranium alone;
(B) Iodate alone and
(C) Uranium + Iodate mixture

\[ [\text{U(VI)}] = 8 \times 10^{-5} \text{M} \]
\[ [\text{IO}_3^-] = 12 \times 10^{-3} \text{M} \]
\[ \text{pH} = 5.0 \]

Starting voltages: A & B = 0 V vs SCE.
C = -0.3 V vs SCE.
### TABLE III.6.1

Effect of pH on the polarographic behaviour of uranium-iodate system

<table>
<thead>
<tr>
<th>pH</th>
<th>Half-wave potential/Peak potential (mV vs SCE)</th>
<th>Wave height/Peak current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uranium alone</td>
<td>Iodate alone</td>
</tr>
<tr>
<td>3</td>
<td>No wave</td>
<td>An ill-defined wave</td>
</tr>
<tr>
<td>4</td>
<td>No wave</td>
<td>0.60</td>
</tr>
<tr>
<td>5</td>
<td>No wave</td>
<td>0.60</td>
</tr>
<tr>
<td>6</td>
<td>No wave</td>
<td>0.66</td>
</tr>
<tr>
<td>7</td>
<td>No wave</td>
<td>0.75</td>
</tr>
</tbody>
</table>

\[ [\text{U(VI)}] = 8 \times 10^{-5} \text{M}, [\text{I}O_3^-] = 12 \times 10^{-3} \text{M} \]
in Table III.6.1 suggests that this type of behaviour is noticed in a very narrow range of pH 5 - 6. Further the wave noticed at pH 5 has an appreciable size and a defined nature. Therefore, studies on the effect of uranium concentration, iodate concentration, mercury column height, presence of organic co-solvents, sodium chloride, surfactants, acetate concentration and buffer capacity on the characteristics of the wave are investigated and the results are presented in Tables III.6.2 to III.6.9 and figures III.6.2 and III.6.3.

**TABLE III.6.2**

Effect of the mercury column height on the peak current

\[
\begin{align*}
[U(VI)] &= 8 \times 10^{-5} \text{M} \\
[IO_3^-] &= 12 \times 10^{-3} \text{M} \\
pH &= 5.0
\end{align*}
\]

<table>
<thead>
<tr>
<th>Mercury column height (cms)</th>
<th>Peak current (μA)</th>
<th>Peak potential (-V vs SCE.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>27.5</td>
<td>1.30</td>
</tr>
<tr>
<td>70</td>
<td>27.5</td>
<td>1.30</td>
</tr>
<tr>
<td>60</td>
<td>27.5</td>
<td>1.30</td>
</tr>
<tr>
<td>50</td>
<td>27.5</td>
<td>1.30</td>
</tr>
<tr>
<td>40</td>
<td>27.5</td>
<td>1.30</td>
</tr>
</tbody>
</table>
**TABLE III.6.3**

Effect of methanol on the peak current

\[
[U(VI)] = 4 \times 10^{-5} \text{M} \\
[I_{03}^-] = 12 \times 10^{-3} \text{M} \\
\text{pH} = 5.0
\]

<table>
<thead>
<tr>
<th>Percentage of methanol</th>
<th>Peak current ((\mu\text{A}))</th>
<th>Peak potential (-V vs SCE.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>23</td>
<td>1.28</td>
</tr>
<tr>
<td>10</td>
<td>29</td>
<td>1.28</td>
</tr>
<tr>
<td>20</td>
<td>32</td>
<td>1.30</td>
</tr>
<tr>
<td>30</td>
<td>33</td>
<td>1.32</td>
</tr>
<tr>
<td>40</td>
<td>34</td>
<td>1.32</td>
</tr>
</tbody>
</table>

**TABLE III.6.4**

Effect of acetonitrile on the peak current

\[
[U(VI)] = 4 \times 10^{-5} \text{M} \\
[I_{03}^-] = 8 \times 10^{-3} \text{M} \\
\text{pH} = 5.0
\]

<table>
<thead>
<tr>
<th>Percentage of acetonitrile</th>
<th>Peak current ((\mu\text{A}))</th>
<th>Peak potential (-V vs SCE.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>3.5</td>
<td>1.28</td>
</tr>
<tr>
<td>10</td>
<td>9.0</td>
<td>1.30</td>
</tr>
<tr>
<td>20</td>
<td>23.0</td>
<td>1.30</td>
</tr>
<tr>
<td>30</td>
<td>40.0</td>
<td>1.31</td>
</tr>
<tr>
<td>40</td>
<td>43.0</td>
<td>1.32</td>
</tr>
</tbody>
</table>
### TABLE III.6.5
Effect of dimethylformamide on the peak current

\[
\begin{align*}
[U(VI)] &= 4 \times 10^{-5} M \\
[IO_3^-] &= 12 \times 10^{-3} M \\
pH &= 5.0
\end{align*}
\]

<table>
<thead>
<tr>
<th>Percentage of dimethylformamide</th>
<th>Peak current (µA)</th>
<th>Peak potential (V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>23</td>
<td>1.28</td>
</tr>
<tr>
<td>10</td>
<td>38</td>
<td>1.40</td>
</tr>
<tr>
<td>20</td>
<td>46</td>
<td>1.50</td>
</tr>
<tr>
<td>30</td>
<td>47</td>
<td>1.56</td>
</tr>
</tbody>
</table>

### TABLE III.6.6
Effect of gelatin on the peak current

\[
\begin{align*}
[U(VI)] &= 4 \times 10^{-5} M \\
[IO_3^-] &= 12 \times 10^{-3} M \\
pH &= 5.0
\end{align*}
\]

<table>
<thead>
<tr>
<th>Percentage of gelatin x 10^3 M</th>
<th>Peak current (µA)</th>
<th>Peak potential (V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>23</td>
<td>1.28</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>1.30</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>1.32</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>1.34</td>
</tr>
</tbody>
</table>
### TABLE III.6.7

Effect of sodium chloride on the peak current

\[
\begin{align*}
[U(VI)] &= 4 \times 10^{-5} \text{M} \\
[IO_3^-] &= 12 \times 10^{-3} \text{M} \\
pH &= 5.0
\end{align*}
\]

<table>
<thead>
<tr>
<th>Concentration of sodium chloride ($\times 10^2 \text{M}$)</th>
<th>Peak current ($\mu\text{A}$)</th>
<th>Peak potential ($\text{V vs SCE}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>23.0</td>
<td>1.28</td>
</tr>
<tr>
<td>4</td>
<td>23.0</td>
<td>1.27</td>
</tr>
<tr>
<td>10</td>
<td>25.0</td>
<td>1.26</td>
</tr>
<tr>
<td>20</td>
<td>29.0</td>
<td>1.26</td>
</tr>
<tr>
<td>30</td>
<td>30.5</td>
<td>1.24</td>
</tr>
<tr>
<td>40</td>
<td>32.0</td>
<td>1.20</td>
</tr>
</tbody>
</table>

### TABLE III.6.8

Effect of acetate on the peak current

\[
\begin{align*}
[U(VI)] &= 4 \times 10^{-5} \text{M} \\
[IO_3^-] &= 12 \times 10^{-3} \text{M} \\
pH &= 5.0
\end{align*}
\]

<table>
<thead>
<tr>
<th>Concentration of acetate (M)</th>
<th>Peak current ($\mu\text{A}$)</th>
<th>Peak potential ($\text{V vs SCE}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>35</td>
<td>1.35</td>
</tr>
<tr>
<td>0.2</td>
<td>23</td>
<td>1.28</td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### TABLE III.6.9

Effect of buffer strength on the peak current

\[
\begin{align*}
\text{[U(VI)]} & = 4 \times 10^{-5} \text{M} \\
\text{[IO}_3^-\text{]} & = 12 \times 10^{-3} \text{M} \\
\text{pH} & = 5.0
\end{align*}
\]

<table>
<thead>
<tr>
<th>Concentration of buffer (M)</th>
<th>Peak current (μA)</th>
<th>Peak potential (-V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>30</td>
<td>1.30</td>
</tr>
<tr>
<td>0.2</td>
<td>23</td>
<td>1.28</td>
</tr>
<tr>
<td>0.3</td>
<td>12</td>
<td>1.28</td>
</tr>
<tr>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. III.6.2: Dependence of peak current on the concentration of uranium.

\[ [IO_3^-] = 12 \times 10^{-3} \text{M} \]

\[ \text{pH} = 5.0 \]
Fig. III.6.3: Dependence of peak current on the concentration of iodate.

\[ [U(VI)] = 4 \times 10^{-5} \text{M} \]

\[ \text{pH} = 5.0 \]
Discussion

As mentioned earlier, uranium does not produce any polarographic wave under these experimental conditions. It is reported (loc. cit.) in literature that in moderately acid solutions uranium exhibits two waves of equal height corresponding to the reduction of (VI) to (V) and (V) to (IV) states respectively. But in the present instance such a behaviour is not noticed in view of the fact that very dilute solutions of uranium are employed in these investigations. Further, iodate exhibited a reduction wave at about -0.6 V vs SCE. This observation is in agreement with that made by Kolthoff and Orlemann in their investigations on the polarographic reduction of iodate in buffered solutions.

An examination of the data presented in Table III.6.1 reveals that the new wave with a peak is noticed in solutions of pH 5 onwards. However, in solutions of pH 6 and 7, the wave has no defined shape and the currents are also low.

The graph (Fig. III.6.2) showing the dependence of uranium(VI) concentration on the peak current is linear in the range 4 - 20 x 10^{-5} M of the metal ion. A similar relationship is noticed between iodate concentration and the peak current in the range 8 - 14 x 10^{-3} M of the
oxidant (Fig. III.6.3). However, either uranium(VI) or iodate did not show any effect on the peak potential.

Results pertaining to the effect of mercury column show that it has no effect on the peak current (Table III.6.2). This observation suggests that the wave has a kinetic nature.

The polarogram recorded comparatively for a higher concentration of uranium (1 x 10^{-3} M) under the same experimental conditions showed two distinct waves of same height at -0.4 V and -1.2 V vs SCE. Logarithmic analysis of the two waves revealed that each corresponds to a one electron reduction. The two waves, therefore, may be ascribed to the reduction of U(VI) to U(V) and U(V) to U(IV) respectively.

Based on the position of the kinetic wave on the potential axis noticed with uranium(VI) - iodate system and the literature available on similar systems, the following arguments are made to explain the phenomenon.

As discussed in a preceding chapter iodate is reduced in a 6 electron reduction process to result in iodide. Iodide further participates in a reaction with iodate to produce iodine and then iodine cation. Further it is stated that^{15} monovalent iodine complexes with highly
polarisable acid anions such as CN\(^-\), CNO\(^-\), CNS\(^-\) and so on. It is probable that iodine cation is also capable of forming complex with acetate. The pK\(_a\) values\(^{16}\) of hydrogen cyanide, cyanic acid and thiocyanic acid are 9.21, 3.46 and 0.85 respectively. The pK\(_a\) value of acetic acid (4.76) is comparable with those of the other compounds in the series. In view of these facts, it is assumed that I\(^+\) forms a complex of the type [I(CH\(_3\)COO)] similar to [I(CN)], [I(CNO)] and [I(CNS)]. It is probable that the following reactions occur involving [I(CH\(_3\)COO)].

\[
\begin{align*}
U(\text{VI}) + e & \rightleftharpoons U(\text{V}) \text{ (first wave at -0.40 V vs SCE)} \\
U(\text{V}) + e & \rightleftharpoons U(\text{IV}) \text{ (second wave at -1.2 V vs SCE)} \\
U(\text{IV}) + X & \rightarrow U(\text{V}) + \text{Reduction products of } X \quad \text{... Chemical reaction}
\end{align*}
\]

\(X = \) Iodate or a reduction product of iodate such as [I(CH\(_3\)COO)]

The species represented as 'X' is reduced through a fast chemical reaction by U(IV) and is responsible for large currents.
Presence of organic co-solvents is known to influence the kinetic waves to a remarkable extent. Therefore, the effect of methanol, acetonitrile and dimethylformamide is investigated on the catalytic currents. From the data presented in Tables III.6.3, 6.4 and 6.5, it may be concluded that dimethylformamide and acetonitrile caused enhancements in the catalytic currents. Methanol, however, did not show such enhancement. These experimental observations may be attributed to the increased rates of chemical reaction in presence of these solvents. The shift in peak potential with increasing proportions of methanol or dimethylformamide is attributed to the probable unfacile reduction of the species responsible for the catalytic wave.

Addition of gelatin even in small quantities resulted in a distorted shape of the catalytic wave (Table III.6.6). This observation suggests that the wave may be having a surface character.

Surface catalytic waves are influenced to a marked extent when salts like sodium chloride are added to the system. The results relating to the effect of sodium chloride concentration (Table III.6.7) reveal that the peak current increased slightly with increasing salt concentration. This experimental fact confirms the assumption that the wave has a surface character. The
sudden drop in the reduction current with increase of potential resulting in a sharp maximum is attributed to the desorption of the depolariser at high negative potentials.

The results pertaining to the effect of acetate on the peak current (Table III.6.8) show that the latter decreased and finally disappeared as the concentration of acetate is increased. Uranium(VI) is reported\textsuperscript{17} to complex with acetate when the latter is present in excess concentrations. In view of this, it appears that U(VI) is not present as simple UO\textsubscript{2}\textsuperscript{2+} but as an acetate complex in presence of excess acetate. This may be the reason for the disappearance of the catalytic wave at high concentrations of acetate.

Similar observation is made when the concentration of the buffer is increased (Table III.6.9). The same reasoning holds good in the present case also because there is regular increase in the concentration of acetate with buffer strength. However, the decrease in peak currents is not that rapid as is noticed in the case of acetate effect.

Studies in presence of hydroxy acids

Hydroxy carboxylic acids, as reported by Chikryzova et al.\textsuperscript{18} influence polarographic catalytic waves to a marked extent. Therefore effect of salicylic, tartaric, lactic
and maleic acids on the catalytic waves is investigated and the results are presented in Fig. III.6.4. It is noticed from the figure that the peaks completely disappeared in presence of any of these acids. However, waves of small currents are noticed in place of the peaks. Babko et al.\textsuperscript{19} reported that uranium(VI) forms complexes with salicylic and tartaric acids. Therefore U(VI) is not freely available to produce U(V) which in turn is responsible for the catalytic cycle. The low currents noticed in presence of any of these acids may be attributed to the small concentrations of uncomplexed uranium species, available under these experimental conditions.

**Studies in presence of organic chelating agents**

Rao and Rao\textsuperscript{20} reported that oximes and other derivatives of carbonyl compounds which has the ability of complexation with metal ions remarkably influence catalytic waves. Therefore effect of salicylaldoxime, furfural isonicotinoyl hydrazone and EDTA is investigated and the polarograms are shown in Fig. III.6.5. An analysis of the figure suggests that the peak disappeared in presence of any of the chelating agents and waves of low currents are noticed. The same arguments presented under the effect of
Fig. III.6.4: Effect of hydroxy-carboxylic acids on the peak current.

(A) Uranium + iodate

(B) A + Maleic acid; [Maleic acid] = 8 x 10^{-3} M

(C) A + Lactic acid; [Lactic acid] = 20 x 10^{-3} M

(D) A + Tartaric acid; [Tartaric acid] = 8 x 10^{-3} M

(E) A + Salicylic acid; [Salicylic acid] = 5 x 10^{-3} M

Starting voltage = -0.9 V vs SCE.
Fig. III.6.5: Effect of chelating agents on the peak current.

(A) Uranium + iodate; $[\text{U(VI)}] = 4 \times 10^{-5} \text{M}$
$[\text{IO}_3^-] = 12 \times 10^{-3} \text{M}$

(B) A + SAO $[\text{SAO}] = 2 \times 10^{-3} \text{M}$

(C) A + FINH $[\text{FINH}] = 1 \times 10^{-3} \text{M}$

(D) A + EDTA $[\text{EDTA}] = 4 \times 10^{-3} \text{M}$

Starting voltage: $-0.9 \text{ V vs SCE.}$
hydroxy acids hold good even in this case because uranium(VI) is known to complex with oximes and other related compounds\textsuperscript{21}.

In view of the discussions presented above it may be concluded that the presence of simple U(VI) as $\text{UO}_2^{2+}$ is a requisite for the appearance of the catalytic wave.

The catalytic wave has significance in terms of analytical point of view. The peak current varies linearly with uranium(VI) and iodate concentrations in the ranges $4 - 20 \times 10^{-5} \text{M}$ and $8 - 14 \times 10^{-3} \text{M}$ respectively. The details of the experimental procedures and interference of foreign ions for the possible determination of uranium are worked out and the details are presented hereunder.

**Recommended procedure**

1 - 5 ml of uranium(VI) of $1 \times 10^{-3} \text{M}$ concentration, 3 ml of iodate of $0.1 \text{ M}$ concentration and a required volume of distilled water are taken in a 25 ml volumetric flask so that the total volume is always constant. The solution is made up to the mark with a $0.2 \text{ M}$ acetate - acetic acid buffer of pH 5.0. The contents of the flask are transferred to the polarographic cell after thorough shaking. Hydrogen gas is passed for about 15 minutes to remove dissolved oxygen. The polarogram is recorded. The value of standard
deviation calculated for the catalytic peak is $\pm 0.04$ at $4 \times 10^{-5}$ M concentration of uranium.

**Interference studies**

It was found that Cl$^-$, Br$^-$, I$^-$, SO$_4^{2-}$, CO$_3^{2-}$, Zn(II), Cd(II), Cu(II), Cr(III), ferricyanide interfere when their respective concentrations exceed 100-fold concentration of uranium. Mo(VI), V(V), EDTA, thiocyanate, tartrate and oxalate seriously interfere in the determination. W(VI), Ni(II), Co(II), Pt(IV), Fe$^{3+}$, Fe$^{2+}$ and Mn$^{2+}$ do not interfere up to a 10-fold excess.

The present method can be employed for the determination of uranium in the range 238-1190 µg.
REFERENCES


