CHAPTER 4

POLAROGRAPHIC STUDIES ON TUNGSTEN
Tungsten exhibits variable oxidation states, the +6 state and its various reduced species are of analytical interest. Electrochemical measurements of tungsten containing solutions are complicated by the presence of isopoly tungstates and complex ion formation with other ions present in the system. Polarographic behaviour of W(VI) is complicated because the waves are affected by competing isopoly, heteropoly and complexation reactions\textsuperscript{1-3}. Frequently kinetic waves are observed instead of diffusion controlled waves for tungsten in presence of reducible ions. A brief review of the polarographic behaviour of tungsten is presented hereunder.

Polarographic behaviour of tungsten:

A single reduction wave is observed for tungsten(VI) in concentrated hydrochloric acid\textsuperscript{4}. Tungsten(VI) does not produce the reduction wave in neutral and alkaline solutions. A stepwise reduction to +5 and the red +3 states is observed in 12 M hydrochloric acid. Bouchay\textsuperscript{5} investigated the polarographic behaviour of iso and heteropoly acids of tungsten. No polarographic waves are observed for tungsten in ammonia or strongly basic solutions\textsuperscript{6}. Tungsten exhibits a single wave in solutions containing both hydrochloric and oxalic acids. Whereas two waves appear if either
Citric or tartaric acid is used with hydrochloric acid\textsuperscript{7,8}. The hydrochloric acid - tartaric acid solutions are used for determining tungsten in steels\textsuperscript{9} and rocks\textsuperscript{10}.

Catalysing properties of tungsten:

Tungsten catalysed polarographic reduction of hydrogen peroxide was investigated by Koltzoff and Parry\textsuperscript{11}. This is attributed by them to the reduction of peroxy-tungstate species. Laitinen and Zeilger\textsuperscript{12} observed that the diffusion current of perchlorate increased several times in presence of tungsten(VI). Tungsten(VI) causes an appreciable increase in the reduction currents of chlorate. The tungsten(VI) catalysed reduction of iodate was studied by Murthy\textsuperscript{13}. 
Experimental

Sodium tungstate solution (1 x 10^{-4} M) prepared in distilled water is used in the studies. To different aliquots of tungstate solution taken in a 25 ml standard flask, 3 ml of chlorate solution (0.8 M) and distilled water are added so that the total volume of the contents is always constant. The contents of the flask are made up to the mark with acetate buffer of pH 4. The solution is thoroughly shaken and transferred into the polarographic cell. Pure nitrogen gas is bubbled through experimental solution to remove dissolved oxygen and the polarogram is recorded.

Results and Discussion:

Typical polarograms of tungsten(VI) solution (a), chlorate solution (b) and tungsten(VI)—chlorate mixture (c) recorded in acetate - acetic acid buffer solution of pH 4 are presented in Fig. III.4.1. An examination of polarograms reveals that neither tungsten nor chlorate produce any cathodic reduction wave under the present experimental conditions. On the other hand a mixture consisting of tungsten(VI) and chlorate produced a wave with large peak currents at -1.5 V vs SCE. In view of the large peak
Fig. III.4.1 - Typical polarograms of

(a) Tungsten(VI) alone
(b) Chlorate alone
(c) Tungsten(VI) + Chlorate mixture

\[
\begin{align*}
[W(VI)] &= 1 \times 10^{-5} \text{ M} \\
[Clo_3^-] &= 9.6 \times 10^{-3} \text{ M} \\
pH &= 4.0
\end{align*}
\]

Starting voltage - a & b = 0 V vs SCE
\[E = -0.8 \text{ vs SCE}\]
Currents observed the effect of pH on the peak current is studied (Table III.4.1). The results indicate that the wave has a well-defined shape and large currents in solutions of pH 4. Therefore, the effect of various other parameters is investigated only in pH 4.

The peak current is sensitive to the concentration of both tungsten as well as chlorate. A linear relationship is noticed for tungsten and chlorate in the range $1 \times 10^{-6}$ M for W(VI), 3.2 to $12.8 \times 10^{-3}$ M for ClO$_3$ (Fig. III.4.2, 3). This suggests that tungsten(VI) can be determined in the microgram range. However, neither tungsten(VI) nor chlorate showed any remarkable influence on the peak potential.

The effect of the height of the mercury column on the magnitude of the peak current is studied and the results are presented in the table (Table III.4.2). The results indicate that the change in the mercury column height has no influence on the peak currents, and the wave possesses kinetic nature.

It is known that the change in the double layer structure exhibits a pronounced influence on surface catalytic waves. Hence, the effect of sodium chloride on the characteristics of the kinetic wave is studied.
Fig. III.4.2 - Effect of the concentration of tungsten on the peak current

\[ [\text{ClO}_3^-] = 9.6 \times 10^{-3} \text{ M} \]

\[ \text{pH} = 4.0 \]
Fig. III.4.3 - Effect of the concentration of chlorate on the peak current

\[ \text{[W(VI)]} = 1 \times 10^{-5} \text{ M} \]

pH = 4.0
TABLE III.4.1

Effect of pH on the peak current

\[ [W(\text{VI})] = 1 \times 10^{-5} \text{M} \]
\[ [\text{ClO}_3^-] = 9.6 \times 10^{-3} \text{ M} \]

<table>
<thead>
<tr>
<th>pH</th>
<th>Peak height (cm)</th>
<th>Peak potential (V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>No wave</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>3.4</td>
<td>1.45</td>
</tr>
<tr>
<td>4</td>
<td>5.2</td>
<td>1.47</td>
</tr>
<tr>
<td>5</td>
<td>3.1</td>
<td>1.48</td>
</tr>
<tr>
<td>6</td>
<td>No wave</td>
<td>-</td>
</tr>
</tbody>
</table>
### TABLE III.4.2

**Mercury column effect on the peak current**

- $[\text{W(VI)}] = 1 \times 10^{-5} \text{ M}$
- $[\text{ClO}_3^-] = 9.6 \times 10^{-3} \text{ M}$

<table>
<thead>
<tr>
<th>pH</th>
<th>4.0</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Height of mercury column (cm)</th>
<th>Peak height (cm)</th>
<th>Peak potential (V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>13.0</td>
<td>1.47</td>
</tr>
<tr>
<td>80</td>
<td>12.9</td>
<td>1.47</td>
</tr>
<tr>
<td>70</td>
<td>13.1</td>
<td>1.48</td>
</tr>
<tr>
<td>60</td>
<td>13.0</td>
<td>1.48</td>
</tr>
<tr>
<td>50</td>
<td>13.0</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Recorded at 2.5 times lower sensitivities.
The peak current decreased in the magnitude with increasing sodium chloride concentration and the peak is shifted towards positive potential. This suggests that the kinetic wave possesses a surface character. The sudden drop in the reduction current with increase of potential resulting in sharp maximum may be attributed to the desorption of the depolariser at high negative potentials.

Electrochemical investigations of tungsten(VI) solutions are complex owing to the presence of isopoly tungstates. Further it is known that tungsten(VI) exists as condensed species in solutions of pH below 7. The kinetic wave in the present investigations is noticed in solutions of pH 4. Therefore, it is assumed that the reduction of a condensed tungsten species at the d.m.e. and its reoxidation by a chemical reaction involving chlorate is responsible for the appearance of the kinetic wave. The author feels that more convincing explanation could not be offered in view of the inadequate information available.

Effect of methanol on the peak current:

Organic solvents generally known to influence the catalytic waves, by the change in the rate of the chemical reaction. Hence the effect of increasing proportions of
### TABLE III.4.3

**Effect of sodium chloride on the peak current**

- $[\text{W(VI)}] = 1 \times 10^{-5}$ M
- $[\text{ClO}_3^-] = 9.6 \times 10^{-3}$ M
- pH = 4.0

<table>
<thead>
<tr>
<th>$[\text{NaCl}]$ (M)</th>
<th>Peak height (cm)</th>
<th>Peak potential (-V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>13.0</td>
<td>1.47</td>
</tr>
<tr>
<td>0.01</td>
<td>11.9</td>
<td>1.47</td>
</tr>
<tr>
<td>0.02</td>
<td>10.4</td>
<td>1.47</td>
</tr>
<tr>
<td>0.03</td>
<td>7.7</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Recorded at 2.5 times lower sensitivities.
methanol on the peak current is investigated. The data presented in Table III.4.4 reveals that the magnitude of the catalytic wave decreased with increase in the methanol concentration. This may be attributed to the decrease in the rate of the chemical reaction, involving reduced tungsten species and chlorate.

Effect of complexing agent (SAO):

The organic complexing agents are known to influence the polarographic catalytic waves to a marked extent. Therefore the author has studied the effect of salicylaldoxime on the kinetic wave and the results are presented in the table (Table III.4.5). An examination of the data indicates that the peak current increased with the concentration of SAO. The increase in the current is attributed to the formation of surface active ternary complex involving species of tungsten, chlorate and the oxime. Similar observations are reported by Rao in his studies on molybdenum-bromate system.
### TABLE III.4.4

Effect of methanol on the peak current

- $[\text{W(VI)}] = 1 \times 10^{-3} \text{ M}$
- $[\text{ClO}_3^-] = 9.6 \times 10^{-3} \text{ M}$
- pH = 4.0

<table>
<thead>
<tr>
<th>[%] $[\text{CH}_3\text{OH}]$</th>
<th>Peak height (cm$^2$)</th>
<th>Peak potential ($\text{V vs SCE}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>13.0</td>
<td>1.47</td>
</tr>
<tr>
<td>2.5</td>
<td>10.9</td>
<td>1.50</td>
</tr>
<tr>
<td>5.0</td>
<td>8.7</td>
<td>1.53</td>
</tr>
<tr>
<td>7.5</td>
<td>7.3</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Recorded at 2.5 times lower sensitivities.
### Table III.4.5

Effect of salicylaldoxime on the peak current

| [W(VI)] | $1 \times 10^{-5}$ M |
| [ClO$_3^-$] | $9.6 \times 10^{-3}$ M |
| pH | 4.0 |

<table>
<thead>
<tr>
<th>[SAA] x $10^3$ M</th>
<th>Peak height (ems)</th>
<th>Peak potential (-V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>0.7</td>
<td>1.47</td>
</tr>
<tr>
<td>2</td>
<td>2.4</td>
<td>1.90</td>
</tr>
<tr>
<td>4</td>
<td>4.9</td>
<td>1.93</td>
</tr>
<tr>
<td>6</td>
<td>6.9</td>
<td>1.93</td>
</tr>
<tr>
<td>8</td>
<td>7.7</td>
<td>1.93</td>
</tr>
<tr>
<td>10</td>
<td>9.9</td>
<td>1.93</td>
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REFERENCES

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<th>Reference</th>
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