POLAROGRAPHIC STUDY OF IRON (III)—RESACETO-PHENONEOXIME COMPLEX

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ABSTRACT

The polarographic behaviour of Iron (III)—Resacetophenoneoxime complex at pH 5.8 in a supporting electrolyte of 0.1 M sodium perchlorate was studied. The results indicated a diffusion controlled irreversible reduction of the complex. The composition of the complex corresponded to the ratio metal to oxime as 1:1. The stability constant of the complex was $2.78 \times 10^{-5}$.

INTRODUCTION

NEELAKANTAM AND SITARAMAN\(^1\) reported that resacetophenoneoxime gave a purple color with Iron (III), the color intensity was maximum at pH 3.6–7.0 and the reaction was highly sensitive. This reaction was investigated spectrophotometrically by Raja Reddy \textit{et al.},\(^2\) at pH 7.0 in ammonium acetate medium. These authors reported the formation of a 1:1 complex. The present authors carried out a detailed study of the polarographic behaviour of Iron (III)—resacetophenoneoxime complex at pH 5.8. The results obtained are reported in the present paper.

EXPERIMENTAL

\textit{Reagents}

1. Ferric chloride solution was prepared from B.D.H. sample and the solution was standardised by a volumetric method. Concentration of the Iron (III) was $10^{-2}$ M.

2. Resacetophenoneoxime solution (0.1 M) was prepared by dissolving the pure, dry, recrystallised solid in Methanol (E. Merck).

3. Sodium perchlorate (1.0 M) solution was prepared from Reidel sample.

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4. Sodium acetate—acetic acid buffer solution (pH 5.8) was prepared from 1.0 M solutions of AnalaR Sodium acetate and acetic acid.

**Apparatus**

A photographic recording polarograph (L.P. 55) was used for recording polarogram. A pyrex cell with an internal mercury pool anode and dropping mercury cathode was employed in the investigations.

**Procedure**

1. **Polarogram of simple Iron (III).**—1.5 ml. of Iron (III) solution, 2 ml. of buffer solution, 1.0 ml. of sodium perchlorate and 1.0 ml. of pure methanol were pipetted out into the polarographic cell. The total volume of the mixture was kept constant at 10 ml. by adding 4.5 ml. of water. The solution was then deaerated by bubbling pure dry hydrogen for about 20 minutes. The polarogram was recorded photographically. The experiment was repeated thrice for reproducibility. Typical polarogram obtained is presented in Fig. 1. The half wave potential is $-0.315$ volt versus Mercury pool. Plot of log $i/(i_d - i)$ versus $E_{dme}$ is presented in Fig. 2.

2. **Polarogram of Iron (III)—resacetophenoneoxime complex.**—The polarograms of the Iron (III)—resacetophenoneoxime complex were recorded at: (a) different concentrations of the complex, (b) at different heights of mercury reservoir, and (c) at different concentrations of the complexing agent as follows: (a) In the first series of experiments 2 ml. of
buffer solution, \((6 - x)\) ml. of water, \(1\cdot0\) ml. of sodium perchlorate, \(1\cdot0\) ml. of resacetophenoneoxime solution and \(X\) ml. of Iron (III) solution were pipetted out into the cell to make a total volume of 10 ml. It was found that this order of addition of the solutions was essential for the reproducibility of the results. The solution was deaerated by pure dry hydrogen and the polarogram recorded. A typical polarogram obtained is presented in Fig. 1. Plots of wave height \(versus\) concentration and \(\log i/(i_d - i)\) \(versus\) \(E_{dme}\) are presented in Figs. 3 and 4 respectively. (b) In the second
series of experiments the volume of Iron (III) solution was kept constant at 1.0 ml. The polarograms were recorded at different heights of the mercury column, other conditions being the same as in the first one. The results obtained are presented in Table I. (c) The third series of experiments was performed as follows: 2 ml. of buffer solution, 1.0 ml. of sodium perchlorate solution, 'X' ml. of oxime solution, (5.5 - X) ml. of water and
1·5 ml. of Iron (III) solution were pipetted out into the cell to make a total volume of 10 ml. Polarograms were recorded after deaerating the solution. The half wave potentials of the complex at different concentrations of the complexing agent are presented in Table II. A plot between half wave potential and logarithm of the concentration of the complexing agent is presented in Fig. 5.

In all cases the pH (5·8) of the solution was checked up with an "Elico" pH meter model LI-10·A.

RESULTS

**TABLE I**

*Change of diffusion current ($i_d$) with height of mercury reservoir (h)*

<table>
<thead>
<tr>
<th>$h$ (cm.)</th>
<th>$i_d$*</th>
<th>$i_d/h^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>5.7</td>
<td>0.81</td>
</tr>
<tr>
<td>45</td>
<td>5.4</td>
<td>0.81</td>
</tr>
<tr>
<td>40</td>
<td>5.1</td>
<td>0.81</td>
</tr>
<tr>
<td>35</td>
<td>4.8</td>
<td>0.81</td>
</tr>
<tr>
<td>30</td>
<td>4.4</td>
<td>0.82</td>
</tr>
</tbody>
</table>

* Wave height (cm.) is taken.

**TABLE II**

*Half wave potential and an values of the complex at different concentrations of resacetophenoneoxime*

<table>
<thead>
<tr>
<th>Concentration of the oxime ($x10^{-3}$ M.)</th>
<th>Half wave potential ($-E_1$) vs. Hg pool (volts)</th>
<th>$(E_2 - E_1)$ vs. Hg pool (volts)</th>
<th>an</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.45</td>
<td>0.08</td>
<td>0.7037</td>
</tr>
<tr>
<td>2.0</td>
<td>0.47</td>
<td>0.08</td>
<td>0.7037</td>
</tr>
<tr>
<td>3.0</td>
<td>0.49</td>
<td>0.08</td>
<td>0.7037</td>
</tr>
<tr>
<td>4.0</td>
<td>0.50</td>
<td>0.08</td>
<td>0.7037</td>
</tr>
<tr>
<td>6.0</td>
<td>0.52</td>
<td>0.08</td>
<td>0.7037</td>
</tr>
<tr>
<td>8.0</td>
<td>0.53</td>
<td>0.08</td>
<td>0.7037</td>
</tr>
</tbody>
</table>
DISCUSSION

Neither the polarogram of the simple Iron (III) nor the Iron (III)—resacetophenoneoxime complex exhibited a maximum under the experimental conditions. The logarithmic analysis (cf. Fig. 2) of the polarogram of simple Iron (III) gave a straight line with a slope corresponding to one electron. This indicated that Iron (III) under the experimental conditions underwent a reversible reduction to ferrous state. Plot of $\log i/(i_d - i)$ versus $E_{dme}$ for Iron (III)—resacetophenoneoxime complex (cf. Fig. 4), however, gave a straight line with a slope corresponding to a non-integral value for $n$ (number of electrons). This indicated that the slope included the transfer coefficient $\alpha$ besides $n$. The average value of $an'$ obtained from $E_1$ and $E_2$ values of the polarograms using the equation $E_1 - E_2 = \frac{2RT}{n'F} \ln 3$ was 0.7037. This showed that the Iron (III) complex underwent an irreversible reduction. However, the wave height was proportional to the concentration of the complex as shown in Fig. 4. Further $i_d/h^3$ values at different heights ($h$) of mercury column were found constant. These facts confirm that the reduction of the complex is a diffusion controlled one. It is, therefore, concluded that Iron (III)—resacetophenoneoxime complex undergoes, under the experimental conditions, a diffusion controlled irreversible reduction.

The composition of the complex was determined by the method proposed by Subramanya for complexes undergoing irreversible reduction. The method involves the determination of the slope (0.059 $p/an$) of the plot between $E_4$ (complex) and the logarithm of the concentration of the complexing agent, where $p$ gives the number of molecules of the complexing agent per one atom of the metal. In the present investigation, the slope was found to be 0.1 and the value of $p$ was 1.2 ($\approx 1.0$). The composition of the complex corresponded to the ratio metal: oxime as 1:1. The probable structure of the complex is given below.

![Structure of the complex](image)

The results are in agreement with those of Raja Reddy et al. (loc. cit.).
The average value of the stability constant \((K_c)\) calculated from the equation:

\[
E_1^{\text{complex}} - E_1^{\text{simple}} = \frac{RT}{a_nF} \ln k_c - p \frac{RT}{a_nF} \ln [\text{oxime}]
\]

is \(2.78 \times 10^{-5}\).

**REFERENCES**

1. Neelakantam, K. and Sitaraman, M. V.  

2. Raja Reddy, G., Kadarmandalgi, S. G. and Murthy, A. S. R.  

3. Subramanya, R. S.  