Polarographic Study of Zn(II) Complexes of L-Hydroxyproline

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The interaction of zinc(II) with L-hydroxyproline has been studied polarographically at \( \mu = 0.5M \) (NaClO) at 303K. The process is found to be quasi-reversible, diffusion-controlled, two-electron reduction. The kinetic parameters \( \alpha \) and \( K_s \) have been determined by Gellings method and \( K_s \) is of the order of \( 10^{-4} \) cm/sec. The overall formation constants have been determined by De-Ford and Hume's method and confirmed by Mihailov's mathematical method. The formation of two complex species having the composition Zn \([(L\text{-hydroxyproline})]^+ \) and Zn \((((L\text{-hydroxyproline})\text{-})^0 \) with values of overall formation constants \( \beta_1 = 30 \) and \( \beta_2 = 3.5 \times 10^5 \) is observed. The percentage distribution of Zn(II) at different L-hydroxyproline concentrations have been also calculated. Since the reduction is diffusion-controlled Zn(II) can be estimated polarographically in L-hydroxyproline solution.

The complexes Zn(II) with tartrate, citrate, acetate, formate, casein and proteins have been studied by Matsuda, Mulnck and others. The kinetics of the reduction of Zn(II) at d.m.e. in sodium perchlorate, potassium nitrate, potassium chloride and potassium iodide have been studied by Tanaka and Tamanushi in this note are presented our results on the polarographic investigation of the complexation reaction of Zn(II) with L-hydroxyproline. The reduction of Zn(II) was found to be quasi reversible and the composition and stability constants have been determined by De-Ford and Hume method and confirmed by Mihailov's mathematical treatment.

Reagent grade chemicals were used throughout. A solution of zinc nitrate \((M/40)\) was prepared and standardized as usual. A solution of L-hydroxyproline \((0.25M)\) was prepared and different concentrations were used during the experiment. The polarograms were taken at constant ionic strength \((\mu = 0.5M \text{ NaClO}_4)\). Gelatin (0-001%) was used as a maximum suppressor in all the solutions.

All the polarograms were taken at 30°±0.1° with the help of manual polarograph. The d.m.e. had the following characteristics: \( n = 3.448 \text{ mg/sec} \); \( t = 2.32 \text{ sec} \) in open circuit. A H-type cell saturated with sodium chloride agar-agar bridge was used. Purified nitrogen was passed for 20 min before taking each current-voltage readings and IR drop correction was applied.

Solutions containing 0.5 mM Zn\(^{2+}\) and 0.005M, 0.010, 0.015, 0.020, 0.025, 0.03, 0.04, 0.05M hydroxyproline were prepared. Requisite amount of sodium perchlorate was added to keep ionic strength constant at 0.5M. In each case, a single well-defined reduction wave appeared, where half-wave potential was shifted to more negative side and diffusion current was found to decrease with increasing concentration of the ligand. The diffusion current was found to be dependent on the height of the mercury column showing the process to be diffusion-controlled. The decrease in \( i_d/ko \) values realized with increasing hydroxyproline: metal ratio may be attributed to the uptake of the metal ions by the proline, provided factors like viscosity and absorption are not operative. The plots of \( \log (i_d/k_0) \) versus E d.e. were linear with a slope = 0.39±2 mV. The above results lead to the conclusion that although the reduction is diffusion controlled yet it is not a reversible process; hence the reversible half-wave potentials \( (E_1') \) were determined by Gellings Eq. (1)

\[
\lim_{t \to 0} \left[ \frac{E - \frac{RT}{nF} \ln \frac{i_d - i}{i}}{t} \right] = E_1'
\]

\( \alpha \) and \( K_s \), the standard rate constants were calculated using Eq. (2)

\[
\log (Z - 1) = \log \frac{1 - \alpha}{2.303RT} \left( E - E_1' \right) \frac{(1 - \alpha)RT}{2.303RT} \left( E - E_1' \right) \]

where \( \log (Z) \) is considered as the measure of the degree of irreversibility. The values of \( Z \) at various potentials were calculated from experimental data. The values of \( K_s \) and \( \alpha \) were determined by the intercept and slope of the plot of \( \log (Z - 1) \) against \( E \) \( (E_1' - E) \). The plot of \( E_1' \) versus \( -\log C_s \) is a smooth curve, indicating the formation of two or three.

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**Table 1 — Analysis of \( F_d(X) \) Functions and Kinetic Parameters of Zinc-L-Hydroxyproline System**

<table>
<thead>
<tr>
<th>Prolin conc. (M)</th>
<th>(-\frac{E_1'}{V} ) (versus SCE)</th>
<th>( i_{d0} ) (div.)</th>
<th>Slope (mV)</th>
<th>( F_0 ([X]) )</th>
<th>( F_1 (X) )</th>
<th>( F_2 (X) ) ( \times 10^2 )</th>
<th>( \alpha )</th>
<th>( K_s \times 10^6 ) (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0-990</td>
<td>36-5</td>
<td>39.0</td>
<td>43.2</td>
<td>13.18</td>
<td>0-42</td>
<td>1-10</td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>0.995</td>
<td>36-0</td>
<td>38.0</td>
<td>2.245</td>
<td>83.0</td>
<td>35.30</td>
<td>0-40</td>
<td></td>
</tr>
<tr>
<td>0.015</td>
<td>1-000</td>
<td>35-0</td>
<td>40.0</td>
<td>3.526</td>
<td>126.3</td>
<td>35.32</td>
<td>0-35</td>
<td></td>
</tr>
<tr>
<td>0.020</td>
<td>1-005</td>
<td>31-5</td>
<td>39.0</td>
<td>3.995</td>
<td>119.3</td>
<td>35.92</td>
<td>0-32</td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>1-008</td>
<td>35-0</td>
<td>41.0</td>
<td>5.5</td>
<td>150.3</td>
<td>40.10</td>
<td>0-37</td>
<td></td>
</tr>
<tr>
<td>0.030</td>
<td>1-012</td>
<td>35-0</td>
<td>40.0</td>
<td>7.793</td>
<td>169.5</td>
<td>34.81</td>
<td>0-30</td>
<td></td>
</tr>
<tr>
<td>0.040</td>
<td>1-016</td>
<td>34-5</td>
<td>41.0</td>
<td>11.424</td>
<td>208.4</td>
<td>35.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.050</td>
<td>1-021</td>
<td>34-5</td>
<td>41-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

202
more complexes. The composition and stability constants were calculated by De-Ford and Hume's method by plotting $F_2(X)$ versus $C_2$. The results show the formation of two complex species $[Zn(\text{hydroxyproline})]_2^+$ and $[Zn(\text{hydroxyproline})]_{3^+}$ having overall formation constants $\beta_1 = 50$ and $\beta_2 = 4.5 \times 10^3$. The percentage distribution of zinc in various forms as a function of log l-hydroxyproline concentration is graphically shown in Fig. 1. The values of overall formation constants determined by Mihailov's mathematical method are $\beta_1 = 31.9156$, $\beta_2 = 3.49 \times 10^9$, which are in good agreement with the values obtained by graphical method.

The value of $K_r$ was found to be of the order of $10^{-3}$ cm/sec for the reduction of zinc in $0.5M$ NaClO and $10^{-4}$ cm/sec in complexing media, indicating that the irreversibility of electrode process for the reduction of zinc increased in the presence of l-hydroxyproline. The kinetic parameters are given in Table 1.

The direct dependence of $i_b$ on height of mercury (b) shows that viscosity changes are not responsible for the decrease in diffusion current. Similarly, the decrease in the current cannot be attributed to the absorption of l-hydroxyproline molecule by the mercury drop. Sufficient indications of the binding of zinc with hydroxyproline are thus available. However, the most distinctive feature of the present study is that neither the carboxyl nor the hydroxy group offers site for binding of zinc with the hydroxyproline. Thus only the amino group viz. serine methyl ester clearly shows that hydroxyproline coordinates to the metal ion through the amino group only. Since the reduction is diffusion-controlled, Zn(II) can be estimated polarographically in l-hydroxyproline solution.

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Fig. 1 — Percentage distribution of Zn(II) in various forms as a function of log l-hydroxyproline concentration

Redox reactions of hexaisothiocyanatomolybdate(III) with Vanadate, Dichromate, Permanganate & Iodate

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