Polarographic Study of Mixed Ligand Complexes: Cadmium-Glycinate-Bicinate System

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The mixed ligand complexes of glycine and N,N-bis(2-hydroxyethyl) glycine (bicinate) with Cd(II) have been investigated polarographically. The overall formation constants for the simple complexes are: 

$$\log \beta_1 = 4.26, \log \beta_2 = 7.85 \text{ and } \log \beta_3 = 10.07$$

with glycine and 

$$\log \beta_1 = 5.30, \log \beta_2 = 8.01 \text{ and } \log \beta_3 = 9.66$$

with bicinate at 35°C. Three mixed complexes Cd(glycinate)(bicinate), Cd(glycinate)₂(bicinate) and Cd(glycinate)(bicinate)₃ are formed and their overall formation constants are: 

$$\log \beta_{11} = 8.36, \log \beta_{12} = 10.17 \text{ and } \log \beta_{13} = 10.04$$

respectively at 35°C. The positive values of mixing constant and stabilization constant reveal that the mixed complex Cd(glycinate)(bicinate) is more stable than the parent binary complexes.

RESULTS AND DISCUSSION

A solution of Cd(II) in 0.2M sodium perchlorate gave a reversible (slope 32±1 mV) and diffusion-controlled wave with $E_{1/2} = -0.577$ V(vs SCE). The Cd(II)-bicinate and -glycine systems were investigated polarographically at pH 7.74±0.06 and 9.20±0.04, respectively. In the presence of ligand (glycine or bicinate) the reduction of Cd(II) was also reversible and diffusion-controlled.

The half-wave potentials of Cd(II) shifted to more negative values on increasing the free ligand concentration. Since plots of $-E_1$ vs log [free ligand] were smooth curves, the DeFord-Hume method was used to calculate the overall stability constants of the consecutive complexes.

The [free ligand] of glycine was calculated from the reported value of $PK_2$ (9.44) at 35°C. The $PK_2$ value of bicinate (7.98) at 35°C was found by applying the method of Pethe and Mali using reported $PK_2$ value (8.22) at 25°C.

The observed values of stability constants are given in Table 1, which agree fairly with the reported values.

**Mixed Cd(II) - glycinate - bicinate system**

Polarograms were recorded with solutions containing $2 \times 10^{-4}M$ Cd(II), constant [glycinate] and varying [bicinate] at pH 8.12±0.04 and constant [bicinate] and varying [glycinate] at pH 8.46±0.02. The instability was kept constant at 0.2. All the reduction waves were diffusion-controlled and reversible.

The two fixed concentrations of amino acid ions were so chosen that at the lower value 1:1 species and at higher value 1:2 species predominated in the simple systems. The fixed concentrations of glycinate chosen were: $4.37 \times 10^{-4}M$ and $1.75 \times 10^{-3}M$ and those of bicinate were $1.34 \times 10^{-3}M$ and $8.02 \times 10^{-3}M$.

On increasing the concentration of bicinate ion, the half-wave potential shifted towards more negative values and the shift was more marked than in the simple Cd(II)-bicinate system. Similar observations were recorded when the concentration of glycinate ion was increased.

<table>
<thead>
<tr>
<th>Table 1 — Overall Stability Constants of Cd(II) Complexes</th>
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<tbody>
<tr>
<td>System</td>
</tr>
<tr>
<td>Cd(II)-glycinate</td>
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<tr>
<td></td>
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<tr>
<td>Cd(II)-bicinate</td>
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**R**ecently Nozaki et al.¹ have studied the mixed hydroxy complexes of Cu(II), Cd(II) and Pb(II) with N, N-bis(dihydroxyethyl) glycine (bicinate). In the present communication we report the polarographic study of simple and mixed complexes of glycine and bicinate with Cd(II) at 35°C. All the reagents used were of AR grade, and used as such. The ionic strength of all the experimental solutions was kept constant at 0.2 with sodium perchlorate. Stock solution of 0.01M cadmium nitrate was used in all the experiments.

An automatic polarograph type OH—102 (Radelkis, Hungary) was used for recording polarograms. The pH of the solution was measured with the help of a digital pH meter NIG 333. The capillary had the following characteristics at $0.8V$(vs SCE) in 0.02M NaClO₄ at 38.5 cm (corrected) mercury head : $m = 2.54 \text{ mg/sec}$ and $t = 3.21 \text{ sec}$. All observations were made at 35°C ± 0.1°C. The potentials were measured with reference to SCE. The cell resistance was < 450 ohms.

**RESULTS AND DISCUSSION**

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On increasing the concentration of bicinate ion, the half-wave potential shifted towards more negative values and the shift was more marked than in the simple Cd(II)-bicinate system. Similar observations were recorded when the concentration of glycinate ion was increased.

**TABLE 1 — OVERALL STABILITY CONSTANTS OF Cd(II) COMPLEXES**

<table>
<thead>
<tr>
<th>System</th>
<th>Constant Observed at 35°C</th>
<th>Reported Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)-glycinate</td>
<td>log $\beta_1$</td>
<td>4.26</td>
</tr>
<tr>
<td></td>
<td>log $\beta_2$</td>
<td>7.85</td>
</tr>
<tr>
<td></td>
<td>log $\beta_3$</td>
<td>10.07</td>
</tr>
<tr>
<td>Cd(II)-bicinate</td>
<td>log $\beta_1$</td>
<td>5.30</td>
</tr>
<tr>
<td></td>
<td>log $\beta_2$</td>
<td>8.01</td>
</tr>
<tr>
<td></td>
<td>log $\beta_3$</td>
<td>9.66</td>
</tr>
</tbody>
</table>
Smooth curves were obtained when $-E_\frac{1}{2}$ were plotted against $-\log [X]$. The method of Schaap and McMasters' was applied to determine the overall stability constants of the mixed-complexes so formed.

The following values of $A$, $B$, $C$ and $D$ (having their usual significance as in the Schaap and McMasters' original paper) were obtained,

(i) [Glycinate] = $4.37 \times 10^{-4} M$

$A = 11$ (calculated), $B = 3.2 \times 10^5$, $C = 1.087 \times 10^6$ and $D = 2.561 \times 10^6 (\log D = 9.41)$.

(ii) [Glycinate] = $1.75 \times 10^{-4} M$

$A = 313$ (calculated), $B = 7.2 \times 10^9$, $C = 1.225 \times 10^{10}$ and $D = 2.353 \times 10^{10} (\log D = 9.37)$.

From two values of $B$, the overall stability constant of the complex $Cd(bic)\{gly\}$ was found to be $2.67 \times 10^5$ (log $\beta_{bic, gly} = 8.43$) and the overall stability constant for the complex $[Cd(bic)\{gly\}]^2$ was obtained as $1.72 \times 10^{10} (\log \beta_{bic, gly} = 10.25)$.

From values of $C$, we get $1.213 \times 10^{10}$ (log $\beta_{bic, gly} = 10.08$) and $1.091 \times 10^{10}$ (log $\beta_{bic, gly} = 10.04$) as the overall stability constants of the complex species $[Cd(bic)\{gly\}]$ at $4.37 \times 10^{-4} M$ and $1.75 \times 10^{-4} M$ respectively. (Here 'g' stands for glycinate and 'b' for bicinate ion).

Both the log $D$ values agree fairly with the log stability constant of the species $[Cd(bic)\{gly\}]_2$. The average value of log $D$ is 9.39.

The functions $F_{10}$ (gly, bic.) vs [glycinate] were plotted at two different concentrations of bicinate ion. The value of constant $A$ was calculated and the values of constants $B$, $C$ and $D$ were obtained by extrapolating the $F_{10}$ (gly, bic.) functions. The various values of $A$, $B$, $C$ and $D$ are given below:

(i) [Bicinate] = $1.34 \times 10^{-4} M$

$A = 4.66 \times 10^5$ (calculated), $B = 3.00 \times 10^6$, $C = 8.84 \times 10^7$ and $D = 7.81 \times 10^9 (\log D = 9.89)$.

(ii) [Bicinate] = $8.02 \times 10^{-4} M$

$A = 1.06 \times 10^4$ (calculated), $B = 2.25 \times 10^4$, $C = 1.86 \times 10^8$ and $D = 7.12 \times 10^9 (\log D = 9.85)$.

The stability constants of mixed complexes were calculated from the above values and the following values of overall formation constants were obtained:

$log \beta_{bic} = 8.29, log \beta_{bic} = 10.14 \ (at \ both \ the \ fixed \ concentrations \ of \ bicinate \ ion)$

and $log \beta_{bic} = 10.01$.

These values agree well with the values obtained at fixed [glycinate]. The values of log $D$ are in agreement with the stability constant of the simple complex $[Cd(gly)]_2$. The average value of log $D$ is 9.87.

The mean log values of overall stability constants of mixed complex species are given below:

$log \beta_{bic} = 8.36 \ (average), log \beta_{bic} = 10.17 \pm 0.05 \ and \ log \beta_{bic} = 10.04 \pm 0.04$.

The stability of mixed complexes can be compared with that of simple complexes. The equilibrium constant for the reaction (1)

$[Cd(gly)]^+ + [Cd(bic)]^+ \Leftrightarrow [Cd(gly)\{bic\}] + Cd^{2+}$ (1)

is given by the relation:

$\Delta log K = log \beta_{bic} - log \beta_{bic} - log \beta_{bic} = -1.2 \ (2)$

The statistical value for coordination of two different bidentate ligands for an octahedral coordination sphere is $-0.4$ (ref. 8). The higher negative value suggests that mixed complex species is less stable than the simple mono complexes.

The mixing constant $K_m$ (equilibrium constant) for the reaction (3)

$[Cd(gly)]_2 + \frac{1}{2}[Cd(bic)]_2 \Leftrightarrow [Cd(gly)\{bic\}]$ (3)

indicates the relative stability of the mixed complex in solution as compared to the parent binary complexes. This is given by the relation (4)

$K_m = \beta_{bic}/\beta_{bic}$ (4)

The log $K_m$ for the reaction (3) is $8.36 - (7.85 + 8.01) = 0.43$.

The stabilization constant, $K_s$ for the ligands of equal denticity is expressed in the form

$log K_s = log \beta_{bic} - log \beta_{bic} + log \beta_{bic} + log D$ (5)

$log K_s = log K_m - log 2$ (6)

Hence log $K_s = 0.43 - log 2 = 0.43 - 0.30 = 0.13$.

The positive values of mixing constant and stabilization constants show that the mixed complex is somewhat more stable than the simple bis complexes. The positive value of stabilization constant has also been observed by Brookes and Pettit, Gergely and Sovago and Ting and Nancollas.

The log $K$ values for the reactions (7) and (8)

$[Cd(gly)]_2^+ + (bic) \Leftrightarrow [Cd(gly)]_2(bic) + (gly)^-$ (7)

$[Cd(bic)]_2^+ + (gly) \Leftrightarrow [Cd(bic)]_2(gly) + (bic)^-$ (8)

are 0.30 and 0.65 respectively. The positive values suggest that the saturated mixed complex species are more stable than the simple saturated complexes. It is also observed that $[Cd(gly)\{bic\}]$ species is the most stable complex species.

Watters and Dewitt found the following relations for the prediction of stability constants of mixed complexes from statistical factors:

$\beta_{11} = 2 \times 3 \times \beta_{10}^{1/3} \times \beta_{03}^{1/3}$

$\beta_{13} = 3 \times \beta_{03}^{1/3} \times \beta_{03}^{1/3}$ and

$\beta_{21} = 3 \times \beta_{03}^{1/3} \times \beta_{03}^{1/3}$ (9)

The values of stability constants calculated from the above expressions and the experimentally determined values are given below:

<table>
<thead>
<tr>
<th>Expl</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>log $\beta_{bic}$</td>
<td>8.36</td>
</tr>
<tr>
<td>log $\beta_{bic}$</td>
<td>10.17</td>
</tr>
<tr>
<td>log $\beta_{bic}$</td>
<td>10.04</td>
</tr>
</tbody>
</table>

The experimental values of the stability constants of the mixed complex species $[Cd(gly)]_2(bic)^-$ and $[Cd(gly)\{bic\}]_2^-$ are nearly equal to the statistical values. But the experimental value for the mixed
complex species \([\text{Cd(gly)}(\text{bic})]\) is higher than the calculated value. This may be accounted for due to the neutralisation of charge on the ion.

Acknowledgement

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References