Mixed ligand complex formation of nickel(II), copper(II) and zinc(II) with some amino acids and imidazoles

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Proton-ligand stability constants for the amino acids viz., aspartic acid and glutamic acid and three imidazoles, viz., imidazole, 2-methylimidazole and 2-ethylimidazole, hydrolytic constants for the metal ions (Cu²⁺, Ni²⁺ and Zn²⁺) and the stability constants for fifteen binary complexes and eighteen ternary complexes of these metal ions and ligands have been determined by pH-metric measurements in aqueous solutions at 30°C in 0.2M NaNO₃. The calculations have been made using the SCOGS computer programme.

As a part of our continuing studies on complex formation of transition metal ions with amino acids and imidazoles, in the present paper we describe the results of a combined pH-metric and spectrophotometric investigation on the mixed ligand complex formation of Ni²⁺, Cu²⁺ and Zn²⁺ with aspartic acid (Ia) and glutamic acid (Ib), (abbreviated hereafter as AH₂) and imidazoles, viz. imidazole (im, IIa) 2-methylimidazole (2-Me-im, IIb) and 2-ethylimidazole (2-Et-im IIc), (abbreviated hereafter as L), in aqueous solution, at 30°C at a fixed ionic strength, (0.2M NaNO₃). These ligands provide situations favourable for measuring the effect of ligand structure on the stability.

Aspartic acid and glutamic acid have three potential coordination sites, viz., the amino nitrogen and two carboxylic groups. The aspartate ion has been reported to act as tridentate ligand, whereas glutamate with extended side chain has been reported to act both as bidentate and tridentate ligand. Imidazole is present in a number of biological systems and provides a potential binding site for metal ion.

Experimental
All the reagents were of AR grade and their solutions were prepared in doubly distilled CO₂ free water. Metal ions solutions were standardized by the usual procedure.

Procedure
The pH measurements were made with a Systronics pH meter, Model 335 (accuracy ±0.01 pH units) using a special glass electrode (pH 1-14) and a saturated calomel electrode. Temperature was maintained constant at 30±1°C using a Yorko thermostat. Electronic spectra were recorded with a Shimadzu UV-vis, UV-160 recording spectrophotometer using 1 cm quartz cell in aqueous solutions at pH 7.0.

The following metal-ligand mixtures were prepared for the pH-metric study, (i)-0.02(M) HNO₃; (ii)-(i) + 0.005(M) M(NO₃)₂; (iii)-(i) + 0.005 (M) AH₂; (iv)-(iii) + 0.005(M) M(NO₃)₂; (v)-(i) + 0.005(M) L; (vi)-(v) +0.005 (M) M(NO₃)₂; and (vii)-(i) + 0.005(M) AH₂ + 0.005(M) L + 0.005 (M) M(NO₃)₂. The initial volume of all the solutions was 50 ml and required amounts of NaNO₃ were added in each solution to maintain the ionic strength (fixed at 0.2 M NaNO₃). All the solutions were allowed to attain equilibrium, at the experimental temperature (30±1°C) and were titrated with standard 1 M NaOH.

\[
\begin{align*}
\text{H}_3&\text{N}^-\text{CH} \quad \text{COO}^- \\
&\text{(CH}_2\text{)}_n \\
&\text{COO}^- \\
&\text{(I)} \\
&\text{(II)} \\
&\text{(I)} \\
&\text{(II)} \\
&\text{(II)} \\
\end{align*}
\]

(a) n=1, aspartic acid
(b) n=2, glutamic acid

(a) R = H
(b) R = CH₃
(c) R = CH₂CH₃
Table I—Proton-ligand and metal-ligand binary and ternary constants at 30±1°C in aqueous solution, ionic strength, I = 0.2 (M) NaNO₃

(a) Proton-ligand constants

<table>
<thead>
<tr>
<th>Ligand</th>
<th>pKᵢ&lt;sup&gt;+&lt;/sup&gt;</th>
<th>pKᵢ&lt;sup&gt;+&lt;/sup&gt;</th>
<th>pKᵢ&lt;sup&gt;-&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspartic acid (AH&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>1.87</td>
<td>4.00</td>
<td>9.75</td>
</tr>
<tr>
<td>Glutamic acid (AH&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>2.10</td>
<td>3.89</td>
<td>9.65</td>
</tr>
<tr>
<td>Imidazole(LH&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>-</td>
<td>-</td>
<td>7.15</td>
</tr>
<tr>
<td>2-Methylimidazole(LH&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>-</td>
<td>-</td>
<td>8.08</td>
</tr>
<tr>
<td>2-Ethylimidazole(LH&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>-</td>
<td>-</td>
<td>8.05</td>
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</tbody>
</table>

(b) Hydrolytic constants of M²⁺ (aq.) ions

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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</thead>
<tbody>
<tr>
<td>logK&lt;sub&gt;M&lt;/sub&gt;&lt;sup&gt;p&lt;/sup&gt;</td>
<td>-8.10</td>
<td>-6.29</td>
<td>-7.89</td>
</tr>
<tr>
<td>logK&lt;sub&gt;M&lt;/sub&gt;&lt;sup&gt;p&lt;/sup&gt;</td>
<td>-16.87</td>
<td>-13.10</td>
<td>-14.92</td>
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(c) Stability constants of binary complexes

<table>
<thead>
<tr>
<th>A/L</th>
<th>A/L</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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</thead>
<tbody>
<tr>
<td>logK&lt;sub&gt;M&lt;/sub&gt;&lt;sup&gt;M&lt;/sup&gt;</td>
<td>asp&lt;sup&gt;-&lt;/sup&gt;</td>
<td>7.25</td>
<td>8.80</td>
<td>5.78</td>
</tr>
<tr>
<td></td>
<td>glu&lt;sup&gt;-&lt;/sup&gt;</td>
<td>9.90</td>
<td>5.85</td>
<td>4.90</td>
</tr>
<tr>
<td></td>
<td>im</td>
<td>2.78</td>
<td>4.20</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>2-Me-im</td>
<td>3.96</td>
<td>5.32</td>
<td>2.83</td>
</tr>
<tr>
<td></td>
<td>2-Et-im</td>
<td>3.05</td>
<td>5.32</td>
<td>2.80</td>
</tr>
</tbody>
</table>

(d) Stability constants of ternary complexes

<table>
<thead>
<tr>
<th>A</th>
<th>L</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>log&lt;sub&gt;M&lt;/sub&gt;&lt;sup&gt;M&lt;/sup&gt;</td>
<td>asp&lt;sup&gt;-&lt;/sup&gt;</td>
<td>10.13</td>
<td>12.60</td>
<td>8.86</td>
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<tr>
<td></td>
<td></td>
<td>(+0.10)</td>
<td>(-0.40)</td>
<td>(+0.60)</td>
</tr>
<tr>
<td></td>
<td>glu&lt;sup&gt;-&lt;/sup&gt;</td>
<td>8.23</td>
<td>12.25</td>
<td>7.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.40)</td>
<td>(-0.40)</td>
<td>(+1.00)</td>
</tr>
<tr>
<td></td>
<td>im</td>
<td>9.41</td>
<td>13.38</td>
<td>7.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.40)</td>
<td>(-0.39)</td>
<td>(-0.40)</td>
</tr>
<tr>
<td></td>
<td>2-Me-im</td>
<td>9.00</td>
<td>13.36</td>
<td>7.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(+0.10)</td>
<td>(-0.40)</td>
<td>(+1.00)</td>
</tr>
</tbody>
</table>

Standard deviation in the values : ±(0.10.2) in log units.

Spectrophotometric measurements were carried out with the mixture (i), (iv) and (vii) after adjusting their pH as at 7.0.

Proton-ligand and metal-ligand stability constants of binary and ternary complexes were calculated using the SCOOGS computer programme.6

Results and discussion

As the metal-ligand complex formation equilibria and the hydrolytic equilibria of the M²⁺ (aq.) ions are overlapping, the hydroxo species M(OH)<sup>+</sup>, M(OH)<sub>2</sub>, M(A)(OH), M(B)(OH)<sup>+</sup> etc. have been assumed to be present in the complexation equilibria of ternary M/AH₂/L system. Only 1:1:1 ternary (M:AH₂:L) mixture have been used in this study to ensure the exclusive formation of the simplest ternary complex M(A)(B). Considering the pKᵢ<sup>+</sup> value of the ligands and hydrolytic constants of the M²⁺ (aq.) ions, the following species have been considered to exist in the complexation equilibria. M²⁺, AH<sup>-</sup>, AH₂, AH, A⁻, M³⁺, M(OH)<sup>+</sup>, M(OH)<sub>2</sub>, M(A), ML²⁺, M(A)(OH)<sup>+</sup>, M(L)(OH), M(A)(L) and M(A)(L)(OH).

The stability constants, logK<sub>M</sub><sup>M</sup>, logK<sub>M</sub><sup>L</sup>, logK<sub>M</sub><sup>M</sup> (Table I) and the speciation curves (Fig.1) were obtained as computer outputs. logK<sub>M</sub><sup>M</sup> and logK<sub>M</sub><sup>L</sup> values are in good agreement with those reported by other workers.1,7 Complex formation equilibria have been elucidated on the basis of speciation curves (Fig. 1). Stability of ternary M(A)(L) complex was generally characterised on the basis of ΔlogK<sub>M</sub> values6,8,10 calculated using the relation

\[ \Delta \log K_M = \log K_{M \_A \_L} - \log K_{M \_A} - \log K_{M \_L} \] ...

Examination of the speciation curves (Fig. 1a) of Cu²⁺/AH₂/L systems, with A=asp<sup>-</sup>, glu<sup>-</sup> and L= im, 2-Me-im and 2-Et-im, indicates the formation of Cu(A)(L) complexes according to the following equations:
Cu^{2+} + AH_2 ⇌ Cu(A) + 2H^+ ... (2)
Cu(A) + LH^+ ⇌ Cu(A)(L) + H^+ ... (3)

On the other hand, Ni(A) and Zn(A) complexes were formed according to equilibria (4)

\[ M^{2+} + AH = M(A) + H^+ \] ... (4)

The corresponding M(A)(L) complexes with Ni^{2+} and Zn^{2+} were formed according to equilibria of the type (3). However in the Zn^{2+}/AH_2/L systems, there were two additional equilibria,

\[ \text{Zn}^{2+} + AH + LH^+ = \text{Zn}(A)(L) + 2\text{H}^+ \] ... (5)
\[ \text{Zn}(A) + \text{Zn}(L)^{2+} = \text{Zn}(A)(L) + \text{Zn}^{2+} \] ... (6)

leading to the formation of mixed ligand Zn(A)(L) complexes. Hydroxo species \( M(OH)_2^+ \), \( M(OH)_3^- \), \( M(A)(OH)_2^- \), \( M(L)(OH)_2^- \) make their appearance only in the Zn^{2+}/gluH_2/L system.

Relatively higher basicity of 2-Me-im and 2-Et-im as compared to im itself may be due to electron-releasing effects of the Me and Et group in 2 position. In this regard, the two alkyl groups appear comparable. Stability constants of binary M(L) complexes were found to be in the order : 2-Me-im = 2-Et-im > im with regard to the ligands (Table 1). Negative contributions if any due to the alkyl substituents were probably over-compensated by the enhanced basicity of the alkyl substituted imidazoles. Stability of the binary, M(A), M(L) and ternary M(A)(L) complexes fall in the expected order \( \text{Ni(II)} < \text{Cu(II)} < \text{Zn(II)} \). Trends in the log \( \beta^{M_{\text{MAX}}(L)} \) values were found to be same as that of the log \( \beta^{M_{\text{MIN}}(L)} \) values. No definite trend was observed in \( \Delta \log K_M \) values. However, as expected, \( \Delta \log K_M \) values were less negative or positive. This may be attributed to the \( \pi \)-acidic character of the three imidazoles and O' -N coordination of the amino acid.

Electronic spectra of Ni(II)/AH_2/L mixtures were recorded in aqueous solution at pH 7.0 at which the concentration of ternary Ni(A)(L) complexes passes through maximum. The trend in the 10 \( Dq \) values tallies with the stability constants of the complexes. The nephelauxetic ratio (β) for Ni(L) and Ni(A)(L) complexes were found to be in the range 0.75 - 0.84, which suggests considerable covalent character of the metal-ligand bonds. Based on the 10 \( Dq \) values, the present ligands may be arranged in the following spectrochemical series : asp^2<glu^2 and im<2-Me-im<2-Et-im.

Acknowledgement

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References