Statistical and astatistical aspects of formation and stabilities of binary and ternary complexes of iron(II) containing cyclic ketones and N,N; N,O- and O-,O- donor ligands in solution

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Formation constants of binary (ML, ML₂) and ternary, (MAL) complexes where M = Fe(II); L = (O,O- donors): 1,2,3-indantrione monohydrate or ninhydrin (NIN), 3-methyl-1,2-cyclopentanedione (MCPD), 2,3-indolinedione or isatin (ISAT), 2-hydroxy-1,3-indolinedione or N-hydroxyphthalimide (NHP) and A = (i) N,N donors: ethylenediamine (en), 2,2-bipyridyl (bipy), (ii) N,O- donors: alanine (ala), valine (val), (iii) O-,O- donors: oxalic acid (oxa) and catechol (cat) have been determined potentiometrically at 30°C and at an ionic strength of 0.1 M (KNO₃). The stabilities of the Fe(II) binary complexes follow the basicity order: ISAT > MCPD > NIN > NHP. The relative stabilities of the ternary complexes are characterised in terms of the statistical parameter ΔlogK. The stabilities of the ternary complexes, [Fe(II)AL] containing A as N,N and N,O- donors are higher than O-,O- donors. The observed stability order with respect to 'A' is: bipy > en > ala > val > oxa > cat and the stability order with respect to 'L' is: NHP > NIN > MCPD > ISAT. The results obtained in the present study are discussed in the light of statistical and different astatistical factors, such as basicity of the ligands, nature of donor atoms, charge neutralisation on central metal ion, metal-ligand π-interactions, electrostatic and steric effects.

The cyclic di and tri keto compounds ninhydrin (NIN), isatin (ISAT), 3-methyl-1,2-cyclopentanedione (MCPD) and N-hydroxyphthalimide (NHP) are known for their important biological activities, applications in bio-chemical, analytical, industrial and in various other fields. The properties exhibited by these compounds and their derivatives were found to undergo significant changes on complexation. The NIN and ISAT were also found to form their Schiff base complexes with amino acids selectively in the presence of transition metal ions, leading to considerable change in biological activities when compared to their pure forms. However, no significant quantitative studies were made on the formation, stability and relative chelating tendencies of these cyclic ketones in solution. The present work has been carried out pH-metrically to study the nature of formation and stabilities of binary and ternary Fe(II) complexes formed by the ligands (L) NIN, ISAT, MCPD and NHP in the presence of some selected N,N; N,O- and O-,O- donor ligands (A) in solution at 30°C and 0.1M (KNO₃) ionic strength. The metal ion, Fe(II) and the ligands 'A' were chosen in view of their known biological and other important roles, so that the different factors affecting the stability of resultant ternary complexes can be observed.

Materials and Methods

Ninhydrin, isatin and N-hydroxyphthalimide were obtained from E Merck and 3-methyl-1,2-cyclopentanedione from Aldrich. All other chemicals used in the experiment were of reagent grade. All solutions were prepared in CO₂ free doubly distilled water, except those of ISAT and NHP which were prepared in 5% v/v ethanol-water medium. The solutions of Fe(II) ion, KOH, HNO₃ were standardised by known literature methods. The metal solution was also tested qualitatively before each titration to ensure for absence of any Fe(III). Moreover, the oxidation of Fe(II) to Fe(III) could not have occurred since the titrations were performed in nitrogen atmosphere.

The pH measurements were made in 5% v/v ethanol-water medium under nitrogen atmosphere at 30°C and 0.1M (KNO₃) ionic strength on a Century CP 901 (India) digital pH meter consisting of a glass and calomel electrode combination. The pH meter and electrode assembly was calibrated against standard buffers before each titration. The titration procedure and other experimental details are similar to those described earlier. The acid dissociation constants of ligands and stepwise formation constants of binary complexes were determined by Irving-Rossotti method and...
Results and Discussion

The acid dissociation constants of all the ligands (A and L) used in the present study were determined under present experimental conditions and are listed in Table 1. The ligands (Structure 1) NIN, MCPD and ISAT exist in keto and hydroxy forms containing –OH group at 2nd position of 5-membered ring. The pKₐ value determined for these ligands (L) corresponds to the hydroxyl proton and the pKₐ value determined for NHP corresponds to its N – OH proton.

Binary systems

The stepwise formation constants of the 1:1 and 1:2 binary (ML and ML₂) complexes have been evaluated from the experimental data by analysing the titration curves in the pH range of 4.0-6.2 and are presented in Table 1. Similarly the (1:1) formation constants of all other complexes (MA) were also determined under identical experimental conditions (Table 1) for better comparison with the corresponding ternary complexes.

The ligands (Structure 1) NHP and NIN are expected to chelate either through 1,2 or 2,3 donor sites whereas the MCPD and ISAT only through 1,2 and 2,3 donor sites respectively. Thus the NHP and NIN are expected to form stable complexes compared to MCPD and ISAT with respect to structure of the ligands. But practically, the stabilities of the binary complexes, [Fe(II)-L] follow the order, ISAT > MCPD > NIN > NHP

From Table 1, it can be observed that this order is in accordance with the basicities of these ligands (L) and is almost reverse to the order expected based on the structure of the ligands. However, the values of log Kₘ₈ for all the systems according to statistical considerations are lesser than the corresponding log Kₘ₈ for all the systems according to statistical considerations.

Ternary systems

From the pH titration curves, it was found that the formation of ternary complexes, [Fe(II)-AL] occurred in two different ways.

(i) The complexes (MAL) consisting of A=bipy, oxal, cat and L=NIN, MCPD, ISAT and NHP were formed in stepwise equilibria, in which L behaves as a secondary ligand.

\[
M + A = MA; MA + L = MAL
\]

(ii) The ternary complexes involving A=ala, val and L=NIN, MCPD, ISAT and all the complexes

\[
M + L = ML; ML + A = MLA
\]
REDDY et al.: FORMATION CONSTANTS OF BINARY & TERNARY COMPLEXES OF IRON(II) 235

Table 2—Formation constants and \( \Delta \log K \) values of Fe(II) ternary complexes containing cyclic ketones and N,N; N,O- and O',O' donor ligands

<table>
<thead>
<tr>
<th>A</th>
<th>NIN (L)</th>
<th>MCPD (L)</th>
<th>ISAT (L)</th>
<th>NHP (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ala</td>
<td>14.13</td>
<td>-0.62</td>
<td>14.21</td>
<td>+0.50</td>
</tr>
<tr>
<td>val</td>
<td>14.04</td>
<td>+0.59</td>
<td>14.08</td>
<td>+0.43</td>
</tr>
<tr>
<td>en</td>
<td>11.48</td>
<td>+0.66</td>
<td>11.54</td>
<td>+0.52</td>
</tr>
<tr>
<td>bipy</td>
<td>7.23</td>
<td>+0.69</td>
<td>7.31</td>
<td>+0.57</td>
</tr>
<tr>
<td>oxa</td>
<td>5.85</td>
<td>-0.69</td>
<td>5.89</td>
<td>-0.85</td>
</tr>
<tr>
<td>cat</td>
<td>5.05</td>
<td>-1.49</td>
<td>4.82</td>
<td>-1.92</td>
</tr>
</tbody>
</table>

(MAL) containing ‘en’ were found to form in simultaneous equilibria.

\[
M + A + L = \text{MAL (or MLA)} \quad \ldots (3)
\]

In all the systems, distinct inflections were observed in the titration curves indicating the nature of complexation. The formation of ternary complexes was also confirmed from a number of observations\(^{15}\) such as change in intensity of colour, variation in pH range of complexation, shift in pH of precipitation etc., when compared to the corresponding binary complexes. The species distribution curves obtained for some representative systems (Fig. 1) using computer program BEST\(^{17}\) also supports the formation of ternary complexes.

The formation constants of (1:1:1) ternary complexes are presented in Table 2. The \( \Delta \log K \) (statistical parameter) values have been calculated\(^{16}\) from Eqs 4, 5, 6 and are tabulated for quantitative comparison of the stabilities of ternary and binary complexes.

\[
\Delta \log K = \log K_{MAL}^{\text{M}} - \log K_{ML}^{\text{M}} \quad \ldots (4)
\]
\[
\Delta \log K = \log K_{MLA}^{\text{M}} - \log K_{MAL}^{\text{M}} \quad \ldots (5)
\]
\[
\Delta \log K = \log K_{MAL}^{\text{M}} - \log K_{ML}^{\text{M}} \quad \ldots (6)
\]

The data in Table 2 shows that the \( \Delta \log K \) values are greater than the statistical ones, indicating that apart from the statistical factors, the stabilities of the ternary complexes are also governed by some astatistical factors such as basicity of the ligand, charge neutralisation in the complex, metal-ligand \( \pi \)-interactions, electrostatic repulsions and steric factors etc. The positive values of \( \Delta \log K \) indicate that the formation of ternary complexes are more favoured over their binary complexes. The order of stabilities of the ternary complexes, [Fe(II)-(MAL)] with respect to the ligands A is, bipy > en > ala > val > oxa > cat. The higher stabilities of the ‘bipy’ systems can be attributed to the metal-bipy \( d_{\pi}-p_{\pi} \) back bonding\(^{15,16}\), due to which the effective positive charge on the metal ion increases and thus facilitates the formation of stable ternary complexes with O,O' donor ligands (L).
In case of 'en', no such π-interactions are possible and hence relatively smaller ΔlogK values are observed. The positive ΔlogK values for the ternary systems containing N,O- donors (ala and val) can be due to the effective charge neutralisation. The greater stability of 'ala' over 'val' systems can be due to its greater basicity and lesser steric effects compared to valine.

The negative ΔlogK values (lower stability) of ternary complexes, MAL containing O-, O- donors or ligands, A (oxa and cat) is due to increase in electrostatic repulsions between the negatively charged oxygens of both A and L. The more negative ΔlogK values for 'cat' compared to 'oxa' systems can be attributed to the higher charge densities on phenolic oxygens, which results in greater coulombic repulsions. Thus, the decrease in ΔlogK values from A=N,N donors to O-,O- donors through N,O- donors can also be attributed to increase in electrostatic repulsions in their ternary complexes.

The stabilities of the ternary complexes can also be explained in terms of relative binding capacity of the ligands, 'L'. All these ligands NIN, MCPD, ISAT and NHP are O,O- donors which bind either simultaneously or in stepwise manner in the presence of other ligands (A) in different ternary systems. From Table 2, it can be seen that the stabilities of the ternary complexes, MAL follow the order with respect to 'L' as NHP>NIN>MCPD>ISAT. A comparison of this order with those of binary complexes (ML) indicate a reverse trend, which follows the order expected based on the structure of the ligand rather than the basicity order as observed in binary complexes (ML). Moreover, the formation of ternary complexes (MAL) are also favoured over their bis binary complexes, ML₂ which involves greater steric interactions. Thus the chelating tendencies of 'L' were significantly influenced in different complexes due to variety of factors.

During these studies it was also observed that, though the Schiff base formation was established in the synthesis of Schiff base complexes of NIN and ISAT with amino acids in presence of transition metal ions, at different experimental conditions, no such condensation took place under the present experimental conditions and instead ternary complexes were formed. Thus, the ligands (L) NIN/ISAT and (A) ala/val acted as two different sets of ligands in the formation of ternary complexes in their respective systems. Even if the formation of Schiff bases, in trace quantities cannot be ruled out, their existence became difficult due to rapid hydrolysis in aqueous medium under the present experimental conditions.

References
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