STABILITY CONSTANTS OF MIXED LIGAND TRANSITION METAL COMPLEXES

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Abstract: Mixed ligand complexes of some transition metal viz, Cu (II), Ni(II), Co(II), and Zn(II) have been investigated potentiometrically with 2 hydroxy- benzalidine- anthranilice acid (HBBA), pyridine-2, 6 dicarboxylic acid (PDA) and furan-2 carboxylic acid (FCA) in aqueous solution at temperature 25±1°C at an ionic strength of 0.1 mol dm⁻³ (KNO₃) the stability constant of this 1:1:1 ternary complexes have been evaluated by the computational method. The relative order of stability has been observed to be Cu(II)> Co(II)> Zn(II)>Ni(II). Which is in accordance with the increasing (φ) =charge /radius ratio. The changes in thermodynamic parameters (free energy changeΔG⁰, Enthalpy ΔH⁰ and Entropy ΔS⁰) have also been calculated under the same conditions. These compounds are antimicrobial sensitive.

Keywords: Metal ligand complex, Thermodynamic parameters, Antimicrobial

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INTRODUCTION

It is an important characteristic of the transition elements to form numerous co-ordination compounds, in sharp contrast to the s and p- block element. They have small, highly charged ions and vacant d or f-orbital of appropriate energy to accept lone pair of electron denoted by other groups or ligands. The ligands have been chosen because of their ability to forming complexes. A considerable work of binary complexes with metal ion has been reported but work on ternary complexes of transition metal is rather scanty\textsuperscript{1-5}. Besides the geometric co-ordination requirements of the metal ions, the polycladate character of the ligand, leading to different orientation of the side group also influence such interactions. Some mixed ligand ternary complexes\textsuperscript{6-8} of Cu(II), Ni(II), Fe(II), and Cr(II) with EDTA and hydroxy compounds have been reported resulting in which EDTA behaves as primary ligands. Engle and Khandkar\textsuperscript{9}, Kiranmail and coworker\textsuperscript{10}, Valechas & Mangonkar\textsuperscript{11}, Singh & Kumar\textsuperscript{12} have studied on the ternary systems.

Experimental:

All the reagents used were of AR grade. The solution of all the chemicals were prepared in doubly distilled water. The solution of transition metal nitrates were prepared and standardized by oxalic acid. Pyridine-2, 6-dicarboxilic acid was used in its monoprotonated form and prepared in calculated volume of KOH. The solution of FCA, KNO\textsubscript{3} and potassium hydrogen phthalate were prepared by direct weighing method and solution of KOH was prepared by standardization method.

The pH metric titration were carried out by ELICO (LI-613) pH meter fitted with a combined glass calomel electrodes assembly, used for entire pH , range (0 to 14) having an accuracy of ± 0.01 pH unit. The instrument was standardized against potassium hydrogen phthalate solution (0.05M) for pH -4 and standard buffer tablet solution (pH-9). Each titration was repeated at least twice against(0.0.1M) KOH solution at temperature 25±1\textdegree{}C and 40±1\textdegree{}C to ensure the reproducibility of result, keeping the ionic strength at 0.1 mole dm\textsuperscript{-3}(KNO\textsubscript{3}) and total volume (50ml) constant in the being of each titration .The measured pH values were plotted against the moles (m) of base (KOH) added per mole metal ion or ligand as depicted in the figures 1,2,3 and 4 being the representative curves for transition metals and ligands in the system 1: 1:1 M(II)-L-L' where M(II) =Cu(II), Ni(II) , Zn(II) and Co(II), L= PDA , L=FCA/HBAA.

The dissociation constant (Table-1) of PDA, FCA and HBBA were calculated by the method of Chaberck and Martell. The values were calculated from titration curves by the direct algebraic method for mono & dibasic ligands.
For mono-basic ligand-

\[
K_1 = \frac{[aCA + [H^+] - [OH^-]]}{[H^+][aCA + [H^+]]}
\]

\[
CA - [aCA + [H^+] - [OH^-]]
\]

For dibasic ligand-

\[
K_2 = \frac{[aCA + [H^+] - [OH^-]]}{[H^+][aCA + [H^+] - [OH^-]]}
\]

K_1 and K_2 are the first and second dissociation constants.

C_A = Total concentration for ligands

a = Number of moles of alkali added per mole of ligand.

The stability constants (log K_{MLL'}) for ternary mixed ligand complexes were calculated by the method of Ramamoorthy and Santappa^{13} for simultaneous complexation of ligand to the metal ion. The stability constants for the ternary system were calculated by the following expression.
Where $T_M$ = Total, metal ion concentration

$K_1$ and $K_2$ = The first and second dissociation constants of ligand (L)

The average (log $K_{MLL'}$) values were used to calculate the free energy ($\Delta G^0$), Enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) from the van’t Hoff’s isotherm.

The data are tabulated in table 2.

**Table 1 Dissociation constant of PDA, FCA and HBAA**

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$PK_1$</th>
<th>$PK_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25±1°C</td>
<td>40±1°C</td>
</tr>
<tr>
<td>PDA</td>
<td>2.63</td>
<td>2.57</td>
</tr>
<tr>
<td>FCA</td>
<td>2.90</td>
<td>2.75</td>
</tr>
<tr>
<td>HBAA</td>
<td>4.77</td>
<td>4.37</td>
</tr>
</tbody>
</table>

Table 2. The systems of section A and section B were potentiometrically titrated against 0.1M KOH solution at two different temperature Viz. 25±1°C and 40±1°C keeping ionic strength $m$ = 0.1M KNO$_3$ concentration of the metal ions and ligands ($5x10^{-3}$M) and total volume (50ml) constant at the beginning of each titration.
Results and Discussion:

![Chemical Structures](image)

**Section A:**

System 1:1:1M(II) – PDA – FCA

\[ M(\text{II}) = \text{Cu(II)}, \text{Ni(II)}, \text{Zn(II)} \text{ and Co (II)} \]

Curve f-Fig. (1 to 4)

10ml (0.025) Metal nitrate + 5ml (0.1M) KNO₃ + 10ml (0.025M) PDA + 10 ml (0.025M) FCA + diluted to 50 ml.

Curve (fig. 1 to 4) indicating the pH metric titration of 1:1:1 M(II) - PDA – FCA ternary system. The initial lowering of pH in this curve with comparison of curve of curve ‘d’ and ‘e’ (1:1 M(II) - PDA), [1:1, M(II) – FCA] followed by an inflection at \( m = 3 \) may by explained to the simultaneous addition of both the ligands to the metal ions forming 1:1:1 tenary complexes in solution.

One more inflection on this curve- f at \( m = 5 \) may probably be attributed to the decomposition of previously formed 1:1:1, ternary complex into metal hydroxide and free ligands.

\[
\begin{align*}
\text{M}^{\text{II}} + \text{PDA} + \text{FCA} + 3\text{OH}^- & \overset{0<m<3}{\longrightarrow} [\text{PDA}^{2-} - \text{M}^{2+} - \text{FCA}^-] + 3\text{H}_2\text{O} \\
[\text{PDA}^{2-} - \text{M}^{2+} - \text{FCA}^-] + 2\text{OH}^- & \overset{0<m<5}{\longrightarrow} \text{M(OH)}_2 + \text{FCA}^- + \text{PDA}^{2-}
\end{align*}
\]
Section B:-

System 1:1:1, M\textsuperscript{II}–PDA-HBAA

Curve f (fig 1 to 4)

Replacement of HBAA [10 ml (0.025M)] at the place of FCA

Potentiometric titration of 1:1:1 M\textsuperscript{II}–PDA–HBAA has been exhibited by the curve f (fig 1 to 4) lowering in the initial buffer region and well deflection at m=3 depicted the simultaneous complexation of both the ligands to the metal ion forming 1:1:1 ternary species as below,

M\textsuperscript{II} +PDA HBAA +3OH \rightleftharpoons [PDA2- -M2+ -HBAA] 3 H\textsubscript{2}O

Mono basic nature of HBAA is indicates the negligible ionization of the phenolic proton evidenced by the calculated percentage ionization (0.002%) at pH=7.85.

The simultaneous formation of ternary species may be further supported by the following facts-

1- Non-appearance of any solid phase during the formation of ternary species.

2- Constancy observed in the calculated values of formation constant.

It can be correlated in terms of increasing ionic potential (Φ) of the metal ion. The values of free energy change (ΔG\textsuperscript{0}), enthalpy (ΔH\textsuperscript{0}) and entropy (ΔS\textsuperscript{0}) of the resulting ternary complexes are recorded in table 2. The calculated ΔG\textsuperscript{0} has been found to be negative in all the systems indicating the spontaneity of the complex formation, calculated positive values of entropy (ΔS\textsuperscript{0}) indicates the formation of ternary complexes in the solution. The negative enthalpy (ΔH\textsuperscript{0}) values indicate the exothermic nature of the reaction.

CONCLUSION:

On the basis of above study the stability of various ternary complexes have been found in the order Cu(II)>Co(II)>Zn(II)>Ni(II). The observed order of stability of complexes may be correlated in terms of increasing polarisability of metal ion due to their decrease in size and increasing ionic potential (Φ) = charge/radius ratio. These compounds are antimicrobial sensitive and have great role in the preparation of antimicrobial medicines.\textsuperscript{14}

REFERENCES:


