

POLAROGRAPHIC STUDIES OF MIXED LIGAND COMPLEXES OF IN(III) WITH HISTIDINE AND PHTHALIC ACID

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ABSTRACT

Polarography investigations have been carried out on the ternary complexes formation of In(III) with Phthalic acid and Histidine at different concentrations of weak ligand (Phthalic acid) at 298 K temperature. The complexes have been studied polarographically at the DME, $\mu = 1M$ (KCl). The stability constants of In(III) with phthalic acid and amino acid was determined by method of deford and Hume while the stability constants of mixed ligand complexes have been evaluated by the method of Schapp and mcmasters. The reduction of the system in each case is quasireversible and diffusion controlled involving three electrons. The startical and electrostatic effects have also been discussed by using these stability constants. The mixing constants (Km) and stabilization constant (Ks) were calculated for comparative study of simple and mixed ligand complexes.

Keywords: Polarography Study, In(III), phthalic Acid, Histidine, Quasireversible Iron, Ternary Complex Diffusion Controlled.

Introduction

Complex forming species in biological material are numerous e.g. Amino acids, peptides, proteins, carboxylic acids, organic phosphates, nucleic acids. Since living organisms contains millions of protein made by simple amino acids, studies on mixed ligand complexes having at least one ligand as amino acid are of considerable interest. For an improved understanding of the driving forces leading to mixed ligand complexes in biological systems. We have carried out detailed studies on the formation equilibrium of binary and ternary complexes of In(III) with phthalic acid as primary ligand and Histidine as secondary ligand by polarography method.

Histidine (symbol His) is an α -amino acid that is used in the biosynthesis of proteins. Histidine is involved in a wide range of metabolic processes in the Histidine is used for rheumatoid arthritis allergic diseases, ulcers and anemia caused by Kidney failure or Kidney dialysis. Histidine is also responsible for keeping a normal pH of 7 is the by shutting protons to maintain a base in tissue and blood. Histidine is also vital in hemoglobin molecule that helps to shuttle oxygen around this body.

Schapp and mcmasters method has been used to calculate the formation constants of mixed-ligand complexes¹. The study of ternary complexes of different metal ions with amine acids and carboxylic acids have been carried out by many workers²⁻⁵. A study of stability constants of [Zn]-mixed ligand complexes of systems have been carried out by many workers⁶⁻⁷. Mixed ligand complexes of Pb(II) and Tl(I) with disuccinic acid and some amino acids in aqueous medium have been studied by K.K. Gupta and many authors⁸. Investigations on stability constants of Pb(II), Tl(I) and In(II) with Mercator succinic

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acid and succinic acid involving different amino acids have carried out by many workers⁹⁻¹¹. The stability constants of different mixed ligand systems of Cd(II) have been reported by many workers¹²⁻¹⁵.

Mixed ligand complexes of Cadmium with pyridine, amino acids, and many other ligands have been studied by many researchers.¹⁶⁻³³

In continuation of this work the present paper deals with the study of In(II) ion with amino acid (Histidine).

Experimental

A d.c. Manual polarograph with scale lamp type galvanometer. Kclsaturated calomel electrode, copper connecting wires and potentiometers was used to record polarograms. The test solutions was placed in an H-type cell with S.C.E. through an agar-agar saturated kclsalt bridge. Prior to polarography examination, purified nitrogen was streamed through the test solutions for 10 minutes to remove the dissolved oxygen. The current variation as a function of applied potential was then plotted to obtain the polarograms.

The capillary of the polarograph is having the following characteristics at height of mercury column (h_{hg}) of 95 cm.

$$M = 4.66 \text{ mg/sec}$$

$$T = 3 \text{ Sec.}$$

All chemicals used of AR grade and all solutions were prepared in conductivity water. The Phthalic acid and amino acid were used as complexing agents. Kcl used as supporting electrolytes to maintain the ionic strength of the solution at 0.1M. The temperature was maintained constant with ± 0.1 °C variation by using ultra Haake type thermostat.

Result and Discussion

Simple Systems

The stability constants of In(III) with phthalic acid and amino acid (Histidine) were determined by the method of deford and Hume. The values of formation constants of simple systems are recorded in Table-I.

Table 1: Stability constants of In(III) with Phthalic acid and Histidine

System	Log β_1	Log β_2	Log β_3
In(III) Phthalic Acid	1.675	2.729	4.338
In(III) Histidine	2.240	3.352	4.431

Mixed Ligand System

The maximum coordination numbers of In(III) is six [In(Pht)(his)] , [In(Pht)(His)₂] and [In(Pht)₂(His)]. Complexes would be expected with the bidentate ligand. In all the systems, solutions containing 1mm, 1M kcl was used. The two values (0.04 M and 0.2M) of weaker ligand (Phthalic acid) at constant concentration were used in study the mixed system of In-Phthalic acid-Histidine, while varying the concentration of the second ligand (Histidine). The slope of the straight line for the plot of E_{de} Vs $\log i/(i_d-i)$ in each case showing that the three electrons reduction is quasireversible.

In the presence of weaker ligand (Phthalic acid) there is a greater shift in half wave potential than in the absence. It favoured mixed ligand complex formation. The extended Schaap and mcmasters treatment was applied to the $E_{1/2}$ data and $F_{10}X_{1Y}$ function and linders graphical extrapolation method was applied to calculate A, B, C and D.

The stability constants β_{11} and β_{12} were calculated by using two values of B at two different concentrations and two values of C gave two values of β_{21} which will agree with each other. The mean value of log D is in well agreement with the log β_{30} . Values are recorded in the **Table 2, 3, 4.**

The Schemes 1-2 represent the results where the log values of the equilibrium constants are numerical.

**Table 2: Values of A, B, C and D for In-Phthalic acid-Histidine System
Phthalic acid concentration = 0.04M.**

System	Log A	Log B	Log C	Log D
In(III)-Pht-Histidine	0.041	2.486	3.553	4.414

**Table 3: Values of A, B, C and D for In-Phthalic acid-Histidine System
Phthalic acid Concentration = 0.2 M**

System	Log A	Log B	Log C	Log D
In(III) - Pht-Histidine	0.176	3.221	3.947	4.431

Table 4: Stability constants of mixed ligand complexes of In-Phthalic acid-Histidine system.

System	Log β_{11}	Log β_{12}	Log β_{21}
In(III)-Pht-Histidine	3.357	4.413	4.519

Scheme 1, can interpret the mixed ligand complex formation.

Entropy and electrostatic effects must be related to the largest part of the difference in logk therefore, charged complexes are formed. Amino Acids have a tendency to be added with [In(Phthalic acid)] and [In(Amino acid)] which can be compared.

Preference of the mixed-ligand complexation can be explained by the addition of Phthalic acid with [In(III)(amino acid)] and [In(III)(Phthalic acid)] and the logk values (1.117) and (1.054) for [In(III) Phthalicacid-Histidine] at different concentration of weak ligand respectively.

The formation of the metal weakers ligand [In(Phthalic acid)] and metal stranger ligand [In(Histidine)] complexes by adding a weaker ligand (Phthalic acid) can be interpreted with log K values (1.054) and (1.117) for the systems of In(III)-Phthalic acid-Histidine at 0.04M and 0.2M concentration of Phthalic acid, respectively.

The addition of the Phthalic acid to [In(Phthalic acid)₂], [In(Phthalic acid)(Histidine)] and [In(Histidine)₂] can be described with the help of log K (1.609) (1.056 and 1.67) for In(III). Phthalic acid-Histidine system and indicate that the addition of bio carboxylic acids are preferred to a weaker ligand.

[In(III)(Histidine)₂ (Phthalate)] are more stable than [In(III)-(Histidine)₃] complexes because the values of β_{21} are higher than β_{30} .

The disproportion constant K can be used to express the tendency of formation of simple and mixed ligand complexes for the equilibrium $2[\text{In(III)-Histidine}(\text{Phthalate})] = \text{In(III)-(Histidine)}_2 + \text{In(III)}(\text{Phthalate})_2$ calculation of the disproportion constants can be calculated by the equations.

$$\text{Log } X_{11} = 2 \log \beta_{11} - (\log \beta_{20} + \log \beta_{02})$$

$$\text{Log } X_{12} = 3 \log \beta_{12} - (\log \beta_{30} + 2 \log \beta_{03})$$

$$\text{Log } X_{21} = 3 \log \beta_{21} - (2 \log \beta_{30} + \log \beta_{03})$$

The calculated values of the log X_{11} , log X_{12} and log X_{21} are (=0.446, 0.132) and (0.357) for In(III)-Phthalic acid-Histidine at 0.04 M and 0.2M concentration of phthalic acid, respectively. These data revealed that all the ternary complexes are more stable.

The $\Delta \log K$ values can be calculated from the equations.

$$\Delta \log K_{11} = \log \beta_{11} = (\log \beta_{10} + \log \beta_{01})$$

$$\Delta \log K_{12} = \log \beta_{12} = (\log \beta_{10} + 2 \log \beta_{02})$$

$$\Delta \log K_{21} = \log \beta_{21} = (\log \beta_{20} + 2 \log \beta_{01})$$

The values of $\Delta \log K_{11}$, $\Delta \log K_{12}$ and $\Delta \log K_{21}$ are (-0.558, = 3.285) and (-0.508) for In(III)-(Histidine)-(Phthalic acid) system. Higher value of $\Delta \log K$ proved that the ternary complexes are more stable than expected from the statistical reasons.

The mixing constants are introduced for comparing the stability of simple and mixed ligand complexes.

$$K_m = \beta_{11}$$

$$(\beta_{02} \cdot \beta_{20})^{1/2}$$

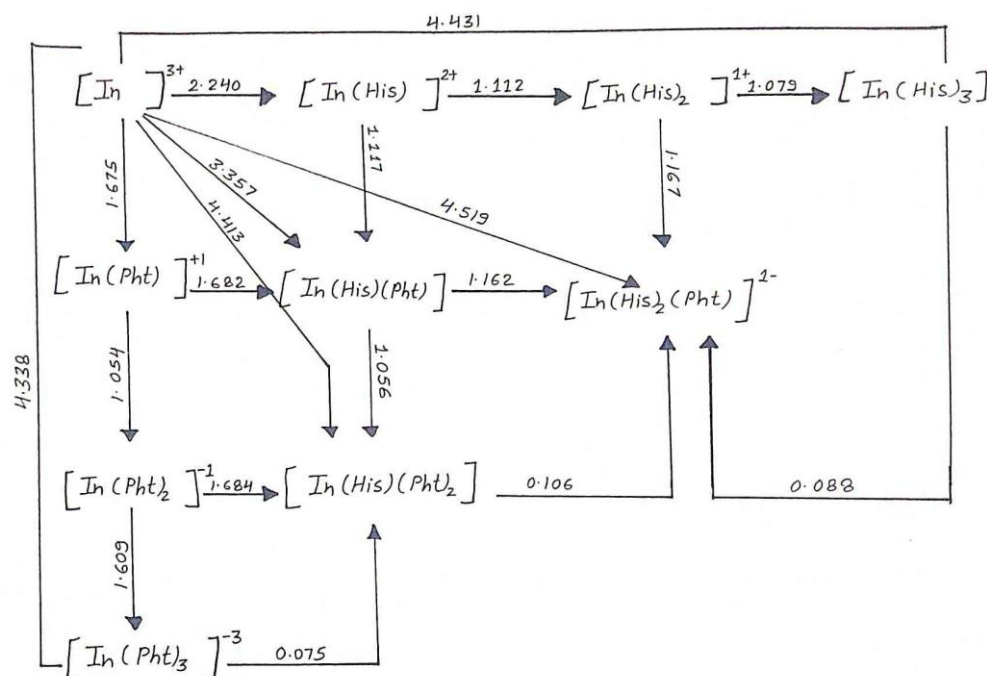
And the stabilization constants

$$\text{Log } K_s = \log K_m - \log 2$$

The log K_m value is (0.3175) and log K_s value is (0.0165) for In(III) – Phthalic acid – Histidine. The values of mixing and stabilization constant reveals that the ternary complexes are more stable than the binary complexes. The values of log K_m and log K_s are tabulated in Table 5.

Table 5: Values of the mixing constant (log Km) and stabilization constants (log Ks) for In(III) – Phthalic acid-Histidine system

System	Log Km	Log Ks
In(III) – pht-Histidine	0.3175	0.0165



Scheme 1: In(III) – Phthalic acid – Histidine system at 298K

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