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Formation constants of mixed ligand complexes of indium (III) with some amino acids (alanine, phenylalanine and serine) and phthalic acid at DME

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ABSTRACT

A polarographic study of In(III) with some amino acids (DL-Alanine, L-Serine, L-Phenylalanine) and Phthalic acid have been carried out separately at ionic strength kept constant ($\mu = 1$) by using KCl at 298K. The reduction of all the systems have been found to be quasireversible and diffusion controlled involving three electrons. The stability constants were determined by for the simple system of In(III) with phthalic acid and In(III) with amino acids first by method of DeFord and Hume and then the stability constants of mixed ligand complexes have been evaluated by the method of Schaap and McMaster.

Key words: In(III), Phthalic acid, DL-Alanine, L-Serine, L-Phenylalanine, Formation constants, Mixed ligand complexes, Polarographic study.

INTRODUCTION

Mixed ligand complexes are formed in solutions containing metal ion with two or more different ligands. A number of reviews have appeared on the stability of mixed ligand complexes. The kinetics of ligand interactions, structure and isomerism and analytical applications of certain types of reactions[1]. Most of the earlier studies on mixed ligand complexes are of spectrophotometer measurements[2,3]. Mixed ligand complexes of Rb and Cs metal salts of some organic acids have been studied with Quinaldinic acid N-oxide and 1, 10-Phenanthroline by many worker[4,5,6]. Formation constants of mixed ligand complexes of Cu(III) with β-Picoline, glycolate and lactate have been studied by P.K.S. Chauhan and coworkers[7]. Mixed ligand complexes of some transition metal chelates and Alkaline earth metal chelates have been carried out by many workers.[8,9] Stability constants of Cd(II) complexes with pyridine and some amino acids and Pb(II) complexes with b-Picoline and some amino acids have been studied by R. K. Paliwal and coworkers[10,11,12]. Mixed ligand complexes of Copper glycinate with Picolinic acid, Quinaldinic acid, Picolinic acid N-oxide, Quinaldinic acid-N-oxide and with O-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol and 1-nitroso-2-naphthol have been carried out by D. Prakash and coworkers[13,14]. The study of ternary complexes of different metal ions with amino acids and bicarboxylic acids have been carried out by many workers[15-18]. Study of biologically important ligands with different metals and their ability of complexation have been carried out by many workers[19,20]. Many workers studied the stability constants of Cd(II) and Pb(II) ion with amino acids and some bicarboxylic acids at DME[21-23].

The literature survey reveals that there is insufficient study and lack of data on the phthalic acid amino acids mixed complexes of In(III).

EXPERIMENTAL

The test solution were prepared in measuring flasks of pyrex glass using conductivity water. The solutions contain 1mM of In(III) with varying concentrations of strong ligands (DL-Alanine, L-Serine and L-Phenylalanine) and fixed concentrations of weak ligand (Phthalic acid). KCl used as supporting electrolyte to maintain the ionic strength of the solution at 0.1 M and 0.002%. The temperatures was maintained constant with in ± 0.1°C variation by using ultra Haake type thermostat.

A d.c. manual polarograph with scale lamp type galvanometer, KCl saturated calomel electrode, copper connecting wires and potentiometer was used. The test solution was placed in an H-type cell coupled with S.C.E. through an agar-agar, saturated KCl salt bridge. Prior to polarographic examination, purified nitrogen was streamed through the test solution for 10 minutes to remove the dissolved oxygen. The current variation as a function of applied potential was then plotted to obtain the polarogram.

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

$$m = 4.66 \text{ mg/Sec.}$$
$$t = 3 \text{ Sec}$$

RESULTS

Simple Systems

The simple complexes of In(III) with DL-Alanine, L-Serine, L-Phenylalanine and Phthalic acid were first investigated and their overall formation constants were evaluated by the DeFord and Hume's method[24].

In the case of each ligand In(III) forms 1:3 highest complex species. In all the case, the

Table 1: Stability constants of In(III) with PA and amino acids

System	Logβ_1	Logβ_2	Logβ_3
In-Phthalic acid	1.675	2.729	4.338
In-Alanine	5.218	5.944	7.544
In-Phenylalanine	2.626	3.511	5.079
In-Serine	3.103	4.124	5.612

Table 2: Values of A,B,C, and D for In-PA-Amino acid systems PA concentration = 0.04M

System	LogA	LogB	LogC	LogD
In-PA-Alaninate	1.812	5.246	6.392	7.556
In-PA-Phenylalaninate	0.079	2.906	3.543	5.167
In-PA-Serinate	0.146	3.246	4.147	5.591

Table 3: Values of A,B,C, and D for In-PA-Amino acid systems PA concentration = 0.2M

System	LogA	LogB	LogC	LogD
In-PA-Alaninate	2.041	5.440	6.945	7.568
In-PA-Phenylalaninate	0.054	3.839	3.968	5.170
In-PA-Serinate	0.531	3.959	4.491	5.602

reduction of simple complexes was diffusion controlled as revealed by straight line plots of i_d Vs $\sqrt{h_{eff}}$ and indicates the reduction is quasireversible. The values of formation constants of simple systems are presented in Table 1.

Mixed systems

The maximum co-ordination number of Indium is six [In (Amino acid)], [In (PA)(Amino acid)$_2$] and [In $(PA)_2$ (Amino acid)] complexes would be expected with the two different bidentate ligands. In all the systems solution containing 1.0 mM In(III), 1M KCl was used. The two values (0.04M and 0.2M) of weaker ligand (PA) at constant concentration were used to study the mixed system of In-PA-Amino acids, while varying the concentration of the second ligand (PA) in each case. The slope of the straight line was 40 mV for the plot of E_{d-e} vs log i/i_d-i in each case showing that the three electron reduction is quasireversible.

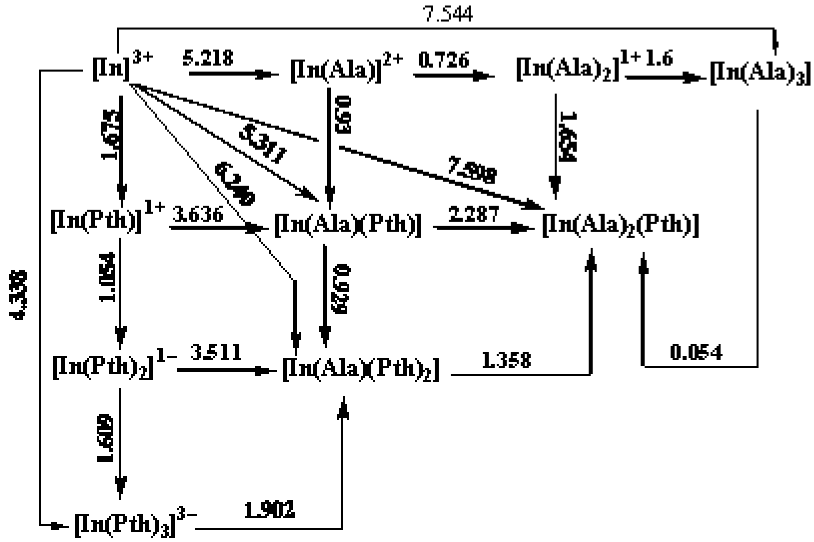
In the presence of weaker ligand (PA) there is a greater shift in half wave potential than in its absence. It favoured mixed ligand complex formation. The extended Schaap and McMasters treatment was applied to the $E_{½}$ data and F_{10}[X,Y]

Table 4: Stability constants of mixed ligand complexes of In-PA-Amino acids system

System	Logβ_1	Logβ_2	Logβ_3
In-PA-Alaninate	5.311	6.240	7.598
In-PA-Phenylalaninate	3.585	5.155	5.179
In-PA-Serinate	3.750	5.225	5.644

Table 5: Values of the mixing constant (logK_m) and stabilization constant (logK_s) for Indium-PA-Amino acids systems

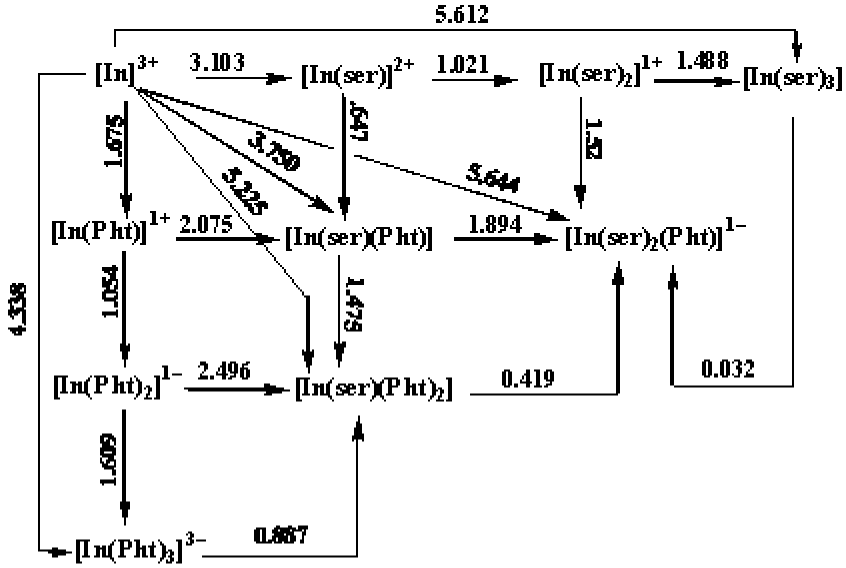
Systems	LogKm	logKs
In-PA-Alaninate	0.974	0.673
In-PA-Phenylalaninate	0.465	0.164
In-PA-Serinate	0.323	0.022



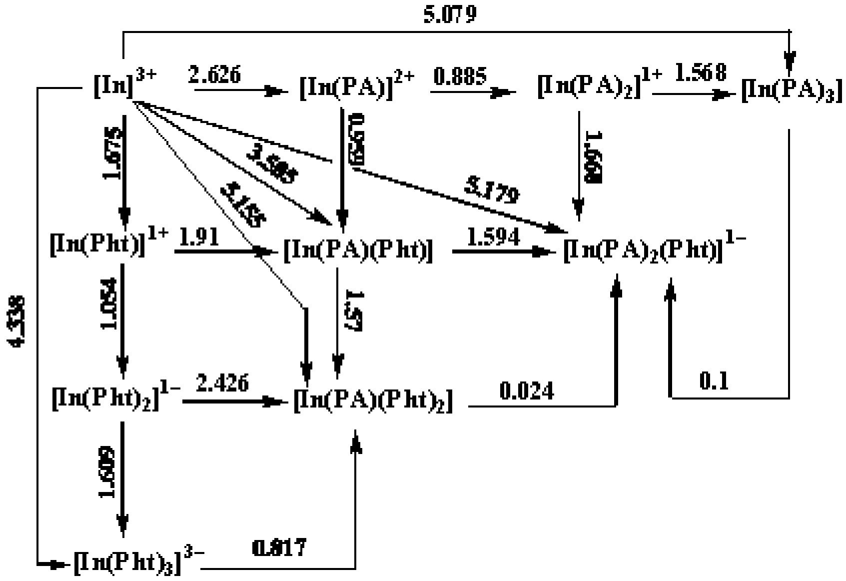
Scheme 1: In(III)-Phthalic acid-DL-Alanine system at 298K

function and Lendend's graphical extrapolation method was applied to calculate A,B,C and D[25,26]. The Stability Constants b_{11} and b_{12} were calculated by using two values of b at two different concentrations and two values of C gave two values of b_{21} which well agree with each other. The mean values of logD is in well agreement with the $\log b_{30}$. values are given in the form of Table 2 to 4.

The Schemes 1-3 represent the results where the log values of the equilibrium constants are numerical.

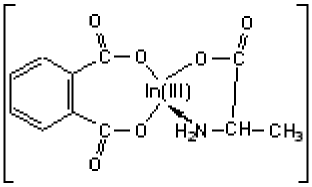


Scheme 2: In(III)-Phthalic acid-L-Serine system at 298K

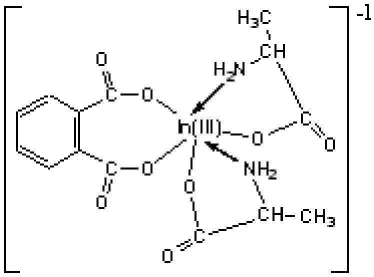


Scheme 3: In(III)-Phthalic acid-L Phenylalanine System at 298K

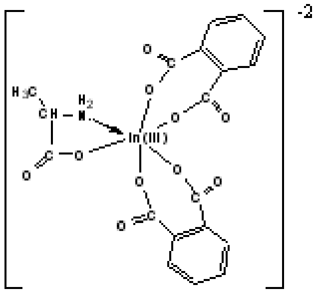
The tentative structure of metal ligand complexes are shown below:-
[In(III)- Phthalic acid-Alanine] complexes



[1:1:1 Complex]

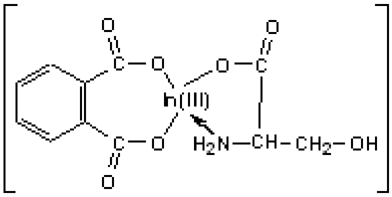


[1:1:2 Complex]

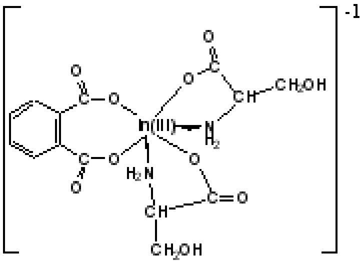


1:2:1 Complex

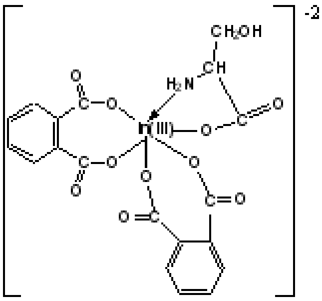
[In(III)-Phthalic acid-Serine] complexes



[1:1:1 Complex]

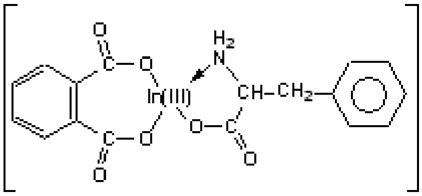


[1:1:2 Complex]

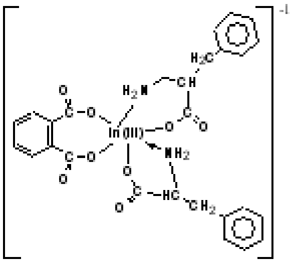


1:2:1 Complex

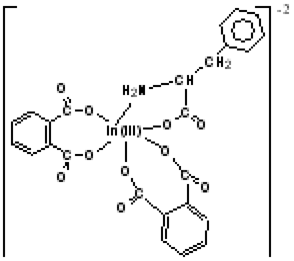
[In(III)-Phthalic acid-Phenylanine] complexes



[1:1:1 Complex]



[1:1:2 Complex]



1:2:1 Complex

DISCUSSION

Scheme 1-3 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 formed.

Amino acids have a tendency to be added with [In(PA)] and [In (Amino acid)] which can be compared.

Preference of the mixed ligand complexation can be explained by the addition of PA with the In(Amino acid) and In (PA) and the logK values (0.93, 1.054),(0.959, 1.054) and (0.647, 1.054) for Indium-PA-Alaninate, Indium-PA-

Phenylalninate and Indium-PA-Serinate systems, respectively.

The addition of the PA to $In(PA)_2$, In(PA) (Amino acid) and In(Amino acid)$_2$ can be described by the help of logK (1.609,0.929, 1.654), (1.609, 1.57, 1.668) and (1.609, 1.475, 1.52) for Indium-PA-Alaninate, Indium-PA-Phenylalaninate and Indium-PA-Serinate, respectively and indicates that addition of bicarboxylic acids are preferred to a weaker ligand.

The logK values for addition of (PA) to $In(PA)_2$, In(Amino acids, PA) and In(Amino acids)$_2$ are (1.609, 0.929, 1.654), (1.609, 1.57, 1.668) and (1.609, 1.475, 1.52) complexes respectively showing that addition of Phthalate ion is preferred. [In(Amino acid)$_2$(PA)] are more stable than [In(Amino acid)$_3$] complexes because the values of b_{21} are higher than b_{30}.

The disproportion constant K can be used to express the tendency of formation of simple and mixed ligand complexes for the equilibrium.
2[In(Amino acid) (PA)] = In(Amino acid)$_2$ + $In(PA)_2$
calculation of the disproportion constants can be made by the equations.

$$\text{Log } X_{11} = 2\log\beta_{11} - (\log\beta_{20} + \log\beta_{02})$$
$$\text{Log } X_{12} = 3\log\beta_{12} - (\log\beta_{30} + \log\beta_{03})$$
$$\text{Log } X_{21} = 3\log\beta_{21} - (2\log\beta_{30} + \log\beta_{03})$$

The calculated values of the $\log X_{11}$, $\log X_{12}$ and $\log X_{21}$ are (1.948, 2.498, 3.367), (0.93, 1.701, 1.025) and (0.646, 1.409, 1.417) for Indium-PA-Alaninate, Indium-PA-Phenylalaninate and Iudium-PA-Serinate, respectively. These reveal that all the ternary complexes are more stable.

The Δ logK values can be calculated from the equations

$$\Delta\log K_{11} = \log\beta_{11} - (\log\beta_{10} + \log\beta_{01})$$
$$\Delta\log K_{12} = \log\beta_{12} - (\log\beta_{10} + \log\beta_{02})$$
$$\Delta\log K_{21} = \log\beta_{21} - (\log\beta_{20} + \log\beta_{01})$$

The values of $\Delta\log K_{11,}$ $\Delta\log K_{12}$ and $\Delta\log K_{21}$ are (-1.58, -1.7,-0.021), (-0.716, -0.20, -0.007) and (-0.028, -0.607, -0.155) for Indium-PA-Alaninate, Indium-PA-Phenylalaninate and Indium-PA-Serinate respectively. Higher values of DlogK 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.

$$K_m = \frac{\beta_{11}}{(\beta_{02}, \beta_{20})^{1/2}}$$

and the stabilization constants

$$\log K_s = \log K_m - \log 2$$

The $\log K_m$ values are (0.974, 0.465, 0.323) and $\log K_s$ values are (0.673, 0.164, 0.022) for Indium-PA-Alaninate, Indium-PA-Phenylalaninate and Indium-PA-Serinate respectively. 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.

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