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POLAROGRARPHIC DETERMINATION OF THE FORMATION CONSTANTS OF THE MIXED LIGAND COMPLEXES OF CD (II) WITH ITACONIC ACID AND SOME AMINO ACIDS (ASPARGINE AND GLUTAMINE)

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ABSTRACT

A polarographic study of Cd(II) with some amino acids and Phthalic acid have been carried out separately at ionic strength kept constant (μ = 1) by using KC1 at 298K. The stability constants of Cd(II) with Itaconic acid and some amino acids were determined by the method of DeFord and Hume while the stability constants of mixed-ligand complexes have been evaluated by the method of Schaap & McMaster's. The reduction of the system in each case is reversible and diffusion controlled, involving two electrons. The statistical 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: Itaconic acid, electrochemical, mixed-ligand complexes, Polarographic study, reversible reduction and Cd(II).

INTRODUCTION

Mixed-ligand complexes are formed in solutions containing metal ion with two or more different ligands. Polarography plays very important role in identification of mixed-ligand complexes of different kinds. Many workers [1-4] have studied biologically active metal complexes of aminoacids which are important in anlaytical, biochemical and pharmaceutical fields [5-7] and attract wide attention in different fields of research. Most of the earlier studies on mixed-ligand complexes are of spectrophotometer measurements[8,9]. Mixed-ligand complexes of Rb and Cs Metal salts of some organic acids have been studied by many workers[10,11,12.] Stability constants of mixed-ligand complexes of Cd(II) and Cu(II) have been studied by many workers [13-16]. The study of ternary complexes of different metal ions with amino acids and bicarboxylic acids have been carried out by many workers [17-20]. Study of biologically important ligands with different metals and their ability of complexation have been carried out by many workers[21,22]. Electroanalytical investigations on some complexes of Cd(II)-Tyrptophan-Bicarboxylic acids have been carried out by Bhavna Yadav and C.P. Singh Chandel.[25,26]

Study of stability constants of [Zn-L-Amino Acidate-Vitamin-PP] Systems have been carried out by K. Rai, F. Khan.[27] Mixed-ligand complexes of Pb(II) and Tl(I) with this discuccinic acid and some amino acids in aqueous medium have been studied by K.K. Gupta, T. Gaur, E. Dadhich using Polarographic method.[28] Polarographic determination of Stability constants of mixed ligand complexes of Zn(II) have been carried out by many authors.[29].

The survey of literature reveals that there is lack of data on the mixed ligand complexes of Cd(II) ion with amino acids and Ita conic acid. Hence the present work has been undertaken for the study.

2. Experimental

A. d.c. manual polarograph with scale-lamp type galvanometer, KC1 saturated calomel electrode, copper connecting wires and potentiometer was used to record polarograms. The test solution was placed in an H-type cell coupled with S.C.E. through an agar-agar saturated KC1 salt bridge. Prior to polarographic examination, purified nitrogen was streamed through the test solution

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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 mg/sec

t = 3 sec

All chemicals used were of AR grade and all solutions were prepared in conductivity water. The Itaconic acid and amino acids were used as complexing agents. KC1 used as supporting electrolyte to maintain the ionic strength of the solution at 0.1M. The temperature was maintained constant with in ± 0.1°C variation by using ultra Haake type thermostat.

3. Results and Discussion

3.1 *Simple systems:*

The stability constants of Cd(II) with Itaconic acid and amino acids (Asparagine and Glutamine) were determined by the method of DeFord and Hume [24]. The values of formation constants of simple systems are recorded in Table 1.

Table 1: Stability constants of Cd(II) with Itaconic acid and amino acids.

System	log β_1	logβ_2	log β_3
Cd(II)-Itaconic acid	1.676	2.730	4.338
Cd(II)-Asparagine	4	6.204	9.414
Cd(II)-Glutamine	2.917	3.727	5.851

3.2 *Mixed-ligand systems:*

The maximum co-ordination number of Cd(II) is six [Cd(Ita)(amino acid)], [Cd(Ita)(amino acids)$_2$] and [Cd(Ita)$_2$(amino acids)] complexes would be expected with the two different bidentate ligands. In all the systems, solutions containing 0.5 mM Cd(II), 1 M KC1 was used. The two values (0.04 M and 0.2 M) of weaker ligand (Itaconic acid) at constant concentration were used to study the mixed system of Cd-Itaconic acid-amino acids, while varying the concentration of the second ligand (Glutamine, Asparagine) in each case. The slope of the straight line was 31 ± 1 mV for the plot of E_{de} VS log $i/(i_d-i)$ in each case showing that the two electron reduction is reversible.

In the presence of weaker ligand (Itaconic acids) 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_{12} data and $F_{10}[X,Y]$ function and Lendend's graphical extrapolation method was applied to calculate A, B, C and D [25,26].

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 well agree with each other. The mean value of log D is in well agreement with the log β_{30}. Values are recorded in the Tables 2-4.

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 Cd-Itaconic acid—amino acids systems. Itaconic acid concentration = 0.04 M

System	log A	log B	log C	log D
Cd(II)-Ita-Asparaginate	1.65	4.25	8.05	9.39
Cd(II)-Ita-Glutaminate	0.11	3.03	4.47	5.81

Table 3: Values of A, B, C and D for Cd-Itaconic acid-amino acids systems. Itaconic acid concentration = 0.2M

System	log A	log B	log C	log D
Cd(II)-Ita-Asparaginate	2.39	5.19	8.74	9.41
Cd(II)-Ita-Glutaminate	0.39	3.65	5.18	5.84

Table 4: Stability constants of mixed ligand complexes of Cd-Itaconic acid-amino acids systems.

System	log β_{11}	logβ_{12}	log β_{21}
Cd(II)-Ita-Asparaginate	4.786	6.527	9.447
Cd(II)-Ita-Glutaminate	3.544	4.875	5.782

Schemes 1-2 can interpret the mixed-ligand complex formation. Entropy and electrostatic effects must be related to the largest part of the difference in log K therefore, charged complexes are formed. Amino acids have a tendency to be added with [Cd(Itaconic acid)] and [Cd(Amino acids)] which can be compared.

Preference of the mixed-ligand complexation can be explained by the addition of Itaconic acid with Cd(II) (amino acids) and Cd(II) (Itaconic acid) and the log K values (2.204, 0.786) and (0.697, 0.627) for cadmium-Itaconic acid-Asparaginate and cadmium-Itaconic acid -Glutaminate systems respectively.

The formation of the metal weaker ligand [Cd(Itaconic acid)] and metal stronger ligand [Cd(Amino acids)] complexes by adding a weaker ligand (Itaconic acid) can be interpreted with log K values (1.054, 3.111) and (1.054, 1.869) for the systems of Cadmium(II)-Itaconic acid-Asparaginate and Cadmium(II)-Itaconic acid-Glutaminate respectively.

The addition of the Itaconic acid to Cd(Itaconic acid)$_2$, Cd (Itaconic acid, Amino acids) and Cd(Amino acid)$_2$ can be described with the help of log K (2.663, 1.741, 3.243) and (2.663, 1.331, 3.502) for Cadmium(II)- Itaconic acid-Glutaminate respectively and indicate that the addition of bicarboxylic acids are preferred to a weaker ligand.

The log K values for addition of Itaconic acid to Cd(II)-(Itaconic acid)$_2$ Cd(II)-(Amino acids, Itaconate) and Cd(II)-(Amino acids)$_2$ are (2.663, 1.741, 3.243) and (2.663, 1.33, 2.238) Itaconate ion is preferred.

[Cd(II)-(Amino acids)$_2$(Itaconate)] are more stable than [Cd(II)- (Amino acids)$_3$1 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[Cd(II)-(Amino acid)(Itaconate)] = Cd(II)-(Amino acids)$_2$ + Cd(II)- (Itaconate)$_2$ calculation of the disproportion constants can be calculated by the equations

$\log x_{11} = 2 \log \beta_{11} — (\log\beta_{20} + \log \beta02)$

$\log x_{12} = 3 \log \beta_{12} — (\log\beta_{30} + 2 \log \beta03)$

$\log x_{21} = 3 \log \beta_{21} — (2 \log\beta_{30} + \log \beta03)$

The calculated values of the log X_{11}, log X12 and log X21 are (0.640, 1.491, 5.175) and (0.632, 0.098, 1.308) for Cadmium(II)-Itaconic acid-Asparaginate and Cadmium(II)-Itaconic acid-Glutaminate respectively. These data revealed that all the ternary complexes are more

stable.

The A logK values can be calculated from the equations.

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

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

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

The values of $\Delta \log K_{11}$, $\Delta \log K_{12}$ and $\Delta \log K_{21}$ are (-0.885,-0.202, 1.56) and (-2.108, -6.706, -6.072) for Cadmium(II)-Itaconic acid-Asparaginate and Cadmium(II)-Itaconic acid-Asparaginate and Cadmium(II)-Itaconic acid- Glutaminate, respectively Higher values of Δ 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.

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

and the stabilization constants

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

The $\log K_m$ values are (0.320 and 0.316) and $\log K_s$ values are (0.019 and 0.015) for Cadmium(II)-Itaconic acid-Asparaginate and Cadmium(II)-Itaconic acid-Glutaminate, 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 Ks

are tabulated in Table 5.

Table 5: Values of the mixing constant ($\log K_m$) and stabilisation constants ($\log K_s$) for cadmium-Itaconic acid-Amino acids sytems.

System	Log K_m	log K_s
Cd(II)-Ita-Asparaginate	0.320	0.019
Cd(II)-Ita-Glutaminate	0.316	0.015

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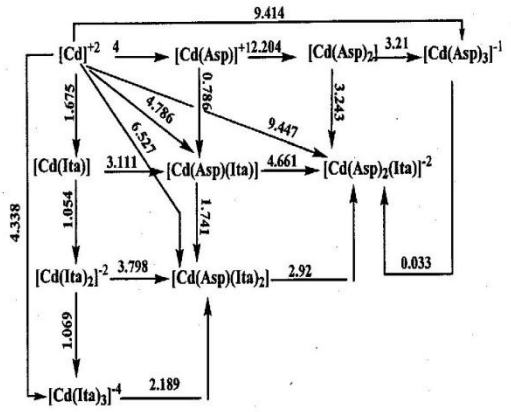
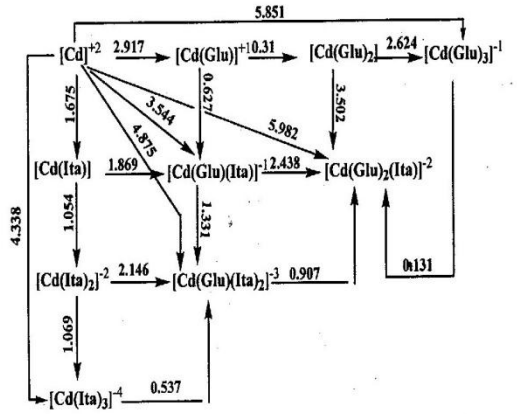


Scheme 1. Cd(II)-Ita-Asparaginate system.



Scheme 2. Cd(II)-Ita-Glutaminate System.

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