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Stability Constants of Ternary Complexes of Cd(II) with Itaconic Acid and Some Amino Acids: A Polarographic Approach

CHANCHAL KARADIA and O.D. GUPTA*
Department of Chemistry, University of Rajasthan, Jaipur-302 055, India
E-mail: gupta_od@yahoo.co.in

A polarographic study of Cd(II) with some amino acids (alanine, phenylalanine and tyrosine) and phthalic acid have been carried out separately at ionic strength kept constant ($\mu = 1$) by using KCl at 298 K. The stability constants of Cd(II) with itaconic acid and some amino acids were measured by the method of DeFord and Hume while the stability constants of mixed complexes have been evaluated by the method of Schaap & McMaster's. The reduction of the system in each case is reversible and diffusion control, involving two electrons. The statistical and electrostatic effects have also been discussed by using these stability constants. The mixing constants (K_m) and stabilization constant (Ks) were measured for comparative study of simple and mixed ligand complexes.

Key Words: Itaconic acid, Electrochemical, Mixed complexes, Polarographic study, Reversible reduction and Cd(II), L-Tyrosine, L-Phenylalanine, L-Alanine.

INTRODUCTION

Mixed ligand complexes are formed in solutions containing metal ion with two or more different ligands. Polarography plays important role in identification of mixed ligand complexes of different kinds. Many workers[1-4] have studied biologically active metal complexes of amino acids 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]. Stability constants of mixed ligand complexes of Cd(II) and Cu(II) have been studied in past[12-14]. The study of ternary complexes of different metal ions with amino acids and bicarboxylic acids have also been reported[14-17]. Study of biologically important ligands with different metals and their ability of complexation have been carried out by many workers[18,19].

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

EXPERIMENTAL

A d.c. manual polaograph with scale lamp type galvanometer, KCl saturated calomel electrode, copper connecting wires and potentiometer was used to record polarogram. 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 min 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.

$$m = 4.66 \text{ mg/s} \qquad t = 3 \text{ s}$$

All chemicals used were of AR grade and all solutions were prepared in double distilled water. Itaconic acid and amino acids were used as complexing agents. KCl used as supporting electrolyte to maintain the ionic strength of the solution at 0.1 M and 0.002 %. The temperature was maintained constant within ± 0.1 °C variation by using ultra Haake type thermostat.

RESULTS AND DISCUSSION

Simple systems: The stability constants of Cd(II) with itaconic acid and amino acids (alanine, phenylalanine and tyrosine) were determined by the method of DeFord and Hume[20]. The values of formation constants of simple systems are presented in Table-1.

TABLE-1
STABILITY CONSTANTS OF Cd(II) WITH ITACONIC ACID AND AMINO ACIDS

System	log β_1	log β_2	log β_3
Cd-Itaconic acid	1.676	2.730	4.338
Cd-Alanine	5.399	7.899	9.748
Cd-Phenylalanine	3.977	4.397	6.544
Cd-Serine	4.000	6.204	9.414

Mixed systems: The maximum coordination number of cadmium is six [Cd(Ita)(amino acid)], [Cd(Ita)(amino acids)$_2$] and [Cd(Ita)$_2$(amino acids)] and complexes would be expected with the two different bidentate ligands. In all the systems solution containing 0.5 mM Cd(II), 1 M KCl 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 (itaconic acid) 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 $E_{1/2}$ data and $F_{10}[X,Y]$ function and Lendend's graphical extrapolation method was applied to calculate A, B, C and D[21,22].

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 1og D is in well agreement with the log β_{30}. Values are given in the form of Tables 2-4.

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-Ita-Alaninate	2.830	5.601	8.515	9.732
Cd-Ita-Phenylalaninate	0.959	4.007	5.267	6.579
Cd-Ita-Serinate	1.653	4.251	8.055	9.397

TABLE-3
VALUES OF A, B, C AND D FOR Cd-ITACONIC ACID-AMINO ACIDS SYSTEMS;
ITACONIC ACID CONCENTRATION = 0.2 M

System	log A	log B	log C	log D
Cd-Ita-Alaninate	3.653	6.558	9.121	9.740
Cd-Ita-Phenylalaninate	1.176	4.227	5.916	6.588
Cd-Ita-Serinate	2.397	5.196	8.749	9.414

TABLE-4
STABILITY CONSTANT OF MIXED LIGAND COMPLEXES OF
Cd-ITACONIC ACID-AMINO ACIDS SYSTEMS

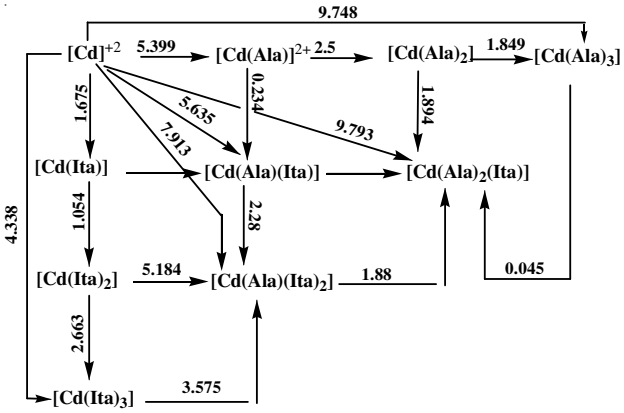
System	log β_{11}	log β_{12}	log β_{21}
Cd-Ita-Alaninate	5.633	7.913	9.793
Cd-Ita-Phenylalaninate	4.079	5.096	6.602
Cd-Ita-Serinate	4.786	6.527	9.447

The **Schemes I** and **II** represent the results where the log values of the equilibrium constants are numerical.

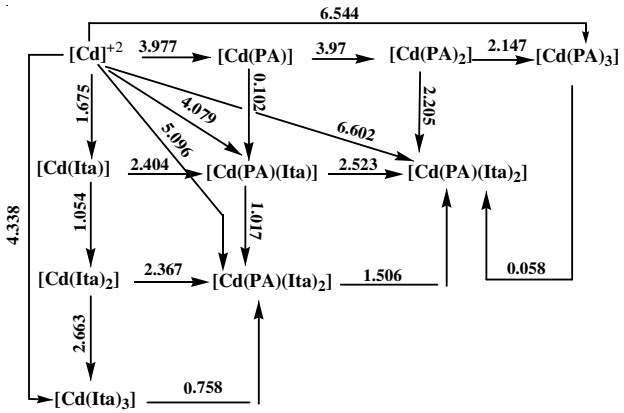
Schemes I-III can interpret the mixed ligand complex formation. Entropy and electrostatic effects must be related to the largest part of the difference in log K therefore, charged complexes formed.

Amino acids have a tendency to be added with [Cd(itaconic acid)] and [Cd(amino acids)] which can be compared.

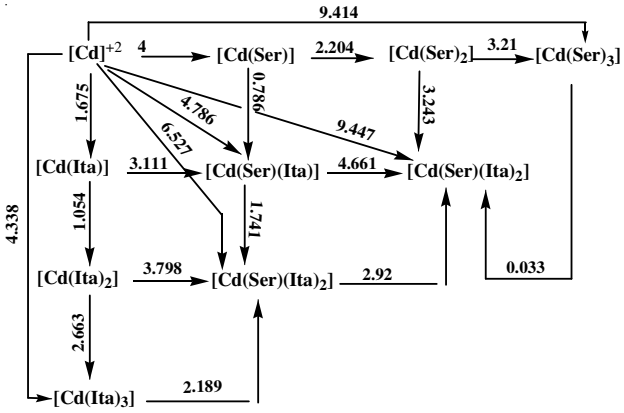
Preference of the mixed ligand complexation can be explained by the addition of itaconic acid with Cd (amino acids) and Cd (itaconic acid) and the log K values (2.5, 0.234) (0.42, 0.102) and (2.204, 0.786) for cadmium-itaconic acid-alaninate, cadmium-itaconic acid-phenylalaninate and cadmium-itaconic acid-serinate systems, respectively.



Scheme-I: Cd-Ita-Alaninate system



Scheme-II: Cd-Ita-Phenylalaninate system



Scheme-III: Cd-Ita-Serinate system

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 (2.663, 5.184) (1.054, 2.404) and (1.054, 3.111) for the systems of cadmium-itaconic acid-alaninate, cadmium-itaconic acid-phenylalaninate and cadmium-itaconic acid-serinate, 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 by the help of log K (2.663, 2.280, 1.894) (2.663, 1.017, 2.205) and (2.663, 1.741, 3.243) for cadmium-itaconic acid-glutaminate, respectively and indicates that the addition of bicarboxylic acids are preferred to a weaker ligand.

[Cd(Amino acids)$_2$(itaconate)] are more stable than [Cd(amino acids)$_3$] 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[Cd(Amino acid) (itaconate)] = Cd (amino acids)$_2$ + Cd(itaconate)$_2$ calculation of the disproportion constants can be made by the equations

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

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

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

The calculated values of the log X_{11}, log X_{12} and log X_{21} are (0.636, 5.314, 5.542) (1.032, 0.0707, 2.38) and (0.640, 1.491, 5.175) for cadmium-itaconic acid - alaninate, cadmium-itaconic acid-phenylalaninate and cadmium-itaconic acid- serinate, respectively. The reveal that all the ternary complexes are more stable.

The Δ log K values can be calculated from the equations.

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

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

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

The values of $\Delta \log K_{11}$, $\Delta \log K_{12}$ and $\Delta \log K_{21}$ are (-1.44, -0.214, 0.219) (-1.572, -1.609, 0.53) and (-0.885, -0.202, -1.56) for cadmium-itaconic acid-alaninate, cadmium-itaconic acid-phenylalaninate and cadmium-itaconic acid-serinate, 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.

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

and the stabilization constants

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

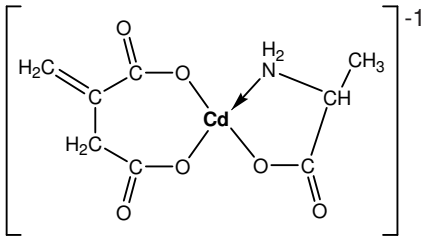
The log K_m values are (0.319, 0.516 0.320) and log K_s values are (0.018, 0.215, 0.019) for cadmium-itaconic acid-alaninate, cadmium-itaconic acid-phenylalaninate and cadmium-itaconic acid-serinate, respectively. The values of mixing and stabilization constant reveals that the ternary complexes are more stable than the binary complexes. The values of log K_m and log K_s are tabulated in Table-5.

TABLE-5
VALUES OF THE MIXING CONSTANT (log K_m) AND STABILIZATION CONSTANTS (log K_s) FOR CADMIUM-ITACONIC ACID-AMINO ACIDS SYSTEMS

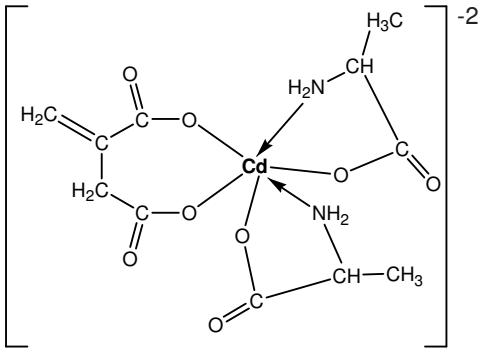
System	log K_m	log K_s
Cd-Ita-Alaninate	0.319	0.018
Cd-Ita-Phenylalaninate	0.516	0.215
Cd-Ita-Serinate	0.320	0.019

The tentative structure of metal complexes are shown below:

[Cd-Itaconic acid-alanine] complexes



[1:1:1 Complex]



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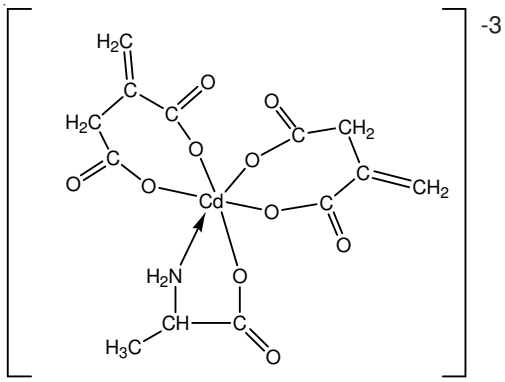
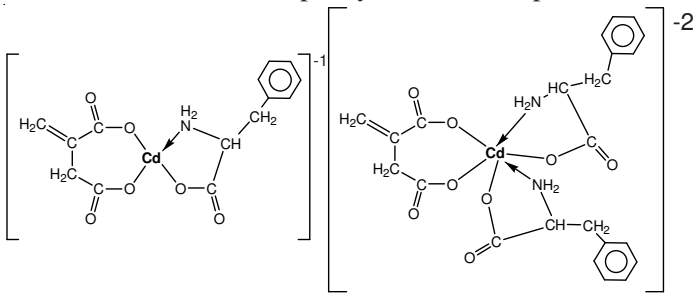


[1:2:1 Complex]

[Cd-Itaconic acid-phenylalanine] complexes



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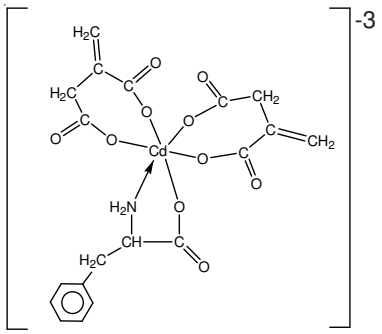
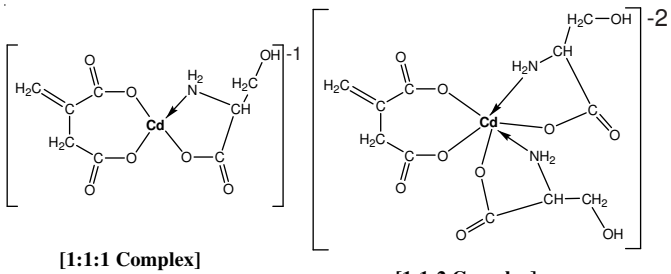
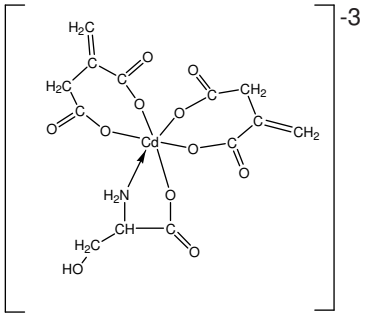


[1:2:1 Complex]

[Cd-Itaconic acid-serine] complexes



[1:1:1 Complex] **[1:1:2 Complex]**



[1:2:1 Complex]

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REFERENCES

1. R. Andreoli, L. Benedeti, G. Grandi, Baltistuzzi and G. Gavioli, *Electrochim. Acta*, **29**, 227, (1984).
2. R.S. Saxena and S.K. Dhawan, *Trans. SAEST*, **18**, 131 (1983).
3. M.Y. Mazumdar and B.I. Nemadi, *J. Electrochem. Soc. (India)*, **30**, 316 (1981).
4. M.D. Manuvrarui, Iseam and B.G. Bhat, *Trans SAEST*, **16**, 215 (1981).
5. R.N. Patal, H.C. Panday and K.B. Panday, *Bull. Electrochem.*, **12**, 612 (1996).
6. F. Khan and P.L. Sahu, *Ultra Scientist Phys. Sci.*, **12**, 106 (2000).
7. B.K. Singh, C.L. Jain and R.S. Sindhu, *Trans SAEST*, **30**, 4 (1995).
8. G. Schwarzenbach and A. Will, *Helv. Chem. Acta*, **34**, 528 (1951).
9. G. Schwarzenbach and J. Heller, *Helv. Chem. Acta*, **34**, 576 (1951).
10. D. Prakash, A.K. Gupta, S. Kumar and A.K. Yadav, *Orient. J. Chem.*, **18**, 295 (2002).
11. D. Prakash, K.B. Sinha, Brahmeshwar and R. Pravesh, *Orient. J. Chem.*, **21**, 77 (2005).
12. P.K.S. Chauhan, A. Verma and R.K. Paliwal, *Orient. J. Chem.*, **21**, (2005).
13. A. Verma, P.K.S. Chauhan and R.K. Paliwal, *Orient. J. Chem.*, **20**, (2004).
14. M.K. Verma and C.P.S. Chandel, *Orient. J. Chem.*, **21**, 22 (2005).
15. V. Malhotra and C.P.S. Chandel, *J. Ultra Scientist Phy. Sci.*, **18**, 203 (2006).
16. K.R. Jangid and C.P.S. Chandel, *Ultra Chemist*, **2**, 113 (2006).
17. V. Malhotra and C.P.S. Chandel, *Bull. Electrochem.*, **22**, 301 (2006).
18. S.K. Singh and C.P.S. Chandel, *Bull. Electrochem.*, **17**, 265 (2001).
19. C.P.S. Chandel and S.K. Singh, *Orient. J. Chem.*, **17**, 239 (2001).
20. D.D. DeFord and D.N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
21. B. Schaap and D.L. McMasters, *J. Am. Chem. Soc.*, **83**, 4699 (1961).
22. I. Lenden, *Phys. Chem.*, **188**, 160 (1941).

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