Oriental Journal of Chemistry Vol. **24**(3), 1001-1008 (2008)

Electrochemical studies on mixed-ligand complexes of Cd(II) with itaconic acid and some amino acids

CHANCHAL KARADIA and O.D. GUPTA*

Department of Chemistry, University of Rajasthan, Jaipur - 302 004 (India).

(Received: September 20, 2008; Accepted: November 24, 2008)

ABSTRACT

A polarographic study of Cd(II) with some amino acids and Itaconic acid have been carried out separately at ionic strength kept constant (μ = 1) by using KCl at 298K. DeFord and Hume's method is used to calculate the stepwise formations constants of simple systems (Cd-amino acids and Cd-Itaconic acid) while the stability constants of mixed complexes have been evaluated by the method of Schaap & McMaster's. The reduction of Cd(II) ion is found to be reversible and diffusion controlled involving two electrons in each case. The statistical and electrostatic effects have also been discussed by using these stability constants. The mixing constant (Km) and stabilization constant (Ks) were measured for comparative study of simple and mixed ligand complexes.

Key words: Amino acids, Itaconic acid, Cd(II), mixed ligand complexes, reversible reduction, 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. Mixed ligand complexes play very important role in biological process[1,2]. Biologically active metal complexes of amino acids are important in analytical biochemical and pharmaceutical fields[3-5]. Most of the earlier studies on mixed ligand complexes are of spectrophotometer measurements[6,7]. 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 workers[8,9,10]. Formation constants of glycolate and lactate have been studied by P.K.S. Chauhan and coworkers[11]. Mixed ligand complexes of some transition metal chelates and Alkaline earth metal chelates have been carried out by many workers[12,13]. Stability constants of Cd(II) complexes with pyridine and some amino acids and Pb(II) complexes with β-Picoline and some amino acids have been studied by R.K. Paliwal and coworkers[14-16]. The study of ternary complexes of different metal ions with amino acids and bicarboxylic acids have been carried out by many workers[17-20]. The survey of literature reveals that there is a lack of data on the mixed ligand complexes of Cd(II) ion with amino acids and Itaconic acid. Hence, the present work is undertaken for the studies.

EXPERIMENTAL

All chemicals used were of AR-grade and all solutions were prepared in double distilled water. The Itaconic acid and amino acids were used as complexing agents. KCl used as supporting electrolyte to maintain the ionic strength of the solution at 0.1M and 0.002%. The temperature 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 mg/sec

t = 3 sec.

RESULTS

Simple systems

The formation constants of the complexes of Cd-Itaconic acid and Cd-amino acids (L-Tyrosine and L-Phenylalanine) were determined by the

Table 1: Stability constants for simple systems

Systems	log β_1	log β_2	log β_3
Cd-Itaconic acid	1.675	2.729	4.338
Cd-Tyrosine	5.399	7.899	9.748
Cd-Phenylalanine	3.977	4.397	6.544

Table 1(A): Data and results for Cd-Phenylalanine-Itaconic acid system

Itaconic acid = 0.04M, temp. = 298K

C_x (moles/lit.)	$\Delta E_{1/2}$	log I_m/I_c	F_{00}	$F_{10} \times 10^3$	$F_{20} \times 10^4$	$F_{30} \times 10^6$
0.000	-	-	-	-	-	-
0.001	0.0311	0.0040	11.371	10.371	19.120	-
0.002	0.0396	0.0040	22.134	10.567	19.362	-
0.003	0.0446	0.0057	33.310	10.770	19.667	3.8
0.004	0.0480	0.0293	44.945	10.986	20.161	4.1
0.005	0.0506	0.0447	57.025	11.205	20.500	4.0
0.006	0.0529	0.0532	69.548	11.424	20.743	3.7
0.007	0.0544	0.0774	82.845	11.663	21.195	3.8

log A (cal.) = 0.653 log B = 4.007 logC = 5.26 logD = 6.57

Table 1(B): Data and results for Cd-Phenylalanine-Itaconic acid system

Itaconic acid = 0.2M, temp. = 298K

C_x (moles/lit.)	$\Delta E_{1/2}$	log I_m/I_c	F_{00}	$F_{10} \times 10^3$	$F_{20} \times 10^4$	$F_{30} \times 10^6$
0.000	-	-	-	-	-	-
0.001	0.037	0.0089	18.72	17.728	82.88	3.80
0.002	0.046	0.0091	38.13	18.565	83.27	3.88
0.003	0.052	0.0099	59.22	19.409	83.66	3.88
0.004	0.055	0.0299	82.05	20.263	84.07	3.90
0.005	0.058	0.0466	106.61	21.122	84.44	3.88
0.006	0.061	0.0544	132.95	21.992	84.87	3.95
0.007	0.062	0.0784	161.07	22.868	85.26	3.94

log A (cal.) = 0.732 log B = 4.227 logC = 5.916 logD = 6.588

method of DeFord and Hume[21]. The values of formation constants of simple systems are presented in Table 1.

Mixed systems

In all the systems solution containing 0.5 mM Cd(II), 1M KCl was used. The mixed systems of Indium-Amino acids–Itaconic acid were studied by keeping be concentration of weaker ligand (Itaconic acid) constant at two values (0.04M and 0.2M) while varying the concentration of the second ligand (amino acids). In each case a single well defined wave was obtained. The plots of E_{de} vs log i/i_d-i were straight line with a slope of 30±2 mV showing that the three electrons reduction was reversible. The increase in diffusion current, directly proportionality to the square root of the effective height of mercury column indicated that the reduction was entirely diffusion controlled.

Half wave potential was shift to more negative side with increase in amino acid concentration, this shift in half wave potential is greater in the presence of the weaker ligand (Itaconic acid) than its absence. It signified mixed ligand formation.

The extended Schaap & Mcmasters[22] treatment was applied to evaluate the F_{00}, F_{10}, F_{20} and F_{30} (Table A to D). Lenden's[23] graphical extrapolation method (graph- a to d) has applied on F_{00}, F_{10}, F_{20} and $F_{30,}$ respectively to calculate the

Table 1(C): Data and results for Cd-Tyrosine-Itaconic acid system

Itaconic acid = 0.04M temp. = 298K

C_x (moles/lit.)	$\Delta E_{1/2}$	log I_m/I_c	F_{00}	$F_{10} \times 10^5$	$F_{20} \times 10^7$	$F_{30} \times 10^9$
0.000	-	-	-	-	-	-
0.001	0.084	0.0302	716.63	7.156	-	-
0.002	0.097	0.0499	2137.3	10.681	33.42	4.7
0.003	0.106	0.0719	4277.2	14.254	34.19	5.2
0.004	0.112	0.0777	7181.7	17.951	34.88	5.4
0.005	0.118	0.0887	10877.2	21.752	35.51	5.4
0.006	0.122	0.1008	15375.4	25.624	36.04	5.4
0.007	0.125	0.1095	20728.7	29.611	36.59	5.4
log A (cal.) = 2.301		log B = 5.601	logC = 8.515	logD = 9.732		

Table 1(D): Data and results for Cd-Tyrosine-Itaconic acid system

Itaconic acid = 0.2M temp. = 298K

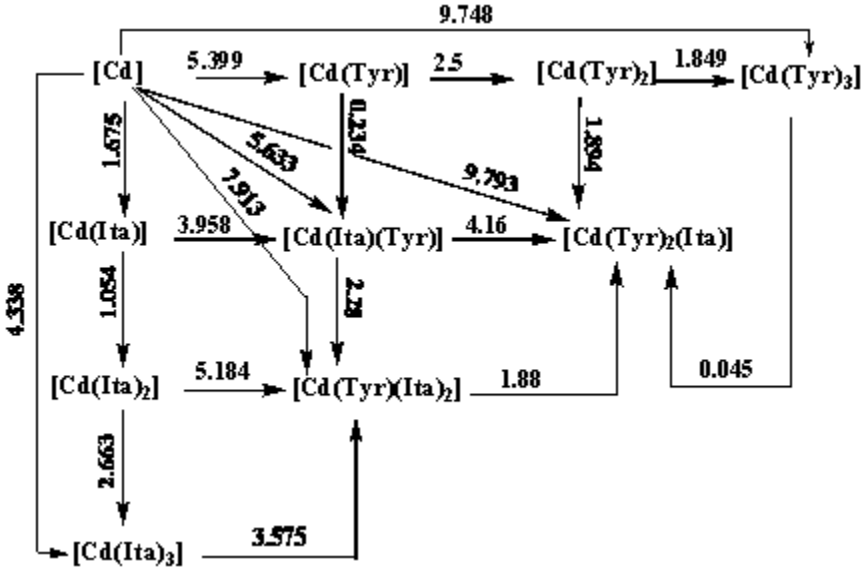
C_x (moles/lit.)	$\Delta E_{1/2}$	log I_m/I_c	F_{00}	$F_{10} \times 10^5$	$F_{20} \times 10^7$	$F_{30} \times 10^9$
0.000	-	-	-	-	-	-
0.001	0.0109	0.0009	4944.2	4.94	132.6	-
0.002	0.120	0.0339	12563.1	6.28	133.1	5.2
0.003	0.127	0.0341	22895.5	7.63	133.8	5.5
0.004	0.133	0.0375	35966.1	8.99	134.3	5.5
0.005	0.137	0.0507	51820.3	10.36	134.9	5.5
0.006	0.141	0.0727	70485.5	11.74	135.5	5.6
0.007	0.144	0.0766	91960.2	13.13	135.9	5.5
log A (cal.) = 3	log B = 6.55		logC = 9.72		logD = 9.74	

values of A, B, C and D at two concentrations of Itaconic acid for each system.

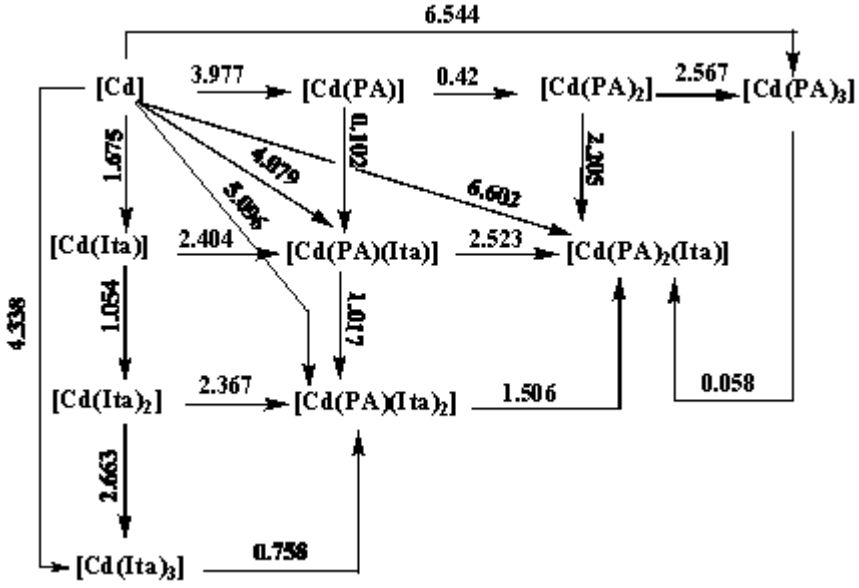
The overall stability constant β_{11}, β_{12} and β_{21} were calculated from the two values of B at two concentrations and are presented in Table 2. The mean value of D is in well agreement with the log β_{30}.

Table 2: Stability constants of mixed systems

Systems	log β_{11}	log β_{12}	log β_{21}
Cd-Tyrosine-Itaconic acid	5.633	5.096	6.602
Cd-Phenylalanine-Itaconic acid	4.079	7.913	9.793



Scheme 1: Cd(II)-Itaconate-Tyrosinate system at 298K



Scheme 2: Cd(II)-Itaconate-Phenylalanate acid System at 298K)

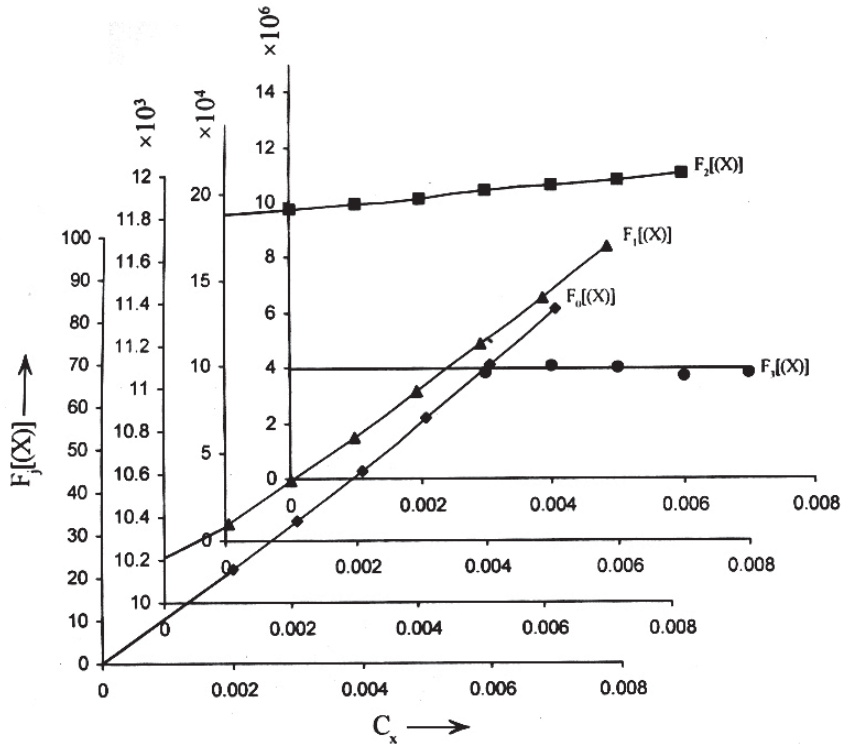


Fig. a : Plots of $F_j[(X)]$ vs C_x for Cd(II) - Itaconic acid-Phenylalanine system at 298 K (Itaconic acid = 0.04 M)

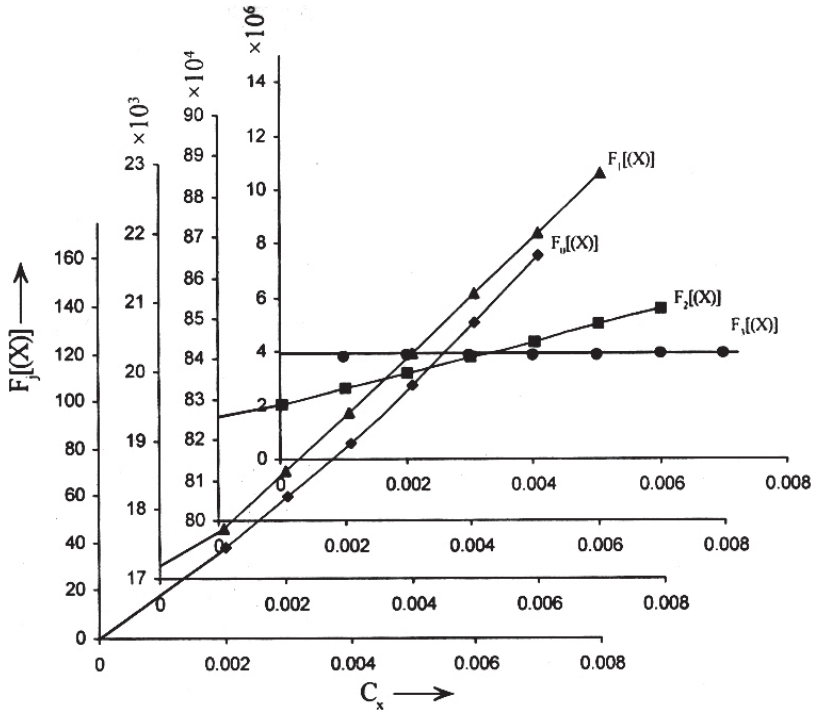


Fig. b: Plots of $F_j[(X)]$ vs C_x for Cd(II) - Itaconic acid-Phenylalanine system at 298 K (Itaconic acid = 0.2 M)

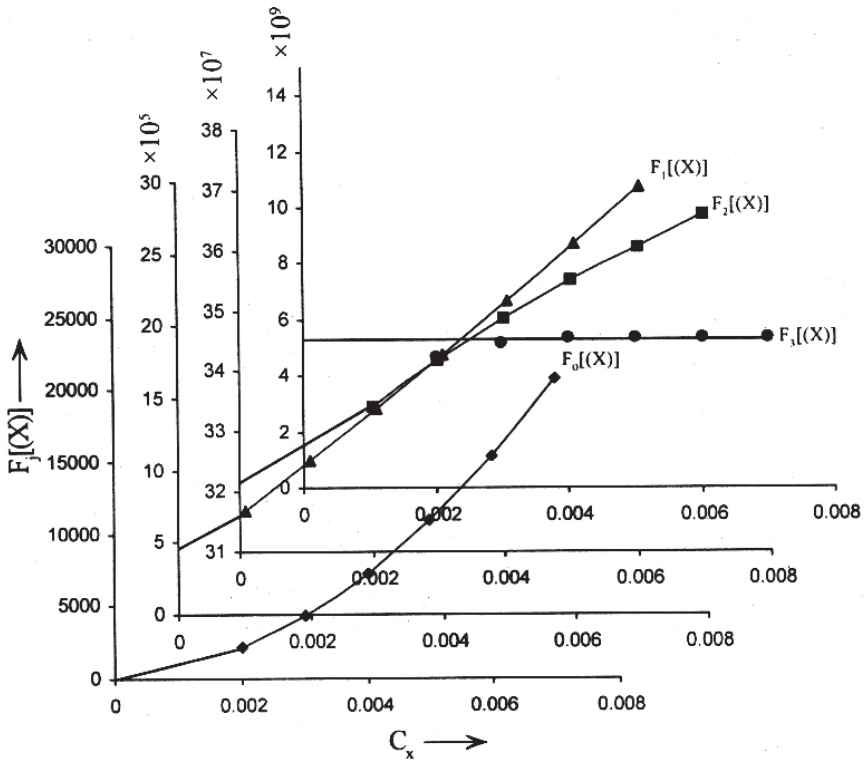


Fig. c : Plots of $F_j[(X)]$ vs C_x for Cd(II) - Tyrosine-Itaconic acid system at 298 K (Itaconic acid = 0.04 M)

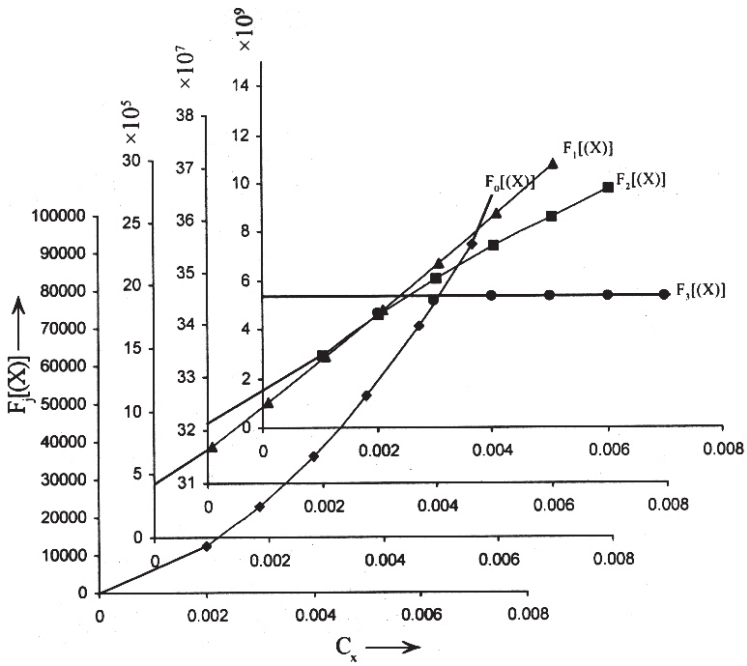


Fig. d: Plots of $F_j[(X)]$ vs C_x for Cd(II) - Tyrosine-Itaconic acid system at 298 K (Itaconic acid = 0.2 M)

DISCUSSION

The formation of mixed ligand complexes can be explained by considering Scheme 1 to 3. The tendency to add (X-amino acids) to Cd[X] and Cd[Y] (Y = Itaconic acid) can be compared. The logarithm values of stability constants of stability constants of the above complexes are - (2.5, 3.958) and (0.42, 2.404) for Cd-tyrosine-Itaconic acid, and Cd-phenyalanine-Itaconic acid systems respectively indicating that mixed ligand complexation is favoured by the addition of opposite ligand.

The tendency to add to CdX and CdY can also be compared. logK values are (0.234, 1.054) and (0.102, 1.054) for Cd-Itaconic acid-tyrosineand Cd-Itaconic acid-Phenylalanine systems respectively. Indicates that the formation of $Cd(Y)_2$ favoured over Cd(X,Y).

For comparing the stability of simple and mixed ligand complexes, it is convenient to measure the mixing constants.

$$K_m = \frac{\beta_{11}}{\sqrt{\beta_{02} \times \beta_{20}}}$$

and the stabilization constants

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

The $\log K_m$ values are (0.974, 0.465) and the logKs values are 0.673, 0.164 for Cd-Itaconic acid-L-Tyrosine, and Cd-Itaconic acid-L-Phenylalanine systems respectively. The positive values of mixing and stabilization constatns shows that the binary complexes are more stable.

The tendency to form mixed ligand complexes in solution could be expressed quantitatively in other approach compares the difference in stability (ΔlogK). The Δ log K values can be obtained using the following 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 observed values of $\Delta\log K_{11}$, $\Delta\log K_{12}$ and $\Delta\log K_{21}$ are (1.58, 1.70, 0.021) and (0.716, 0.20, 0.007) for Cd-Itaconic acid-Tyrosine and Cd-Itaconic acid-Phenylalanine systems, respectively. The ΔlogK values are higher than statistical value, which again proves that the ternary complexes are more stable than expected from statistical reasons.

ACKNOWLEDGEMENTS

One of the authors (Chanchal Karadia) is thankful to the Head, Department of Chemistry, University of Rajasthan, Jaipur for providing facilities to carry out this research work and to CSIR for the award of SRF (NET).

REFERENCES

1. Sigel, H., *Metal Ions in Biological System*, Marcel-Dekker Vol. (2): New York (1973).
2. Sigel, H., *Coordination Chemistry*, Pregamon, 20th edi., pp. 27, Oxford (1970).
3. Patel, R.N., Pandey, H.C. and Panday, K.B., *Bull. Electrochem*., 12612 (1996).
4. Khan, F. and Sahu, P.L., *Ultra Scientist Phys. Sci.*, **12**: 106 (2000).
5. Singh, B.K., Jain, C.L. and Sindhu, K.S., *Trans SAEST*, **30**: 04 (1995).
6. Schwarzebach, G. and Will, A., *Helv. Chem. Acta*, **34**: 528 (1951).
7. Schwarzenbach, G. and Heller, J. *Helv. Chem. Acta*, **34**: 576 (1951).
8. Prakash, D., Gupta, A.K., Kumar, S. and Yadav, A.K., *Oriental J. Chem.*, **18**(1): (2002).
9. Prakash, D., Gupta, A.K. Kumar, S. and Yadav, A.K., *Oriental J. Chem.*, **18**(1): (2002).
10. Prakash, D., Sinha, K.B., Brahmeshwar and Pravesh, R., *Oriental J. Chem.*, **21**(1): (2004).
11. Chauhan, P.K.S., Verma, A. and Paliwal, R.K., *Oriental J. Chem.,* **20**(1): (2004).
12. Prakash, D., Amir, N. and Eqbal, E., *Oriental J. Chem.*, **19**(3): 2003.
13. Prakash, D., Singh, R.N., Kumari, S. and Pravesh, R., *Oriental J. Chem.*, **19**(3): (2003).

14. Verma, A., Chauhan, P.K.S. and Paliwal, R.K., *Oriental J. Chem.*, **20**(2): (2004).
15. Verma, A., Chauhan, P.K.S. and Paliwal, R.K., *Oriental J. Chem.*, **20**(2): (2003).
16. Verma, M.K., Chandel, C.P.S., *Oriental J. Chem.*, **21**(1): (2004).
17. Verma, Mahendra Kumar and Chandel, C.P. Singh, *Oriental J. Chem.*, **21**(1): 9-20 (2005).
18. Malhotra, Vijay and Chandel, C.P. Singh, *J. Ultra Scientist Phy. Sci.*, **18**(2): 203-214 (2006).
19. Jangid, Kana Ram and Chandel, C.P. Singh, *Ultra Chemist*, **2**(2): 113-126 (2006).
20. Malhotra, Vijay and Chandel, C.P. Singh, *Bull. Electrochem.*, **22**: 301 (2006).
21. DeFord, D.D. and Hume, D.N., *J. Amer. Chem. Soc.*, **73**: 5321 (1951).
22. Schaap and McMasters, *J. Amer Chem. Soc.*, **83**: 4699 (1961).
23. Lenden, I. *Phys. Chem.*, **188**: 160 (1941).