RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.2, No.4 (2009), 853-860
ISSN: 0974-1496
CODEN: RJCABP

ELECTROCHEMICAL STUDIES OF Pb(II) AND Cd(II) IN PRESENCE OF BIPYRIDYL IN AQUEOUS MEDIA

Usha Nakra and O.D. Gupta*
Department of Chemistry University of Rajasthan, Jaipur (Rajasthan) 302004
E-mail : gupta_od@yahoo.com

ABSTRACT

Lead(II) and Cadmium(II) complexes with Bipyridyl have been investigated polarographically using Potassium Chloride as supporting electrolyte in aqueous media at 293K and 303K and pH 6.0 to 6.4. Both Lead(II) and Cadmium(II) formed 1:1, 1:2 and 1:3 complex species in aqueous medium with Bipyridyl. DeFord and Hume's method and Mihailov's method have been applied for the determination of stability constants. Kinetic parameters were evaluated for the reduction process at d.m.e. The stability constants of Pb(II) complexes with Bipyridyl at 293K using DeFord and Hume's method are 1.4344, 3.0853 and 4.9867 and using Mihailov's method are 1.4237, 3.1789 and 4.7580.The stability constants of Pb(II) complexes with Bipyridyl at 303K are 1.264, 2.875 and 4.7556 and by using Mihailov's method are 1.956, 2.976 and 4.5213. The stability constants of Cd(II) complexes with Bipyridyl at 293K using DeFord and Hume's method are 2.0211, 3.4026 and 6.3459 and using Mihailov's method are 1.956, 4.077 and 6.0219. The stability constants of Cd(II) complexes with Bipyridyl at 303K using DeFord and Hume's method are 1.810, 3.313 and 6.294 and using Mihailov's method are 1.672, 4.004 and 6.161.
Keywords: Electrochemical study, lead, cadmium, bipyridyl.

INTRODUCTION

There have been a number of electroreduction studies on simple[1-4] and mixed[5-14] ligand complex formation by different methods. The polarographic behaviour of Pb(II) and Cd(II) have been studied at D.M.E and it was observed that both Pb(II) and Cd(II) reduced reversibly involving two electrons as revealed by the plots of log $i/i_d - i$ Vs $E_{d.e.}$. The reduction was found to be diffusion controlled as revealed from the straight line plot of i_d Vs square root of effective height of mercury column ($h_{eff}^{1/2}$), In this paper the composition, stability constants and thermodynamic parameters of Lead(II) and Cadmium(II) with Bipyridyl have been reported.

EXPERIMENTAL

A.R. grade chemicals were used. The solvents used were purified by standard methods. The concentration of Lead(II) and Cadmium(II) in their respective solutions is 0.5 mM and the concentration of Bipyridyl varies from 0.001M to 0.009M. Potassium Chloride of concentration 0.1 M was used as supporting electrolyte to maintain the constant ionic strength (μ=1) of the solution and 0.002 % Triton X -100 was used as a maxima suppressor. A manual polarographic set up was used for recording polarograms. The dropping mercury electrode had the characteristics m = 1.75 mg / sec and t = 3.8 sec. (in open circuit). The measurements were done at constant temperatures [293K and 303K] maintained by using Haake-type ultra-thermostat. Before examining the solutions polarographically, purified nitrogen gas was passed through each solution for 20-30 minutes (according to solvent) to remove dissolved oxygen. The gradual increase in current with increase in potential was recorded and plotted to obtain the polarogram for the solution. At this particular pH, solutions were showing measurable negative shift in half-wave potential and decreasing diffusion current of Pb(II) on addition of the ligand Bipyridyl to solutions containing 0.5 mM Pb(II) in aqueous medium, confirmed complexations between Pb(II) and Bipyridyl. The decreasing diffusion current of Cd(II) on addition of the ligand Bipyridyl to solutions containing 0.5 mM Cd(II) in aqueous medium, also comfirmed complexations between Cd(II) and Bipyridyl.

DeFord and Hume's method and Mihailov's method were applied to determine the composition (metal ligand ratios) and overall stability constants of metal complexes.

The various polarographic measurements and $F_j[(X)]$ functions values at 293K and 303K for complexes of Pb(II) and Bipyridyl have been recorded in Tables 1 and 2, respectively. The Mihailov's constants ‘a’ and ‘A’ at 293K and 303K have been recorded in Tables 1.1 and 2.1, respectively. The results have also been shown graphically in Figures 1 and 2. The various polarographic measurements and $F_j[(X)]$ functions values at 293K and 303K for complexes of Cd(II) and Bipyridyl have been recorded in Tables 3 and 4, respectively. The Mihailov's constants ‘a’ and ‘A’ at 293K and 303K have been recorded in Tables 3.1 and 4.1, respectively. The results have also been shown graphically in Figures 3 and 4.

RESULTS & DISCUSSION

The plots of $F_0[(X)]$ Vs C_x were smooth curves in all solutions, showing the formation of more than one complexes in aqueous media. Further analysis showed the presence of three consecutive complexes in aqueous media, since the plots of F_1 [(x)] and F_2 [(x)] Vs ligand concentration (Bipyridyl) were a curve and a straight line with a slope, respectively and the plot of $F_3[(x)]$ Vs [Bipyridyl] was a straight line parallels to ligand concentration (axis) (without slope). The Plots of F_j [(x)] Vs Bipyridyl on extrapolation to [x] = 0 resulted in the values of β_j.

The overall formation constants determined at 293K and 303K for Pb(II)-Bipyridyl complexes enabled to calculate the thermodynamic functions values which are recorded in Table-A.

Table-A

Complex Species	ΔG^0 (-) (KCals/mol)	ΔH^0 (-) (KCals/mol)	ΔS^0 (-) (Cals/mol/deg)
MX_1	2.0518	39.3657	0.1273
MX_2	3.8477	40.2203	0.1241
MX_3	5.7711	40.4483	0.1183

M = Lead (II), X = Bipyridyl

The thermodynamic functions values for Cd(II)-Bipyridyl complexes are recorded in Table-B

Table -B

Complex Species	ΔG^0 (-) (KCals/mol)	ΔH^0 (-) (KCals/mol)	ΔS^0 (-) (Cals/mol/deg)
MX_1	2.0518	39.3657	0.1273
MX_2	3.8477	40.2203	0.1241
MX_3	5.7711	40.4483	0.1183

M = Cadmium (II), X = Bipyridyl

The order of stability constants of Bipyridyl with these metals is Cd(II) > Pb(II)

Table-C: Stability constants of Pb(II),Cd(II) complexes formed with Bipyridyl at 293K

Metal ion	Ligand	Electrolyte	Stability constant		
			$\log\beta_1$	$\log\beta_2$	$\log\beta_3$
Pb(II)	Bipyridyl	KCl	1.434	3.085	4.986
Cd(II)	Bipyridyl	KCl	2.021	3.402	6.345

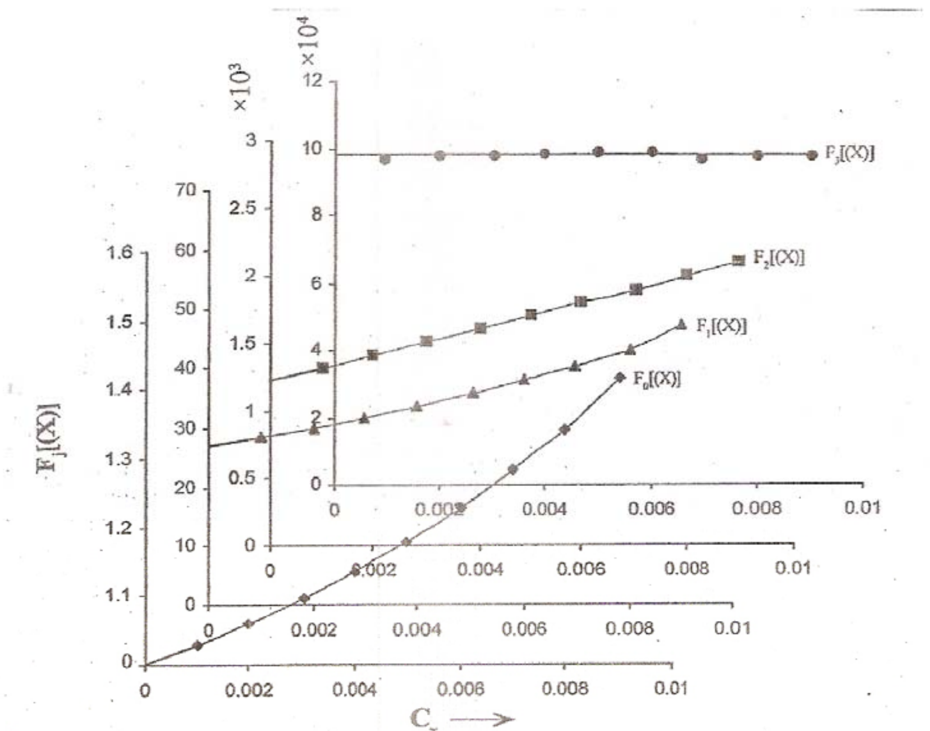

Fig. 1 : Plot of $F_j[(X)]$ vs. C_x for Pb(II)-Bipyridyl system at 293K in aqueous medium.

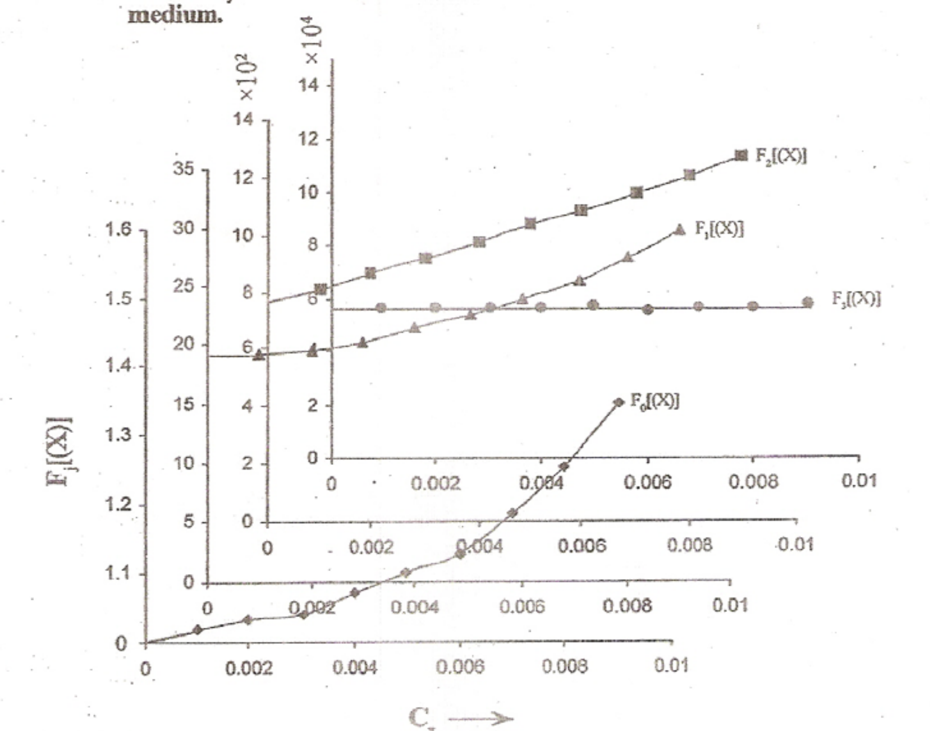

Fig. 2 : Plot of $F_j[(X)]$ vs. C_x for Pb(II)-Bipyridyl system at 303K in aqueous medium.

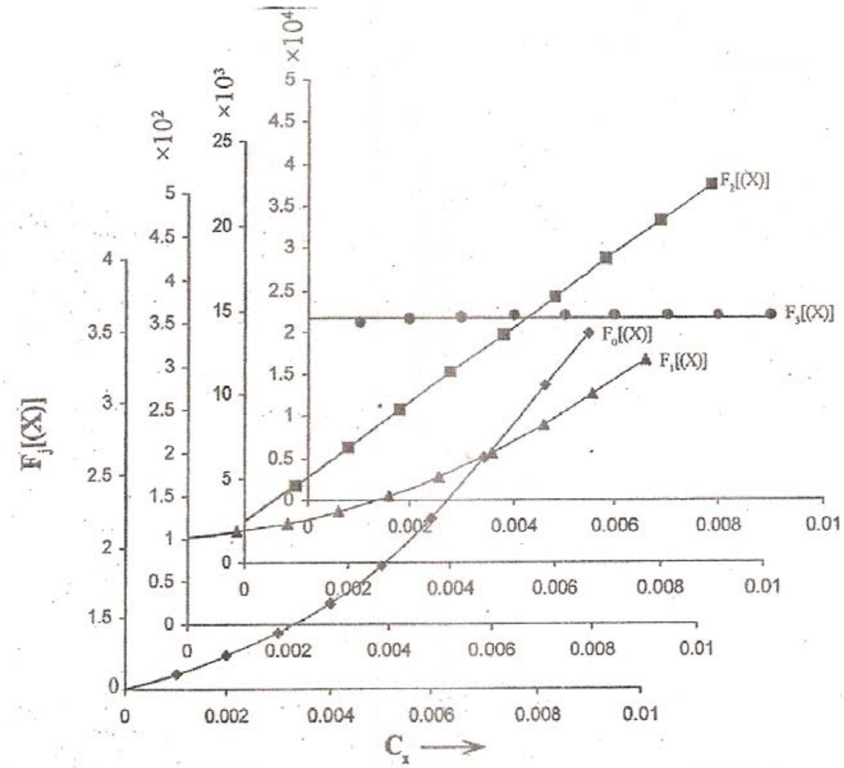

Fig. 3 : Plot of $F_j[(X)]$ vs. C_x for Cd(II)-Bipyridyl system at 293K in aqueous medium.

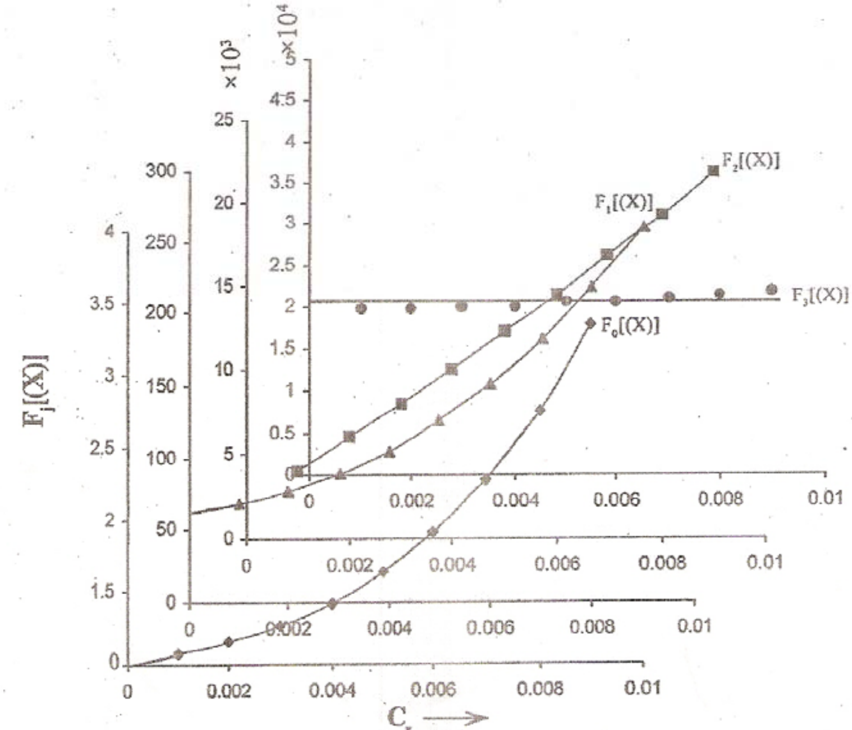

Fig. 4 : Plot of $F_j[(X)]$ vs. C_x for Cd(II)-Bipyridyl system at 303K in aqueous medium.

On comparing the

datas recorded in the tables C and D it is clear that increase in temperature results in the decrease in stability of complex species. At both temperatures Cd(II) forms more stable complexes with Bipyridyl as compared with Pb(II). This may be attributed to the differences in ionic size and binding energy of metal ions.

ACKNOWLEDGEMENT

The authors are thankful to the Head, Chemistry Department, University of Rajasthan, Jaipur for providing the necessary facilities to carry out the research work.

REFERENCES

1. K.D. Gupta and J.N. Gaur, *Indian J. Chem*, **16,** 74 (1978).
2. K.D. Gupta, O.D. Gupta and J.N. Gaur, *J. Electrochem. Soc., India*, **27**, 265 (1978).
3. K.D. Gupta, O.D. Gupta and J.N. Gaur, *J. Electrochem, Soc. India* **27**, 58 (1978).
4. K.D. Gupta, O.D Gupta and J.N. Gaur, *Trans of SAEST*, **14**, 121 (1979).
5. K.D. Gupta and J.N. Gaur, *Montash fur Chem. Austia* **56**, 457 (1979).
6. K. Singh, C.L. Jain and R.S. Sindhu, *Trans SAEST*, **30**, 4 (1995).
7. B.R. Rodriguez, Amaro, M. Sanchez, E.Munoz, J.J. Ruiz and L.Camcho, *J. Electrochem soc.*, **14,** 2132 (A) (1996).
8. D.G. Peters and E.R. Davidson, *J. Elecroanal Chem.*, **16,** 500 (2001).
9. F.M. Ortiz, M.L. Alcaraz and I. Roca, *Electrochem Acta,* **45**, 387 (1999).
10. M.K. Singh, A.Das, R.Laskar and B. Paul, *J. Indian Chem. society* **85,** 485-490 (May 2008).
11. Afroza Khanam and Farid Khan, *J. Indian Chem. Society* **85**, 89-91, (Jan 2008).
12. Amit Verma, P.K.S. Chouhan and R.K. Paliwal, *Oriental Journal of Chemistry*,**20 (2)** (2004).
13. Amit Verma, P.K.S. Chouhan and R.K. Paliwal, *Oriental Journal of Chemistry*, **20 (2)** (2004).
14. Zine A.M., *Asian Journal of Chemistry*, **18(4)**, 2902-2906 (2006).

Table-1: Polarographic measurements and $F_j[(X)]$ function values for Pb(II)-Bipyridyl system at 293K in aqueous media.
[Pb(II)]= 0.5 mM, μ=1

Cx (Moles/Litre)	i_d (divisions)	$E_{1/2}$ (-v vs S.C.E.)	$F_0[(X)]$	$F_1[(X)]$	$F_2[(X)] \times 10^3$	$F_3[(X)] \times 10^4$
0.000	89	0.4000	-	-	-	-
0.001	88	0.4002	1.0285	28.50	1.314	9.70
0.002	87	0.4004	1.0600	30.01	1.412	9.76
0.003	85	0.4006	1.0951	31.72	1.510	9.79
0.004	82	0.4005	1.1345	33.63	1.610	9.82
0.005	81	0.4008	1.1787	35.75	1.712	9.87
0.006	79	0.4011	1.2283	38.05	1.811	9.89
0.007	77	0.4013	1.2832	40.46	1.896	9.69
0.008	77	0.4019	1.3400	43.18	1.999	9.77
0.009	75	0.4022	1.4146	46.07	2.098	9.78

log β_1 = 1.4344; log β_2 = 3.0853;log β_3 = 4.9867
C_x = Bipyridyl concentration, moles.litre^{-1}

Table-2:Polarographic measurements and $F_j[(X)]$ function values for Pb(II)-Bipyridyl system at 303K in aqueous media.
[Pb(II)]= 0.5 mM, μ=1

Cx (Moles/Litre)	i_d (divisions)	$E_{1/2}$ (-v vs S.C.E.)	$F_0[(X)]$	$F_1[(X)]$	$F_2[(X)] \times 10^2$	$F_3[(X)] \times 10^4$
0.000	91	0.3980	-	-	-	-
0.001	91	0.3981	1.0191	19.16	8.067	5.68
0.002	88	0.3981	1.0401	20.08	8.637	5.68
0.003	86	0.3984	1.0633	21.12	9.208	5.69
0.004	84	0.3984	1.0890	22.27	9.778	5.69
0.005	82	0.3985	1.1177	23.55	10.383	5.76
0.006	80	0.3985	1.1492	24.86	10.849	5.58
0.007	78	0.3986	1.1848	26.40	11.488	5.70
0.008	77	0.3989	1.2240	28.00	12.052	5.69
0.009	44	0.5735	1.2682	29.80	12.717	5.79

log β_1 = 1.264; log β_2 = 2.875; log β_3 = 4.7556
C_x = Bipyridyl concentration, moles.litre^{-1}

Table-1.1:Mihailov constant 'a' for various combinations of Bipyridyl concentrations and 'A' at various Bipyridyl concentrations at 293 K for
Pb(II)-Bipyridyl system in aqueous media.

S.No.	Combinations of Bipyridyl Concentrations (Moles/Lit.)	'a'	Concentration of Bipyridyl (Moles/Lit.)	'A'
1	0.001 0.002	100	0.001	0.2222
2	0.002 0.003	107	0.002	0.2348
3	0.003 0.004	114	0.003	0.2339
4	0.004 0.005	118	0.004	0.2340
5	0.005 0.006	122	0.005 0.006	0.2345 0.2355
6	0.006 0.007	120	0.007	0.2362

Average 'a' = 105, Average 'A' = 0.1716

Table-2.1:Mihailov constant 'a' for various combinations of Bipyridyl concentrations and 'A' at various Bipyridyl concentrations at 303 K for
Pb(II)-Bipyridyl system in aqueous media.

S.No.	Combinations of Bipyridyl Concentrations (Moles/Lit.)	'a'	Concentration of Bipyridyl (Moles/Lit.)	'A'
1	0.001 0.002	95	0.001	0.1723
2	0.002 0.003	99	0.002	0.1714
3	0.003 0.004	102	0.003	0.1726
4	0.004	109	0.004	0.1707

	0.005			
5	0.005 0.006	106	0.005 0.006	0.1711 0.1712
6	0.006 0.007	117	0.007	0.1722

Average 'a' = 105, Average 'A' = 0.1716

Table-3:Polarographic measurements and $F_j[(X)]$ function values for Cd(II)-Bipyridyl system at 293K in aqueous media.[Cd(II)]= 0.5 mM, μ=1

Cx (Moles/Litre)	i_d (divisions)	$E_{1/2}$ (-v vs S.C.E.)	$F_0[(X)]$	$F_1[(X)]$	$F_2[(X)] \times 10^3$	$F_3[(X)] \times 10^4$
0.000	55	0.4890	-	-	-	-
0.001	51	0.4892	1.109	1.096	4.643	2.11
0.002	47	0.4895	1.237	1.187	6.862	2.16
0.003	45	0.4905	1.396	1.323	9.101	2.19
0.004	41	0.4913	1.601	1.503	11.336	2.20
0.005	39	0.4920	1.863	1.727	13.556	2.20
0.006	37	0.4930	2.198	1.997	15.785	2.20
0.007	35	0.4950	2.618	2.312	18.036	2.21
0.008	32	0.4960	3.137	2.671	20.269	2.21
0.009	31	0.4970	3.487	3.073	22.488	2.21

$\log \beta_1 = 2.0211$ $\log \beta_2 = 3.4026$

$\log \beta_3 = 6.3459$

C_x = Alizarin concentration, moles.litre^{-1}

Table-4:Polarographic measurements and $F_j[(X)]$ function values for Cd(II)-Bipyridyl system at 303K in aqueous media.
[Cd(II)]= 0.5 mM, μ=1

Cx (Moles/Litre)	i_d (divisions)	$E_{1/2}$ (-v vs S.C.E.)	$F_0[(X)]$	$F_1[(X)]$	$F_2[(X)] \times 10^3$	$F_3[(X)] \times 10^6$
0.000	58	0.4870	-	-	-	-
0.001	55	0.4871	1.0685	68.57	4.019	1.97
0.002	51	0.4871	1.1532	76.61	6.027	1.98
0.003	47	0.4873	1.2658	88.62	8.021	1.99
0.004	47	0.4888	1.4189	104.7	10.04	1.99
0.005	46	0.4903	1.6308	126.16	12.32	2.05
0.006	43	0.4915	1.9080	151.34	14.46	2.06
0.007	41	0.4932	2.2759	182.28	16.81	2.10
0.008	40	0.4953	2.7491	218.64	19.26	2.15
0.009	40	0.4979	3.3485	260.95	21.82	2.19

$\log \beta_1 = 1.81$; $\log \beta_2 = 3.311$; $\log \beta_3 = 6.294$

C_x = Bipyridyl concentration, moles.litre^{-1}

Table-3.1:Mihailov constant 'a' for various combinations of Bipyridyl concentrations and 'A' at various Bipyridyl concentrations at 293 K for Cd (II) - Bipyridyl system in aqueous media.

S.No.	Combinations of Bipyridyl Concentrations (Moles/Lit.)	'a'	Concentration of Bipyridyl (Moles/Lit.)	'A'
1	0.001 0.002	155	0.001	0.3630
2	0.002	210	0.002	0.3431

	0.003			
3	0.003 0.004	252	0.003	0.3339
4	0.004 0.005	292	0.004	0.3322
5	0.005 0.006	322	0.005 0.006	0.3355 0.3422
6	0.006 0.007	350	0.007	0.3513

Average 'a' = 263, Average 'A' = 0.3420

Table- 4.1:Mihailov constant 'a' for various combinations of Bipyridyl concentrations and 'A' at various Bipyridyl concentrations at 303 K for In (III) - Bipyridyl system in aqueous media

S.No.	Combinations of Bipyridyl Concentrations (Moles/Lit.)	'a'	Concentration of Bipyridyl (Moles/Lit.)	'A'
1	0.001 0.002	217	0.001	0.1277
2	0.002 0.003	284	0.002	0.1145
3	0.003 0.004	342	0.003	0.1070
4	0.004 0.005	417	0.004	0.1033
5	0.005 0.006	445	0.005 0.006	0.1029 0.1033
6	0.006 0.007	533	0.007	0.1053

Average 'a' = 430, Average 'A' = 0.1091

(Received: 9 September 2009 Accepted: 25 October 2009 RJC-457)