ELECTROCHEMICAL STUDIES OF Pb(II) COMPLEXES WITH PYRIDINE IN AQUEOUS MEDIUM AND COMPARISON OF STABILITY CONSTANT VALUES BY MIHAILOV METHOD AND DEFORD AND HUMES METHOD.

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ABSTRACT

The polarographic determination of stability constants of metal complexes of Pb(II) with Pyridine under varying temperatures at 303K and 313K in aqueous medium at 0.1M KCL and at constant pH, have shown the formation of 1:1, 1:2, and 1:3 complexes. The values of stability constants of complexes have been calculated by Deford and Humes method and compared by values calculated by Mihailovs method (mathematical).The changes thermodynamic parameters ΔG, ΔH and ΔS accompanying complexation have been also evaluated at 30°C. The reduction process of Pb(II) in presence of Pyridine was found to be reversible and diffusion controlled involving two electron transfer. The formation constants, $\log\beta_1$ $\log\beta_2$ and $\log\beta_3$ of Pb(II)-Pyridine system at 303K are 5.114, 7.699 and 7.699 and at 313K are 5.068, 7.623 and 11.140 in aqueous medium. It was found that the stability constants of Pb(II) Pyridine system at 303K is more than at the 313K.

Keywords: *Electrochemical Studies,Pyridine,Mihailov method.*

INTRODUCTION

From the survey of chemical literature[1-10], it has been found that there are very few references in literature regarding polarographic studies of the complexation of Pb(II) with some amino acids at different temperatures. The polarographic behaviour of some of the amino acids *viz* Aspartic acid, Glutamic acid, etc., have already been studied by Saxena and Cowokers[11]. Number of electrochemical studies on the behaviour of amino acids and their complexes[12] has been found useful applications in biochemistry and medicine[13]. Present study shows the complexation of Pb(II) with Pyridine an heterocyclic compound which have not been studied.

EXPERMENTAL

Pyridine was supplied by B.D.H. Chemicals Ltd Poole England and all reagents were of Anal grade. Polarograms were recorded on a manual polarograph using a saturated calomel electrode as the reference electrode. The capillary had the following characteristics m=1.96 mg, t=4.10 sec /drop and their stock solutions were prepared in conductivity water. Potassium chloride was used, as a supporting electrolyte to maintain the ionic strength at 1M. The temperature was maintained constant at 303K. A thermostat having an accuracy of ±0.1°C was used to constant temperature of all solution .0.002% Tritron X-100 was used as a maximum suppressor and all polarograph were recorded in an inert atmosphere of Nitrogen at 303K and 313K. Experiments were performed with 0.5mM of metal ion and Pyridine was used as complexing agent whose concentration was varied from 0.001 to 0.007 moles. The $E_{1/2}$ of reduction of metal ligand complex showed a gradual cathodic shift with an increasing ligand concentration. The corresponding plot of $E_{1/2}$ versus –log Cx was smooth curve indicating successive complexation .

DeFord and Hume method hasbeen applied to determine the composition of metal ligand ratio and overall stability constants of metal complexes

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RESULTS AND DISCUSSION

The reduction of Pb(II) complexes with complex with ligand gives well defined wave at d.m.e. The plot of I_d vs $h_{eff}^{1/2}$ was found to be linear indicating the diffusion controlled nature of the electrode process. Conventional value of slope indicating the reversible nature of the electrode process involving two electron transfer process. Plots of $F_0[X]$, $F_1[X]$, $F_2[X]$, and $F_3[X]$ verses [X] when extrapolated to [X] = 0 gave the value of overall stability constant. The plot of $F_3[X]$ is horizontal to the [X] axis indicating the formation of three complexes with metal to ligand ratio of 1:1,1:2 and 1:3. Stability constants values are also calculated by Mihailov′s method given in Table4 and are compared with the values of stability constants calculated by DeFord and Hume′s method given below at both the temperatures 303K and 313K.

Calculations of Constants at 303K

Method	log β_1	log β_2	log β_3
DeFord and Hume	5.114	7.699	11.238
Mihailov	4.761	8.075	11.213

Calculations of Constants at 313K

Method	log β_1	log β_2	log β_3
DeFord and Hume	5.068	7.623	11.140
Mihailov	4.715	8.004	11.116

Effect of Temperature:

It is seen from Table 1and Table 2 that stability constants gradually decreases with rise in temperature showing there by that lower temperature favours the formation of stable complexes . The reduction of Pb(II) ligand complex gives well defined cathodic wave (diffusion controlled) and reversible in each case . $E_{1/2}$ versus – log Cx was smooth curve indicating successive complexation. The logβ values were determined at different temperature 303K and 313K which are summarized in Table 1 and Table 2, respectively.

Thermodynamic Parameters:

Thermodynamic functions such as Free energy (ΔG), Entropy (ΔS) and Enthalpy (ΔH) accompanying complexation are determined at 303K with the help of standard equation. The values of these thermodynamic functions are given in Table 3. The negative values of (ΔG) shows that the reaction tends to proceed spontaneously. The negative value of (ΔH) indicate the exothermic nature of reaction process in fair agreement with increasing stability suggesting lower temperature favours the chelation process. The entropy values indicate that complexation is favoured by enthalpy and entropy factors.

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Table-1: Polarographic measurements and Fj([X]) functions values for the Pb(II)- Pyridine System

[Pb(II)] = 0.5mM, μ=1(KCl), T=303 K

S. No.	Cx (Moles)	I_d (divisions)	$E_{1/2}$ (-V vs S.C.E.)	$F_0([X])$ x 10^3	$F_1([X])$ x 10^5	$F_2([X])$ x 10^8	$F_3([X])$ x 10^{11}
1	0	80	0.3856				
2	0.001	74	0.4612	0.3548	3.5384	2.2384	1.7384
3	0.002	71	0.4822	1.8491	9.2403	3.9701	1.7351
4	0.003	68	0.4959	5.5166	18.3854	5.6951	1.7317
5	0.004	64	0.5057	12.4215	31.0512	7.4378	1.7344
6	0.005	61	0.5135	23.6935	47.3850	9.2170	1.7434

7	0.006	60	0.5202	40.2534	67.0873	10.9645	1.7441
8	0.007	56	0.5251	62.7843	89.6904	12.6272	1.7325
Log β_1	=5.114	Log β_2	=7.699	Log β_3 =	11.238		

Table-2: Polarographic measurements and Fj([X]) functions values for the Pb(II)- Pyridine System

[Pb(II)] = 0.5mM, μ=1(KCl), T=313 K

S. No.	Cx (Moles)	I_d (divisions)	$E_{1/2}$ (-V vs S.C.E.)	F_0([X]) x 10^3	F_1([X]) x 10^5	F_2([X]) x 10^8	F_3([X]) x 10^{11}
1	0	86	0.375				
2	0.001	84	0.4515	0.2985	2.9754	1.8054	1.3854
3	0.002	83	0.4732	1.5114	7.5518	3.1909	1.3855
4	0.003	81	0.4875	4.4740	14.9102	4.5801	1.3867
5	0.004	74	0.4972	10.0573	25.1408	5.9927	1.3932
6	0.005	65	0.5041	19.1036	38.2052	7.4070	1.3974
7	0.006	64	0.5109	32.1322	53.5520	8.7303	1.3851
8	0.007	63	0.5169	50.9444	72.7763	10.2295	1.4014

Log β_1 =5.068 Log β_2=7.623 Log β_3 =11.140

Table-3:Thermodynamic functions (ΔG°, ΔH°, ΔS°) are recorded below.

Temperature	Complex Species	ΔG° KJ / mol	ΔH° KJ / mol	ΔS° KJ /K/mol molmmmolmol
313 K	MX_1	-3402.62	-1943.00	4.78
	MX_2	-4873.90	-817.15	13.3
	MX_3	-5836.38	-617.40	17.2

M = Pb(II), X = Pyridine

Table-4: Mihailov Constant 'a' for various combinations of Pyridine concentrations and 'A' at various Pyridine concentrations at 303K for Pb(II)- Pyridine system

S.No.	Combinations of Concentration of Pyridine (mol^{-1})	'a'	Concentrations of Pyridine (mol^{-1})	'A'
1.	0.001 0.002	3380.5229	0.001 0.002	14.6020 13.6648
2.	0.002 0.003	4184.8648	0.003 0.004	13.6915 13.8486
3.	0.003 0.004	5028.5967	0.005 0.006	14.0430 14.1561
4.	0.004 0.005	6507.3220*	0.007	14.1542
5.	0.005 0.006	6031.9444*	Average 'a' =	3907.68
6.	0.006 0.007	4087.1810	Average 'A' =	14.0229
7.	0.007 0.001	3907.6776		

The value marked asterisk(*) has not been included in average calculations due to its exceptional deviation

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