Determination of stability constants of thallium (I) complexes with 2-amino pyridine and 2-amino-4-methyl pyridine by Deford and Hume's method in aqueous medium

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ABSTRACT

The stability constants of complexes formed by Thallium (I) with 2-amino. Pyridine and 2-amino-4-methyl pyridine have been determined in aqueous medium, the complexes of Tl(I) with 2-amino pyridine and 2-amino-4-methyl pyridine as 1:1, 1:2, have been reported. the values of stability constant of 2-amino pyridine are log β_1=2.14680, log β_2=4.703 at 298K and complexes of Tl(I) with 2-amino-4-methylpyridine have log β_1=2.2170, logβ_2==4.7801 at 298K, respectively were calculated by DeFord and Hume's method.

INTRODUCTION

Many workers[1-2] have studied biologically active metal complexes of amino acids which are important in analytical, biochemical and pharmaceutical fields[3-5] and attracts wide attention in different fields of reasearch. A large number of such complexes have been suitable to investigate the redox properties of new drugs; whcih give insight into it. Electrocanalytical techniques are also used in clinical chemistry and laboratory medicines[6]. Electrode Kinetics of Zn(II) and Ni(II) with amino acids have been studied by P.s. Verma *et al.*,[7-8]. The importance of such compounds has been recognised in biochemical and pharmaceutical fields and attracting wide attention in different fields of research. Polargrahic behaviour of divalent metal ion with acetate[9], isovalerate[10], 1,3-diaminopropane[11] and oxalate[12] has been studied and determined stability constants in aqueous medium. Stanely, E. Mahanan[13] studied in non-aqueous medium, and also investigated some mixed-ligand complexes. Sarkar and Cruck have reported the isolation of complexes of Cu(II) with threonine from normal human serum and have prepared complexes of Cu(II) with amino acids. Mixed-ligand complexes of Cu(II), Zn(II), Ni(II) and Co(II) with wide range of ligands have been studied polarographically in aqueous media[14-20].

Polarographic studies of Histidine with some p-block elements like Ga(III), In(III), Tl (I) have been carried out separately at constant ionic strength (μ=1.0M) by using KCl as supporting electrolyte at 298 K and 308K temperatures[21].

On the basis of these studied thallium (I) amino acids complexes are a part of the accessible physiological role of the elements for most tissues.

In view of the little work done, specially polaroraphically, on the amino acids complexes of Tl (I), the present paper deals with the study of these complexes and determination of stability constants of the resulting compelxes in aqueous medium by graphical method of DeFord and Hume[22].
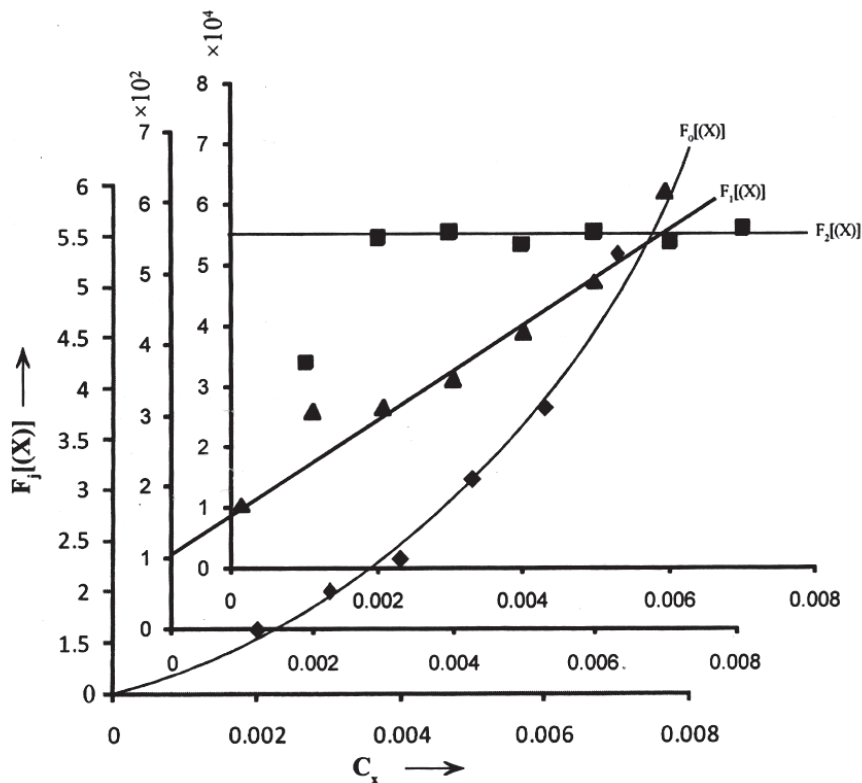
Fig. 1: Plots of $F_j[(X)]$ vs. C_x for Tl(I)-2-amino pyridine system at 298K
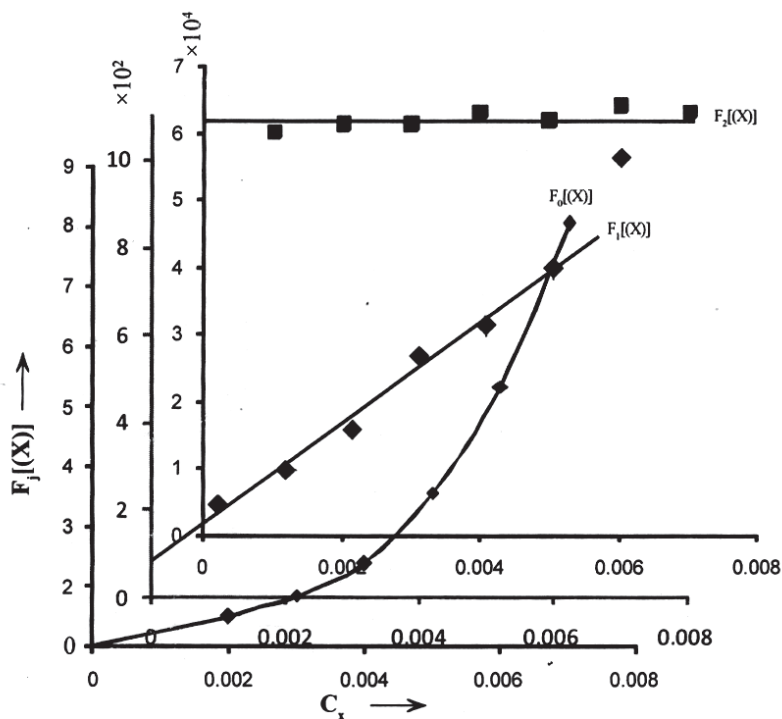

Fig. 2: Plots of $F_j[(X)]$ vs. C_x for Tl(I)-2-amino-4-methyl pyridine system at 298K

Table 1: Stability constants for complexes of TI(I) with 2-amino pyridine and 2-amino-4-methyl pyridine determined by DeFord Hume's and Mihailov method at 298K respectively

System	Temp	$\log\beta_j$	DeFord and Hume	Mihailov
TI(I)-2-amino pyridine	298K	$\log\beta_1$	2.14680	2.2801
		$\log\beta_2$	4.7403	4.5862
Ti(I)-2-amino-4-methyl pyridine		$\log\beta_1$	2.2170	2.2460
		$\log\beta_2$	4.7801	4.8329

Table 2: Polarographic measurement and $F_j[(X)]$ function values for the TI(I)-2-amino pyridine system at 298K

[TI(I) = 0.1 mM, μ=1.0M (KNO$_3$), Temp. 298K

CX (Moles/litre)	E½ (-V vs S.C.E)	$\log I_m/I_c$	$F_0[(X)]$	$F_1[(X)] \times 10^2$	$F_2[(X)] \times 10^3$
0.000	-	-	-	-	-
0.001	0.4600	0.0027	1.1743	1.7430	3.4070
0.002	0.4644	0.0053	1.6098	0.0490	5.4335
0.003	0.4701	0.0078	1.9870	3.0981	5.5260
0.004	0.4835	0.0105	1.9394	3.09081	5.2212
0.005	0.4882	0.0120	3.0831	4.1662	5.5278
0.006	0.49021	0.0157	3.6024	4.3373	5.1891
0.007	0.5024	0.0174	5.3039	6.1484	5.5801

C_X=2-amino pyridin concentration, moles litre^{-1}

Table 3: Polarographic measurement and $F_j[(X)]$ function values for the TI(I)-2-amino pyridine system at 298K

[TI(I) = 0.1 mM, μ=1.0M (KNO$_3$), Temp. 298K

CX (Moles/litre)	E½ (-V vs S.C.E)	$\log I_m/I_c$	$F_0[(X)]$	$F_1[(X)] \times 10^2$	$F_2[(X)] \times 10^3$
0.000	-	-	-	-	-
0.001	0.4700	0.0048	1.2080	2.0801	6.0201
0.002	0.4748	0.0101	1.4965	2.4825	6.1131
0.003	0.4801	0.0155	1.8456	2.8320	6.1172
0.004	0.4855	0.0220	2.3880	3.4721	6.3201
0.005	0.4920	0.0321	3.5579	5.1158	6.1746
0.006	0.5021	0.0421	5.3296	7.2101	6.3901
0.007	0.5121	0.0525	8.0352	10.0501	6.3201

C_X=2-amino pyridin concentration, moles litre^{-1}

**Table 4: Mihailov constant 'a' for various combinations of
2-amino-4-methyl pyridine and 'A' at various concentration
for Tl(I)-2-amino-4-methyl pyridine system at 298K in aqueous medium**

Combination of 2-Amino-4-methyl pyridine (moles litre^{-1})	'a'	concentration of 2-Amino-4-methyl pyridine (moles litre^{-1})	'A'
0.001			
0.002	476.1	0.001	0.1929
0.002			
0.003	373.6	0.002	0.1800
0.003			
0.004	139.3	0.003	0.1685
0.004			
0.005	106.8	0.004	0.1751
0.005			
0.006	778.7	0.005	0.224
0.006			
0.007	577.66	0.006	0.2793
		0.007	0.3486

Average 'a' = 777.84
Average 'A' = 0.2240

**Table 5: Mihailov constant 'a' for various combinations of
2-amino-4-methyl pyridine and 'A' at various concentration
for Tl(I)-2-amino-4-methyl pyridine system at 298K in aqueous medium**

Combination of 2-Amino-4-methyl pyridine (moles litre^{-1})	'a'	concentration of 2-Amino-4-methyl pyridine (moles litre^{-1})	'A'
0.001			
0.002	1000	0.001	0.3718
0.002			
0.003	27.637	0.002	0.55288
0.003			
0.004	277.90	0.003	0.4965
0.004			
0.005	738.10	0.004	0.3359
0.005			
0.006	103.1	0.005	0.5369
0.006			
0.007	205.69	0.006	0.5086
		0.007	0.6614

Average 'a' = 777.84
Average 'A' = 0.2240

EXPERIMENTAL

A CL-362 polargraphic analyser is used to record polarograms, using a saturated calomel electrode as the reference electrode which has a relatively large surface area to inhibit its ready polarisation.

It is essential that the DME has microdimensions so that it is readily polarised. All the chemicals used were of A.R. grade. 2-amino pyridine and 2-amino-4-methyl pyridine were used as complexing agents. Potassium nitrate was used as a supporting electrolyte to maintain the ionic strength constant at 1.0M. Triton X-100 was used to suppress the maxima observed. The concentration of maxima suppressor does not need to exceed 0.01%. The temperature was maintained constant at 298K. The capillary has the following characteristics, m=4.62 mg/s, t=2 sec and h_{eff}= 100 cm. The deaeration was done using N_2 for 15-20 minutes, which was purified by passing through vanadium pentaoxide and water solution.

RESULTS

Current-voltage curves were obtained. The concentration of ligands was varied from 0.001M to 0.007M. The values of the half-wave potentials for metal complexes shifted to more negative values on increasing the concentration of the ligands and diffusion current decreases. TI(I)-2-amino pyridine and TI(I)-2-amino-4-methyl pyridine system, the log plots log i/i_d-i vs E_{dc} indicate that reduction is reversible and diffusion controlled. A plot of $E_{\frac{1}{2}}$ vs log [(X)] resulted a smooth curve indiacting the formation of successive complexes. The method of DeFord and Hume's[22] was applied to determine the values of stability constants. For the varification the mathematical Mihailov's method was also applied to evaluate the stability constants. The stability constants determined by two methods are recorded Table 1.

DISCUSSION

The overall formation constants of the complex were determined by graphical DeFord and Hume's method at 298K. The $F_0[(X)]$ functions values when plotted against C_x (Concentration of ligand), smooth curve passing through the origin was observed. However, $F_1[(X)]$ values on plotting against C_x gave a straight line with slope, which indicates formation of penultimate complex. The plot of $F_2[(X)]$ values C_x gave a straight line parallel to abscissa axis denotes the formation of the the highest stoichiomatric complex species. This proves that overall formation constant for the formation of 1:2 (metal to ligant). For the verifications, the mathematical Mihailov's method was also applied to evaluate the stability constants from $F_0[(X)]$ function values. This involves the evaluation of Mihailov's constant 'a' and 'A' for the various ligand concentrations which have been recorded in Table 4,5 respectively from the average value of 'a' and 'A' stability constants may be determined by expression-

$$\beta_n = \frac{A^{a^n}}{n!}$$

where 'n' is the number of complex formed, which can be known from DeFord and Hume's method. The comparison the overall formation constants determined by both the method are found to be in good agreement.

There is a electron releasing group in the pyridine ring 2-amino pyridine it increase the basicity of both nitrogen atom and increase the stability of complex

ACKNOWLEDGEMENTS

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