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Comparison of stability contant values of Cu(II) complexes with amino acids by DeFord & Hume's and Mihailov's methods

SURESH KUMAR, MEENA, AKHIL K. BARJATYA and O.D. GUPTA*

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

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ABSTRACT

The reduction of Cu(II) with amino acids (glycine, α-alanine and L-valine) was investigated electrochemically. The stability constants of Cu(II) with amino acids were evaluated by the method of DeFord and Hume. These stability constants values were verified by Mihailov's mathematical approach. The reduction of the system in each case is reversible and diffusion controlled, involving two electrons.

Key words: Stability constant, Cu(II) complexes, amino acids.

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 attracted wide attention in different fields of research. Mixed ligand complexes of transition metals with many amino acids have been studied by many workers[6-12]. A large number of such complexes have been studied polarographically during the past decade. Copper-amino acid complexes are a part of the accessible physiological pool of the element for most tissues.[13]

In view of the little work done, especially polarographically, on the amino acids (glycine, α-alanine and L-valine) complexes of Cu(II), the present paper deals with the study of these complexes.

EXPERIMENTAL

A manual polarograph is used to record polarograms, using a saturated calomel electrode as the reference electrode. All the chemicals used were of AR grade. Amino acids were used as complexing agents. Potassium chloride was used as a supporting electrolyte to maintain the ionic strength at 1.0M. Triton X-100 in the final solution sufficed to suppress the maxima observed. The temperature was maintained constant at 300K. The capillary having the following characteristics, m = 2.30 mg/s, t = 3.20 sec. and h = 40 cm, was used. Solution of Cu(II) contains concentration of 5×10^{-4}M.

RESULTS AND DISCUSSION

Current-voltage curves were obtained. The concentrations of amino acids were varied from 0.001M to 0.008M. The values of half-wave potentials for metal ions and their complexes shifted to more negative value on increasing the concentration of ligand. The nature of all the waves were reversible and diffusion controlled. A plot of $E_{1/2}$ vs log[X] resulted a smooth curve indicating the formation of successive complexes. The method of DeFord and Hume's[14] was applied to determine

Table 1: Polarographic measuremetns and $F_j[X]$ values for the Cu(II)-glycinate system

[Cu(II)] = 5x 10^{-4} M, $E_{1/2}$ of Cu(II) = + 0.016 V vs SCE, i_d = 62 div.,
μ = 1.0 M KCl, p = 7.80 ± 0.01, temp. = 300K.

[gly]mol L^{-1}	Δ $E_{1/2}$	logIm/Ic	$F_0[X] \times 10^{10}$	$F_1[X] \times 10^{12}$	$F_2[X] \times 10^{15}$
0.001	0.2717	0.0763	0.1610	1.61092	1.5102
0.002	0.2883	0.1022	0.6196	3.0982	1.4991
0.003	0.2980	0.1296	1.3968	4.6562	1.5187
0.004	0.3048	0.1489	2.4785	6.1962	1.5240
0.005	0.3106	0.1489	3.8901	7.7802	1.5360
0.006	0.3144	0.1796	5.5765	9.2942	1.5323
0.007	0.3177	0.2013	7.5755	10.8222	1.5317
0.008	0.3202	0.2361	9.9136	12.3920	1.5365

Table 2: Polarographic measuremetns and $F_j[X]$ values for the Cu(II)-α-alaninate system

[Cu(II)] = 5x 10^{-4} M, $E_{1/2}$ of Cu(II) = + 0.016 V vs SCE, i_d = 62 div.,
μ = 1.0 M KCl,p = 7.80 ± 0.01, temp. = 300K.

[ala]mol L^{-1} [ala]	Δ $E_{1/2}$ Δ $E_{1/2}$	logIm/Ic logIm/Ic	$F_0[X] \times 10^{10}$ $F_0[X] \times 10^{10}$	$F_1[X] \times 10^{11}$ $F_1[X] \times 10^{12}$	$F_2[X] \times 10^{14}$ $F_2[X] \times 10^{14}$
0.001	0.2609	0.0681	0.0689	6.8899	6.3399
0.002	0.2773	0.0934	0.2590	12.9500	6.2000
0.003	0.2868	0.1203	0.5738	19.1266	6.1922
0.004	0.2935	0.1392	1.0117	25.2925	6.1856
0.005	0.2993	0.1292	1.5745	31.4900	6.1880
0.006	0.3031	0.1691	2.2565	37.6083	6.1764
0.007	0.3064	0.1903	3.0645	43.7785	6.1755
0.008	0.3091	0.2126	4.0095	50.1187	6.1960

Table 3: Polarographic measuremetns and Fj[X] values for the Cu(II)-L-valinate system.

[Cu(II)] = 5×10-4 M, $E_{1/2}$ of Cu(II) = + 0.016 V vs SCE, id = 62 div.,
μ = 1.0 M KCl,p = 7.80 ± 0.01, temp. = 300K.

[val]mol L^{-1}	Δ $E_{1/2}$	logIm/Ic	$F_0[X] \times 10^{10}$	$F_1[X] \times 10^{11}$	$F_2[X] \times 10^{14}$
0.001	0.2512	0.0640	0.0319	3.1899	2.7999
0.002	0.2673	0.0891	0.1180	5.8999	2.7549
0.003	0.2766	0.1156	0.2596	8.6533	2.7544
0.004	0.2834	0.1344	0.4564	11.4100	2.7550
0.005	0.2888	0.1344	0.6941	13.8820	2.6984
0.006	0.2928	0.1640	1.0120	16.8666	2.7461
0.007	0.2962	0.1849	1.3772	19.6742	2.7548
0.008	0.2989	0.2069	1.7903	22.3787	2.7486

Table 4: Mihailov constant 'a' for various combinations of Glycine concentrations and 'A' at various Glycine concentrations at 300 K for Cu(II)-glycinate system

Combinations of Glycine concentrations (M)	'a'	Concentrations of Glycine (M)	'A'
0.001 0.002	22884.61	0.001	4.6761×10^{6}
		0.002	4.6498×10^{6}
0.001 0.003	34475.47	0.003	4.7397×10^{-6}
0.004 0.005	22628.57	0.004	4.7611×10^{-6}
		0.005	4.8011×10^{-6}
0.005 0.006	14419.04	0.006	4.7919×10^{-6}
0.006 0.007	24401.52	0.007	4.7915×10^{-6}
		0.008	$4.8075\times\times10^{-6}$
0.005 0.008	32754.26		
		Average 'a' = 25260.58 Average 'A' = 4.7523×10^{6}	

Table 5: Mihailov constant 'a' for various combinations of glycine concentrations and 'A' at various glycine concentrations at 300 K for Cu(II)-α-alaninate system

Combinations of glycine concentrations (M)	'a'	Concentrations of glycine (M)	'A'
0.001 0.002	22884.61	0.001	4.6761×10^{6}
		0.002	4.6498×10^{6}
0.001 0.003	34475.47	0.003	4.7397×10^{-6}
0.004 0.005	22628.57	0.004	4.7611×10^{-6}
		0.005	4.8011×10^{-6}
0.005 0.006	14419.04	0.006	4.7919×10^{-6}
0.006 0.007	24401.52	0.007	4.7915×10^{-6}
		0.008	$4.8075\times\times10^{-6}$
0.005 0.008	32754.26		
		Average 'a' = 25260.58 Average 'A' = 4.7523×10^{6}	

the values of stability constants of successive complexes. The polarographic measurements have been recorded in Tables 1 to 3 and shown graphically in Figs. 1 to 3.

Mihailov's[15] mathematical approach to evaluate stability constants from $F_0[X]$ functions values, was also explored. From the average values of Mihailov's constant ('A' and 'a'), the stability constants can be determined by the expression

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

Values of 'a'and 'A' were calculated, for various combination of ligand concentrations and at various ligand concentrations, respectively by the expressions :

Table 6: Mihailov constant 'a' for various combinations of glycine concentrations and 'A' at various glycine concentrations at 300 K for Cu(II)-L-valinate system

Combinations of glycine concentrations (M)	'a'	Concentrations of glycine (M)	'A'
0.001	13575.00	0.001	2.7052×10^6
0.002			
		0.002	2.6642×10^6
0.002	15027.27		
0.003		0.003	2.6627×10^6
0.003	15040.90	0.004	2.6626×10^6
0.004			
		0.005	2.6092×10^6
0.001	11920.00		
0.003		0.006	2.6537×10^6
0.004	14092.57	0.007	2.6619×10^6
0.007			
		0.008	2.6558×10^6
0.006	16682.22		
0.008			
		Average 'a' = 14389.66	
		Average 'A' = 2.6594×10^6	

Table 7 : Successive stability constants for ML and ML_2 complexes of Cu(II)-amino acid determined by two methods at 300K

Systems	Methods	Stability constants	
		log β_1	log β_2
Cu(II)-glycinate	DeFord and Hume	11.00	15.18
	Mihailov	11.08	15.18
Cu(II)-α-alaninate	DeFord and Hume	10.74	14.79
	Mihailov	10.78	14.79
Cu(II)-L-valinate	DeFord and Hume	10.79	14.44
	Mihailov	10.58	14.43

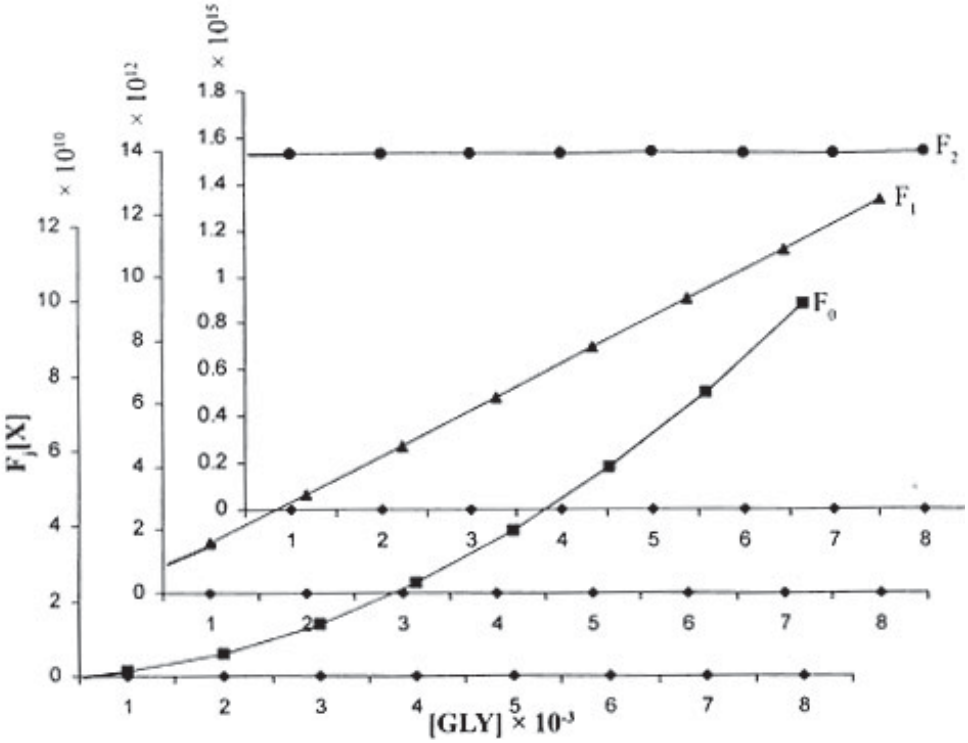

Fig. 1: Plot of F_j [X] vs (GLY) : Cu (II) -glycinate system at 300 K

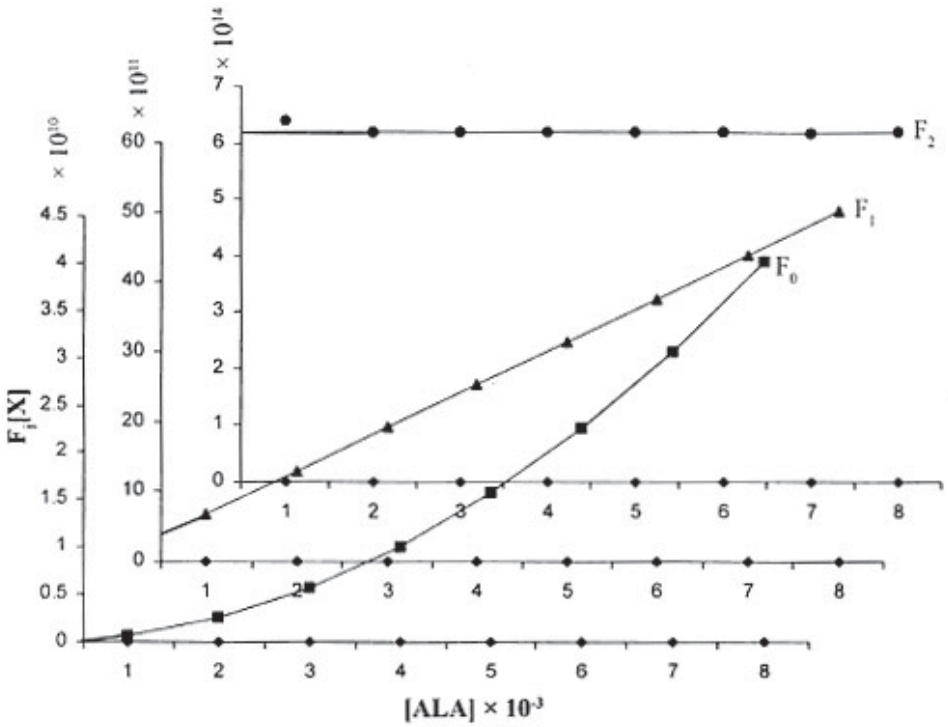

Fig. 2: Plot of F_j [X] vs (ALA) : Cu (II)-α-alaninate system at 300 K

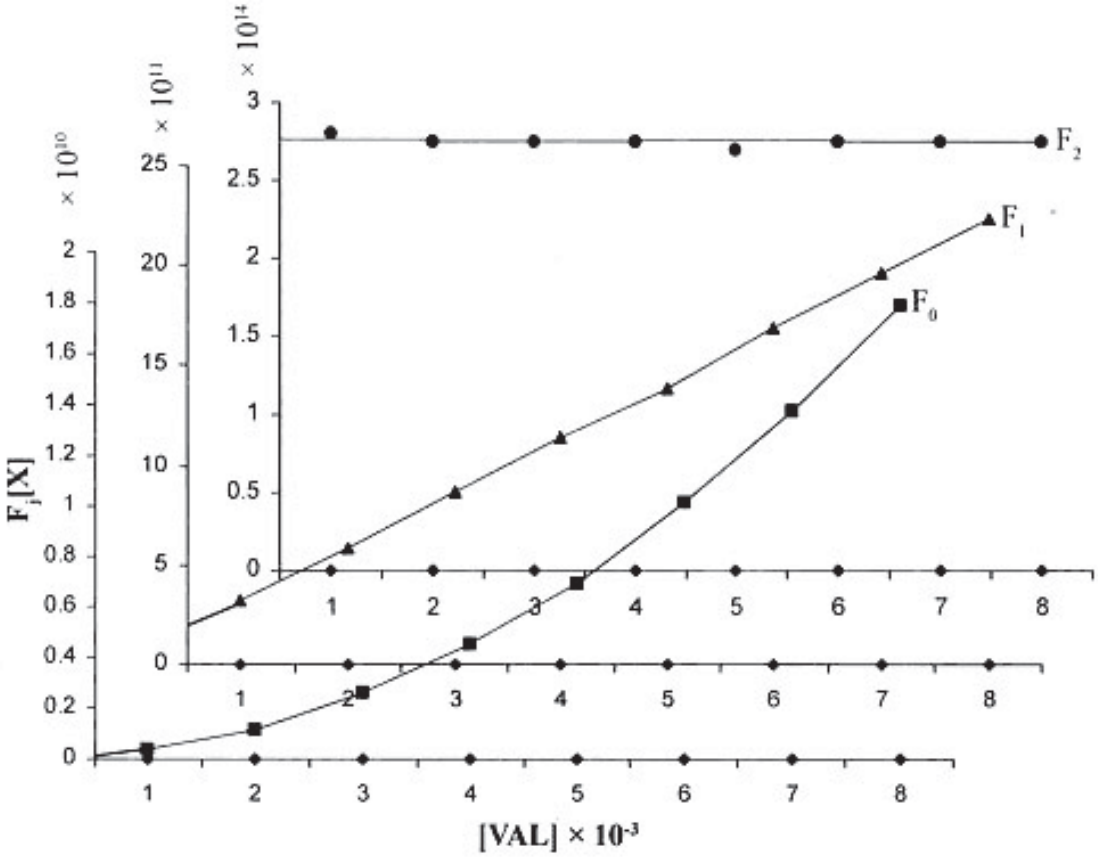

Fig. 3: Plot of F_j [X] vs (VAL) : Cu (II)-L-valinate system at 300 K

$$(f'-1)\left[L'' + \frac{(L'')^2}{2!}a\right] - (f'-1)\left[L' + \frac{(L')^2}{2!}a\right] = 0$$

And for 'A'

$$A\ \frac{(f'-1)}{\Sigma \frac{(L')^n}{n!}\ a^n}$$

where f's are the F_0[X] function and L's are ligand concentrations. Mihailov's constants 'a' and 'A' for various combinations of ligand concentrations and at various ligand concentrations, respectively have been recorded in Tables 4 to 6 together with their average values.

The stability constants obtained by the two methods have been tabulated in Table 7.

A very good agreement can be seen between the values obtained by two methods.

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