POLAROGRAPHIC STUDIES ON AMINO ACID COMPLEXES OF CADMIUM

V.L. Khuspe and B.I. Nemade*

Department of Chemistry, University of Bombay, Vidyanagari, Bombay - 400 098

The reduction of cadmium in presence of glutamic acid, norvaline and isoleucine was found to be reversible in nature. The stability constants of cadmium complexes were found to be $\beta_1 = 1.2 \times 10^4$, $\beta_2 = 1.35 \times 10^6$ and $\beta_3 = 2.0 \times 10^8$ for glutamic acid, $\beta_1 = 1.30 \times 10^4$, $\beta_2 = 3.5 \times 10^6$ and $\beta_3 = 4.7 \times 10^8$ for norvaline and $\beta_1 = 1.5 \times 10^4$, $\beta_2 = 6.2 \times 10^6$ and $\beta_3 = 7.0 \times 10^8$ for isoleucine respectively.

Amino acids are well known for their tendency to form complexes with metals and have great significance in biological, pharmaceutical fields and are directly involved in all the metabolic, enzymatic activities of every living being. Polarographic behaviour and metal complexes of several such amino acids or compounds have been investigated by various research workers[1-11].

EXPERIMENTAL

All current potential curves were recorded on a Manual set up using DME and SCE. The capillary had following characteristics, m = 1.72 mg/sec. and t = 4.0 sec.in 0.5 M potassium nitrate in open circuit. All measurements were carried out at 30 + 0.1°C. The ionic strength was maintained at 0.5 M with potassium nitrate. Gelatin (0.002%) was used as maximum supressor. The pH of the solution was measured with an expanded scale pH meter (Electronic Corporation of India Limited, Hyderabad, Model No. pH 821 B). The pH of the solution was maintained by using CO_2 free sodium hydroxide or dilute perchloric acid solution.

A stock solution of cadmium was prepared by dissolving cadmium nitrate (AR) in double distilled water and was estimated by standard method[12]. L-glutamic acid (E.Merck) DL-Norvaline, AR and L-isoleucine (Fluka) were used without further purification. All other chemicals used were of AR grade. The pK of the ligands were determined seperately by the pH titration technique of Irving and Rossotti[13]. The values are $pK_1 = 2.10$, $pK_2 = 4.11$ and $pK_3 = 9.45$ for glutamic acid, $pK_1 = 2.26$, and $pK_2 = 9.53$ for norvaline and $pK_1 = 2.40$ and $pK_2 = 9.58$ for isoleucine. The concentratrion of ligand ion was calculated from the pH of the solution.

RESULTS AND DISCUSSION

Cadmium gave a well-defined reversible wave in 0.5 M potassium nitrate medium with the half-wave potential at - 0.580 V vs SCE. The reduction remained reversible in the presence of glutamic acid, norvaline and isoleucine but the wave shifted to more negative potentials indicating complexation. (Fig. 1,2&3).

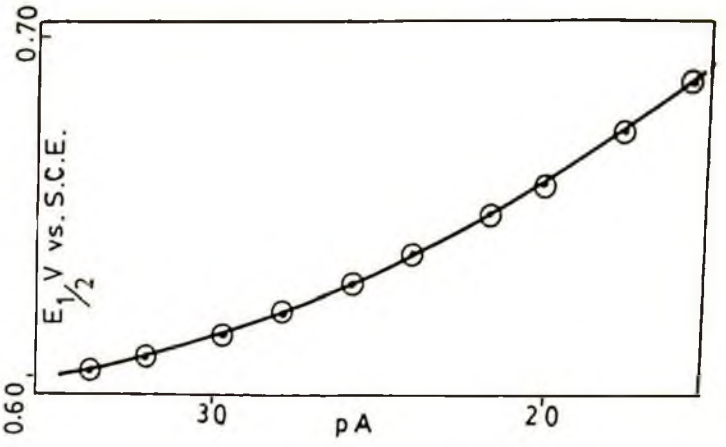


Fig. 1 $E_{1/2}$ vs. pA Cadmium - Glutamic Acid System

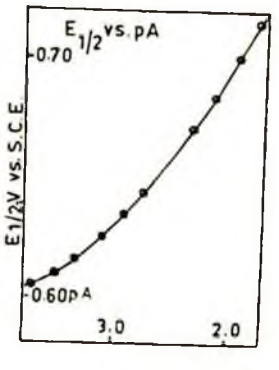


Fig. 2 Cadmium - Norvaline system $E_{1/2}$ vs. pA

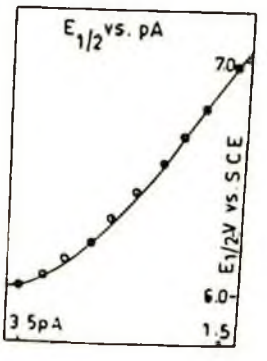


Fig. 3 Cadmium - Isoleucine system $E_{1/2}$ vs. pA

TABLE 1

CADMIUM-GLUTAMIC ACID SYSTEM :
ANALYSIS OF DATA BY DEFORD AND HUME'S METHOD

$m^{2/3}\ t^{1/6}$, 1.80 $mg^{2/3}\ sec^{-1/2}$

μ = 0.5 M KNO_3 Temp = 30°C

pA	F_0 (A)	F_0 (A)x10^{-4}	F_2 (A)x10^{-6}	F_3 (A)x10^{-9}
3.4	6.10	-	-	-
3.2	9.09	1.28	1.30	-
3.0	14.57	1.36	1.57	0.22
2.8	24.18	1.46	1.65	0.19
2.6	43.48	1.67	1.87	0.21
2.4	83.39	2.07	2.18	0.21
2.2	180.9	2.85	2.61	0.20
2.0	455.5	4.54	3.34	0.20
1.8	1309	8.25	4.45	0.20
1.6	4291	17.0	6.32	0.20

$\beta_1 = 1.2 \times 10^4$, $\beta_2 = 1.35 \times 10^6$ and $\beta_3 = 2.0 \times 10^8$

TABLE 2

CADMIUM-NORVALINE SYSTEM :
ANALYSIS OF DATA DEFORD AND HUME'S METHOD

$m^{2/3}\ t^{1/6}$ = 1.80 $mg^{2/3}\ sec^{-1/2}$

μ = 0.5 M KNO_3 Temp. = 30°C

pA	F_0 (A)	F_1 (A)x10^{-4}	F_2 (A)x10^{-6}	F_3 (A)x10^{-8}
3.4	6.4	1.37	-	-
3.2	10.4	1.49	-	-
3.0	18.0	1.70	3.97	0.47
2.8	32.3	1.98	4.26	0.48
2.6	63.3	2.48	4.69	0.47
2.4	138	3.44	5.36	0.47
2.2	339	5.37	6.44	0.47
2.0	951	9.50	8.20	0.47
1.8	2951	18.61	10.92	0.47
1.6	10054	40.02	15.41	0.47

$\beta_1 = 1.30 \times 10^4$, $\beta_2 = 3.5 \times 10^6$ and $\beta_3 = 4.7 \times 10^8$

A plot of the half-wave potential ($E_{1/2}$) vs. pA resulted in a smooth curve indicating the presence of different species whose stabilities do not differ greatly. The data were, therefore, analysed by the method of DeFord and Hume[14] for the Fronaeus function[15] F (A) using the expression

$$F_0\ (A) = \text{antilog}\left[0.4343\ \frac{nF}{RT}\Delta E_{1/2} + \log\frac{i_{d(s)}}{i_{d(c)}}\right]$$

$$= 1 + \beta_1[A] + \beta_2.[A]^2 + \beta_3.[A]^3 + \ldots + \beta_N\ .\ [A]^N$$

where $\Delta E_{1/2}$ refer to the shift in half-wave potentials on complexation and $i_{d(s)}$ and $i_{d(c)}$ are the corresponding diffusion currents. β's refer to the overall stability constants and [A] is the concentration of the ligand. The F_0 (A) functions,

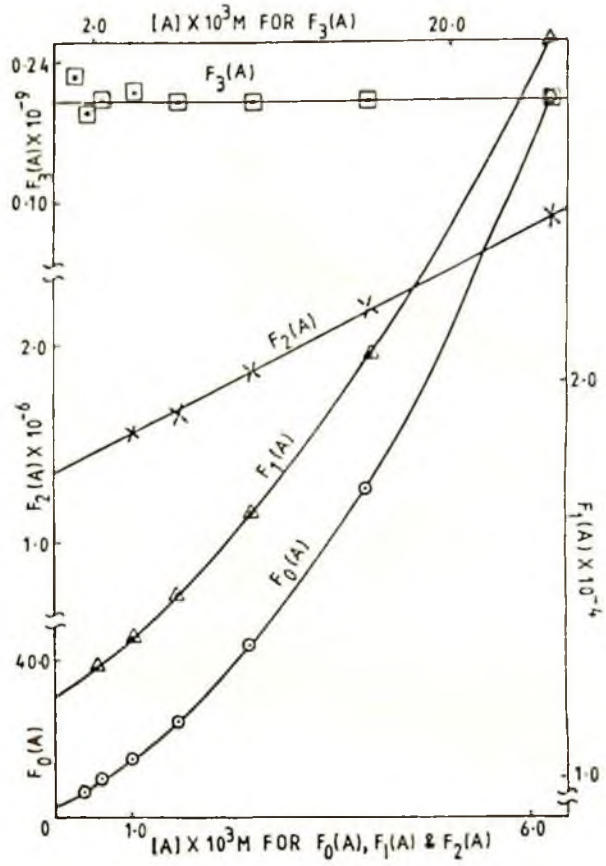


Fig. 4 Cadmium - Glutamic Acid System F Functions

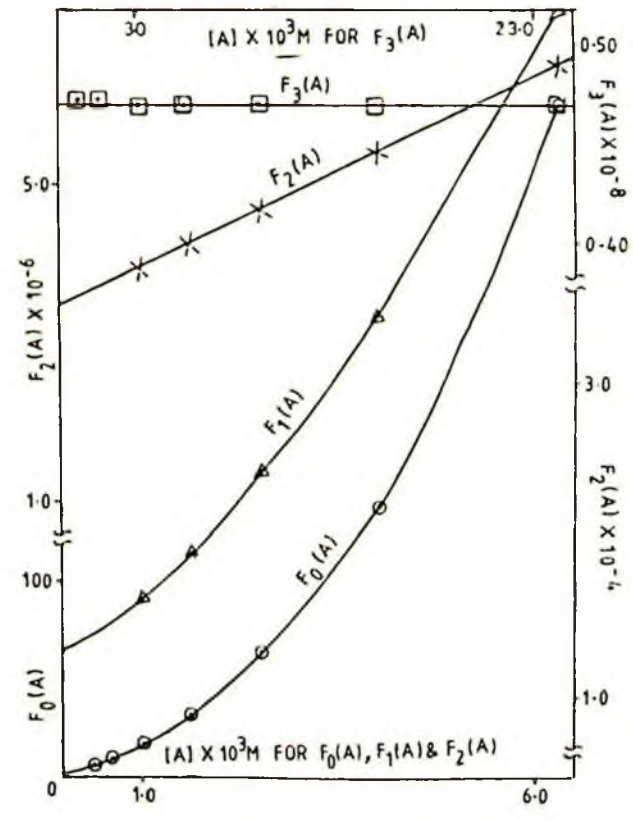


Fig. 5 Cadmium - Norvaline System, F-Functions

TABLE 3

CADMIUM-ISOLEUCINE SYSTEM:
ANALYSIS OF DATA BY DEFORD AND HUMES METHOD

$m^{2/3}\ t^{1/6} = 1.80\ mg^{2/3}\ sec^{-1/2}$

μ = 0.5M KNO_3 Temp. = 30°C

pA	F_0 (A)	F_1 (A)$\times 10^{-3}$	F_2 (A)$\times 10^{-6}$	F_3 (A)$\times 10^{-9}$
3.5	6.38	1.70	6.41	0.66
3.3	10.1	1.82	6.57	0.73
3.1	17.1	2.03	6.74	0.68
2.9	31.1	2.39	7.07	0.69
2.7	60.9	3.00	7.52	0.66
2.3	131	4.13	8.31	0.66
2.3	318	6.34	9.62	0.69
2.1	862	10.84	11.8	0.70
1.9	2553	20.27	14.9	0.69
1.7	8442	42.31	20.4	0.71

$\beta_1 = 1.5 \times 10^4$, $\beta_2 = 6.2 \times 10^6$ and $\beta_3 = 7 \times 10^8$

calculated at different ligand concentrations, were then solved for the stability constants by a graphical procedure (Fig.4,5&6).

The values of the stability constants (Table 1,2 and 3) were checked by calculating the F function and comparing with the experimental values. Three complexes were identified with $\beta_1 = 1.2 \times 10^4$; $\beta_2 = 1.35 \times 10^6$ and $\beta_3 = 2.0 \times 10^8$ for glutamic acid, $\beta_1 = 1.30 \times 10^4$, $\beta_2 = 3.5 \times 10^6$ and $\beta_3 = 4.7 \times 10^8$ for norvaline and $\beta_1 = 1.5 \times 10^4$, $\beta_2 = 6.2 \times 10^6$ and $\beta_3 = 7.0 \times 10^8$ for isoleucine respectively.

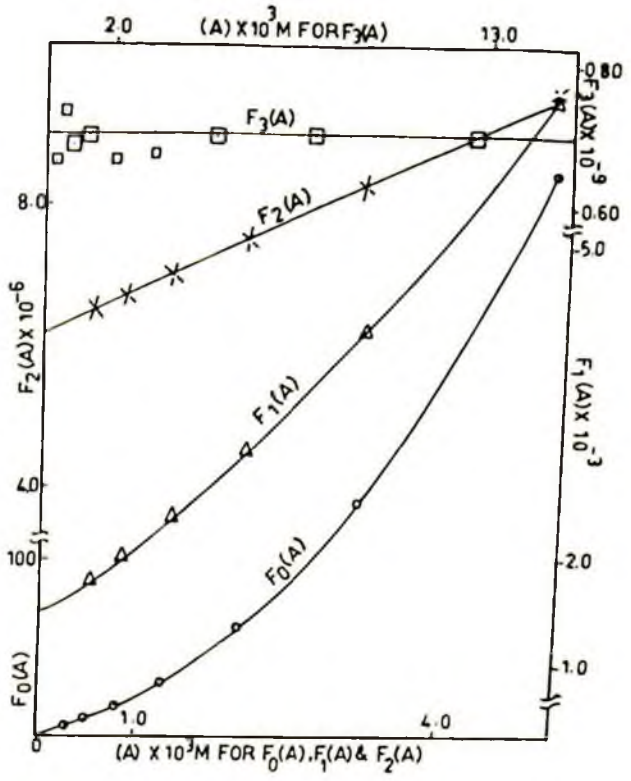


Fig. 6 Cadmium - Isoleucine System F - Functions

Results show that stability of the complexes are in the order: Glutamic acid>Norvaline>Isoleucine indicating that as pK_A values of amino acid increase, the value of stability constant of complex also increases.

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