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Formation of Mixed Complexes of Cadmium(II) with Methyl Imino Diacetic Acid and Some Amino Acids at Dropping Mercury Electrode

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The present investigation describes the polarographic determination of the stability constant of binary and ternary metal complexes of Cd(II) with methyl imino diacetic acid and some amino acids (isoleucinate, valinate, citrullinate, threoninate and serinate) by the treatment of Schaap and McMasters. The reduction of all the complexes has been found to be reversible and diffusion controlled, involving two electrons. The statistical and electrochemical effects have been discussed by using these stability constants.

Key Words: Methyl imino diacetic acid, Amino acids, Polarographically.

INTRODUCTION

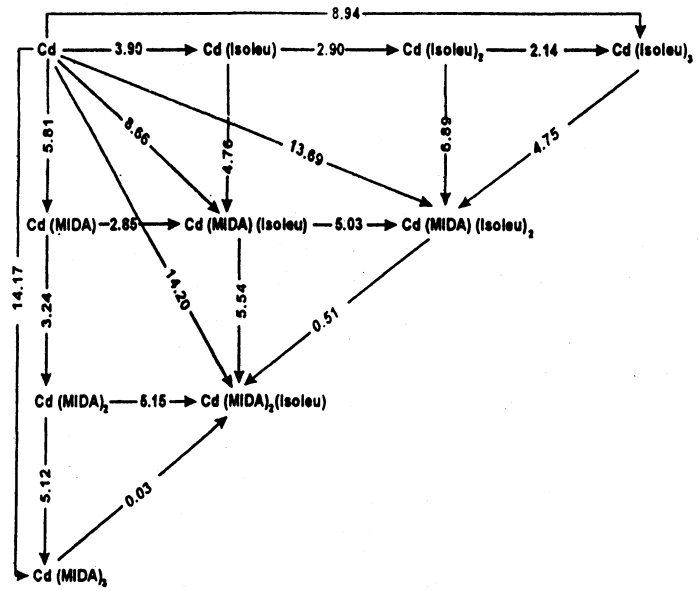
The studies of mixed ligand complexes plays an important role in biological processes[1, 2]. Biologically active metal complexes of amino acids, which are important in analytical, biochemical and pharmaceutical fields[3–5], have been studied by many workers[6–9]. Amino acids, which form stable complexes, have analytical importance in separation of transition metals and rare earths[10]. A study of these complexes is also important in biological chemistry, in that the accumulation of sufficient data on amino acids complexes with metal ions may contribute to a better understanding of the type of linkages involved in metal protein interactions[11]. Studies on mixed ligand complexes of Cd(II) with amino acid and carboxylic acids have been reported by Khan and Nema[12–14]. Mixed ligand complexes of Cu, Cd and Pb with different amino acids and malonic acid and oxalic acid have been reported by Shah[15]. Singh *et al.*[16] have reported mixed ligand complexes of Cd(II) with phthalate and some amino acids. Recently, the studies of amino acids have increased due to their wide application. Reduction of glycinate and alaninate complexes of palladium(II) on a dropping mercury electrode at different temperatures has been studied kinetically by Nikiforova *et al.*[17] The studies of the ternary complexes of different metal ions with amino acids and bicarboxylic acids have been carried out in our laboratory[18–21].

In the present work, it is proposed to undertake comprehensive polarographic studies on the composition and stability of mixed complexes of cadmium(II) with methyl imino diacetic acid (MIDA) and some amino acids.

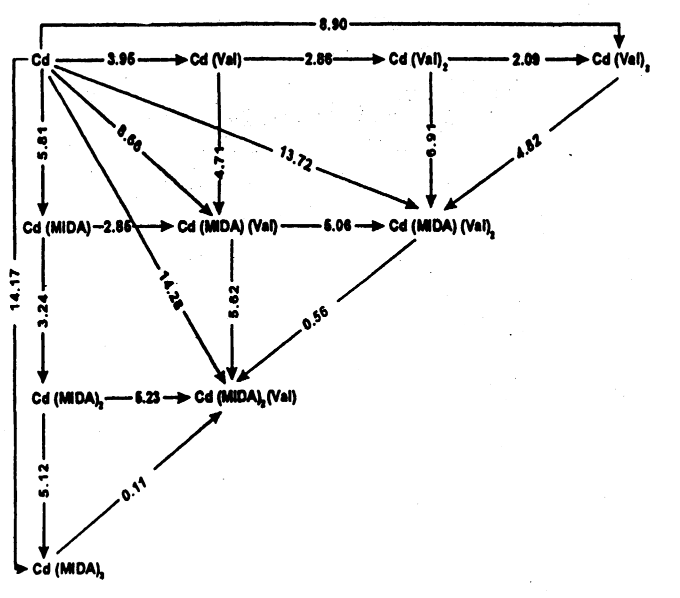
EXPERIMENTAL

All the chemicals (DL-isoleucine, DL-valine, L-citrullinate, DL-threonine, L-serine and MIDA) were used as complexing agents. All the above chemicals were AnalaR grade and their solutions were prepared in double distilled water. KNO_3

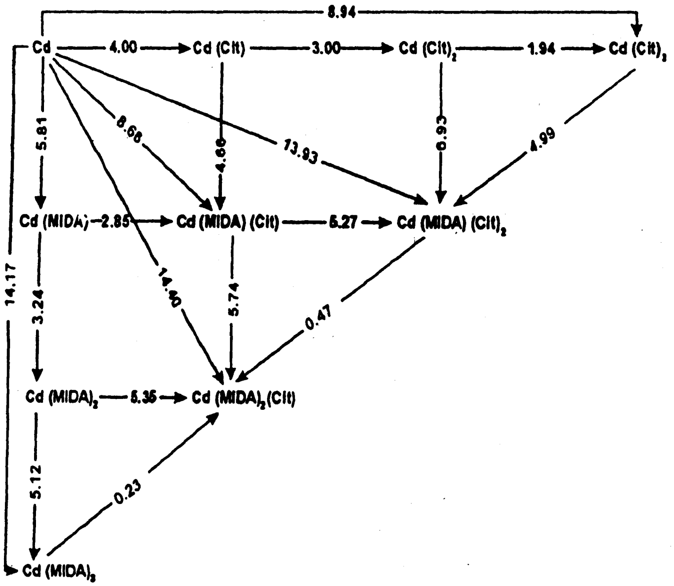
was used as supporting electrolyte. The ionic strength was maintained constant at 0.2 M with KNO_3 in all the systems studied in this communication. Gelatin (0.004 M) in the final solution sufficed to suppress the maxima observed. 5×10^{-4} M concentration of Cd(II) was used in the study. The temperature was maintained constant throughout the investigations at 303 ± 1 K. The experimental techniques were the same as described earlier[22].



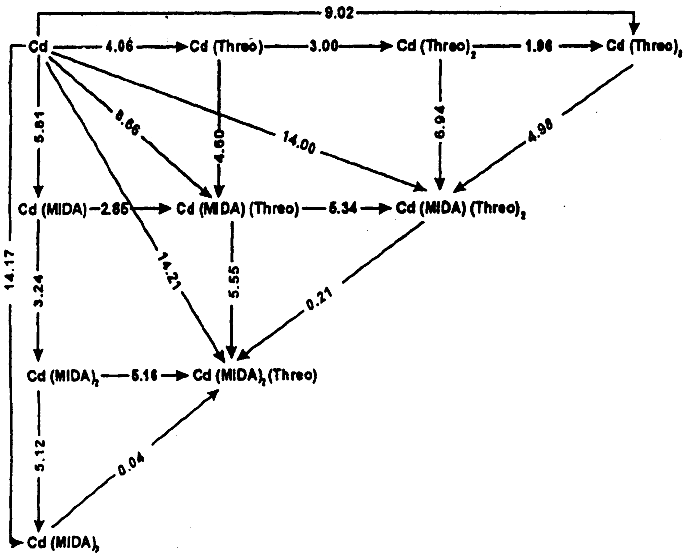
Scheme-1. Cd-MIDA-isoluecinate system



Scheme-2. Cd-MIDA-valinate system



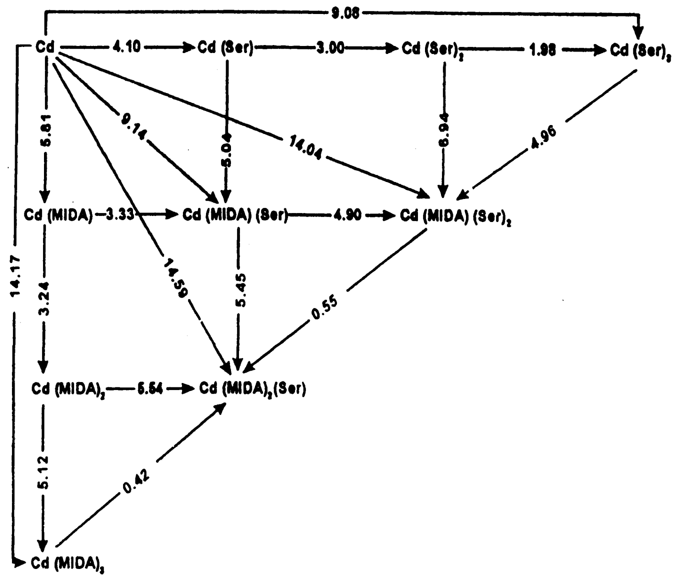
Scheme-3. Cd-MIDA-citrulline system



Scheme-4. Cd-MIDA-threoninate system

RESULTS AND DISCUSSION

Simple Systems: The formation constant of the complexes of Cd(II) with MIDA, isoleucine, valine, citrullinate, threonine and serine acid were determined prior to the study of the mixed ligand systems. The stability constants have been evaluated by the method of Deford and Hume as improved by Irving. The plot of $F_0[X]$ *vs.* [X] results into a curve and has an intercept on $F_0[X]$ axis equal to unity in



Scheme-5. Cd-MIDA-serinate system

all the systems. The plot of $F_1[X]$ axis gives the value equal to β_1 and the plot of $F_2[X]$ *vs.* [X] is a straight line parallel to [X] axis and is independent of [X]. Thus all the complexing agents under study in this paper form 1 : 1, 1 : 2 and 1 : 3 complexes.

The half wave potential of Cd(II) is 0.2 M KNO_3 was measured accurately at the time of running each series of solution and was ranged between –0.579 and –0.583 V *vs.* SCE.

A simple well-defined reduction wave was obtained in all the cases. The wave was found to be diffusion controlled and reversible. The plot of $E_{d.e.}$ *vs.* log i_{d-i} gave a straight line with slope of 30 ± 2 mV.

The results are being summarized in Table-1. The values agree well with those reported in literature.

TABLE-1
STABILITY CONSTANTS OF Cd WITH MIDA AND AMINO ACIDS

Systems	log β_1	log β_2	log β_3
Cd-MIDA	5.81	9.05	14.17
Cd-Isoleucinate	3.90	6.80	8.94
Cd-Valinate	3.95	6.81	8.90
Cd-Citrulline	4.00	7.00	8.94
Cd-Threoninate	4.06	7.06	9.02
Cd-Serinate	4.10	7.06	9.08

Mixed Systems: The formation of three complexes [Cd(MIDA)(amino acid)], [Cd(MIDA)(amino acid)$_2$] and [Cd(MIDA)$_2$(amino acid)] would be expected.

In these studies, on the mixed complex systems, a ligand displacement technique has been used in which a more complexing species is added to a mixture of a metal ion with weaker complexing species.

The concentration of amino acids (weaker ligand) was held constant at 0.01 M and 0.001 M respectively and concentration of MIDA (stronger ligand) was varied over a wide range.

The F_{ij} functions were calculated by Schaap and McMasters treatment and the results are tabulated in Tables 2(A) to 6(B) and the Graphs 1(A) to 5(B). The values of A, B, C and D at the two concentrations of amino acid ions for all the systems and are tabulated in Tables 8(A) and 8(B). The overall stability constants β_{11}, β_{12} and β_{21} have been presented in Table-7.

TABLE-2(A)
DATA AND RESULTS FOR CADMIUM-MIDA-ISOLEUCINATE SYSTEM
Isoleucinate = 0.01, $E_{1/2}[M] = 0.580$ *vs.* SCE

[X] $\times 10^3$	$\Delta E_{1/2}/V$	log I_m/I_c	$F_{00} \times 10^{-6}$	$F_{10} \times 10^{-9}$	$F_{20} \times 10^{-12}$	$F_{30} \times 10^{-14}$	$F_{00} \times 10^{-6}$ (cal)	ΔF%
0.50	0.193	0.03776	2.87653	5.74990	1.69980	1.99*	2.87	0.00
1.00	0.204	0.39100	6.70162	6.70004	1.80040	2.00*	6.65	–0.74
1.50	0.210	0.72020	11.44774	7.63077	1.82050	1.47	11.44	0.00
2.00	0.215	0.08654	17.36161	8.68001	1.89000	1.45	17.38	+0.12
2.50	0.219	0.10417	24.56405	9.82499	1.96999	1.48	24.56	0.00
3.00	0.222	0.13385	33.09710	11.03184	2.04394	1.48	33.09	0.00
3.50	0.225	0.14869	43.09630	12.31277	2.11793	1.48	43.09	0.00
4.00	0.228	0.15272	54.73687	13.68382	2.19595	1.49	54.67	–0.13
4.50	0.230	0.17884	67.75478	15.05627	2.25694	1.46	67.93	+0.26
5.00	0.232	0.20044	83.00036	16.59975	2.33995	1.48	83.00	0.00

A = 1576 (cal) B = 4.90×10^4 C = 1.60×10^{12} D = 1.48×10^{14} *May be deleted

TABLE-2(B)
DATA AND RESULTS FOR CADMIUM-MIDA-ISOLEUCINATE SYSTEM
Isoleucinate = 0.001, $E_{1/2}[M] = 0.580$ *vs.* SCE

[X] $\times 10^3$	$\Delta E_{1/2}/V$	log I_m/I_c	$F_{00} \times 10^{-6}$	$F_{10} \times 10^{-9}$	$F_{20} \times 10^{-12}$	$F_{30} \times 10^{-14}$	$F_{00} \times 10^{-6}$ (cal)	ΔF%
0.50	0.147	0.03108	8.35160	1.66999	23.39980	1.48	8.35	0.00
1.00	0.165	0.06435	35.80139	3.57997	30.79970	1.48	35.80	0.00
1.50	0.177	0.08179	93.45014	6.22990	38.19933	1.48	93.45	0.00
2.00	0.186	0.09598	193.39775	9.61980	45.59900	1.48	192.400	–0.05
2.50	0.193	0.11513	342.74786	13.74985	52.99939	1.48	343.750	–0.05
3.00	0.202	0.12393	698.98845	23.29956	75.99853	2.00*	558.600	–20.08
3.50	0.207	0.14290	1071.00130	30.59999	85.99999	2.00*	848.050	–20.82
4.00	0.208	0.17185	1235.97590	30.89935	75.99837	1.50	1223.2000	–1.03
4.50	0.212	0.17596	1625.11830	37.66925	82.59833	1.48	1695.1500	–0.02
5.00	0.215	0.19913	2249.98700	44.99970	88.99940	1.46	2275.0000	+1.11

A = 16.12 (cal) B = 5.00×10^7 C = 1.60×10^{11} D = 1.48×10^{14} *May be deleted

TABLE-3(A)
DATA AND RESULTS FOR CADMIUM-MIDA-VALINATE SYSTEM
Valinate = 0.01, $E_{1/2}[M]$ = 0.580 *vs.* SCE

[X] $\times 10^3$	$\Delta E_{1/2}$/V	log I_m/I_c	F_{00} $\times 10^{-6}$	F_{10} $\times 10^{-9}$	F_{20} $\times 10^{-12}$	F_{30} $\times 10^{-14}$	$F_{00} \times 10^{-6}$ (cal)	ΔF%
0.50	0.194	0.03979	3.12011	6.23715	1.97430	1.49	3.12	0.00
1.00	0.205	0.04306	7.30146	7.29992	2.04992	1.50	7.30	0.00
1.50	0.212	0.04934	12.66426	8.44182	2.12788	1.52	12.65	–0.08
2.00	0.217	0.06582	19.29345	9.64596	2.19798	1.49	19.29	0.00
2.50	0.221	0.09644	28.12613	11.24984	2.39993	2.00*	27.32	–2.84
3.00	0.224	0.11424	36.87397	12.29081	2.34693	1.49	36.97	0.00
3.50	0.227	0.12931	48.03966	13.72518	2.42148	1.49	48.03	0.00
4.00	0.230	0.13278	60.93685	15.23383	2.49595	1.49	60.93	0.00
4.50	0.232	0.16033	75.67806	16.81700	2.57044	1.49	75.67	0.00
5.00	0.234	0.18096	92.49963	18.49962	2.64992	1.50	92.37	–0.12

A = 1531 (cal) B = 5.25×10^9 C = 1.90×10^{12} D = 1.49×10^{14} *May be deleted

TABLE-3(B)
DATA AND RESULTS FOR CADMIUM-MIDA-VALINATE SYSTEM
Valinate = 0.001, $E_{1/2}[M]$ = 0.580 *vs.* SCE

[X] $\times 10^3$	$\Delta E_{1/2}$/V	log I_m/I_c	F_{00} $\times 10^{-4}$	F_{10} $\times 10^{-8}$	F_{20} $\times 10^{-11}$	F_{30} $\times 10^{-14}$	$F_{00} \times 10^{-4}$ (cal)	ΔF%
0.50	0.149	0.03957	9.92658	1.98497	2.89994	2.00*	9.26	–6.65
1.00	0.168	0.05755	44.35167	4.43499	3.89999	2.00*	39.05	–11.95
1.50	0.178	0.07962	100.38758	6.69239	4.10492	1.47	100.38	0.00
2.00	0.187	0.08878	204.37700	10.21495	4.43997	1.47	204.30	0.00
2.50	0.194	0.10410	361.80953	14.47231	5.57492	1.47	361.81	–0.02
3.00	0.200	0.11237	583.94239	19.46468	6.30989	1.47	583.95	–0.02
3.50	0.205	0.12499	881.73890	25.19249	7.04499	1.47	881.73	0.00
4.00	0.209	0.14907	1266.19930	31.65478	7.77994	1.47	1266.20	0.00
4.50	0.213	0.16286	1775.70170	39.45999	8.64999	1.50	1748.36	–1.54
5.00	0.215	0.22064	2364.32150	47.28459	9.34991	1.49	2339.25	–1.06

A = 17.24 (cal) B = 5.35×10^7 C = 1.90×10^{11} D = 1.47×10^{14} *May be deleted

TABLE-4(A)
DATA AND RESULTS FOR CADMIUM-MIDA-CITRULLINATE SYSTEM
Citrullinate = 0.01, $E_{1/2}[M]$ = 0.580 *vs.* SCE

[X] $\times 10^3$	$\Delta E_{1/2}$/V	log I_m/I_c	$F_{00} \times 10^{-6}$	$F_{10} \times 10^{-9}$	$F_{20} \times 10^{-12}$	$F_{30} \times 10^{-14}$	$F_{00} \times 10^{-6}$ (cal)	ΔF%
0.50	0.200	0.03581	4.89564	9.78733	2.57446	1.49	4.89	0.00
1.00	0.210	0.06065	11.15192	11.14995	2.64995	1.50	11.15	0.00
1.50	0.216	0.08975	18.88295	12.58732	2.72488	1.50	18.88	0.00
2.00	0.221	0.09760	28.20135	14.09969	2.79984	1.50	28.20	0.00
2.50	0.225	0.10776	39.22021	15.68729	2.87491	1.50	39.22	0.00
3.00	0.228	0.13110	52.07868	17.35890	2.95296	1.51	52.05	–0.04
3.50	0.231	0.14085	67.02240	19.14869	3.04248	1.55	66.80	–0.32
4.00	0.233	0.17295	84.11239	21.02760	3.13190	1.58	83.60	–0.60
4.50	0.235	0.19630	103.45465	22.98948	3.21988	1.60	102.54	–0.88
5.00	0.237	0.20756	123.45137	24.74987	3.24997	1.50	123.75	0.00

A = 1971 (cal) B = 8.50×10^9 C = 2.50×10^{12} D = 1.50×10^{14}

TABLE-4(B)
DATA AND RESULTS FOR CADMIUM-MIDA-CITRULLINATE SYSTEM
Citrullinate = 0.001, $E_{1/2}[M]$ = 0.580 *vs.* SCE

[X] $\times 10^3$	$\Delta E_{1/2}$/V	log I_m/I_c	$F_{00} \times 10^{-5}$	$F_{10} \times 10^{-8}$	$F_{20} \times 10^{-11}$	$F_{30} \times 10^{-14}$	$F_{00} \times 10^{-5}$ (cal)	ΔF%
0.50	0.152	0.03557	1.23768	2.47492	3.22984	1.46	1.23	0.00
1.00	0.169	0.06043	4.82014	4.81992	3.95992	1.46	4.82	0.00
1.50	0.180	0.08485	11.84268	7.89497	4.68998	1.46	11.84	0.00
2.00	0.188	0.11445	23.39968	11.69973	5.41986	1.46	23.40	+0.04
2.50	0.195	0.12738	41.21269	16.48495	6.24998	1.50	40.58	–1.52
3.00	0.201	0.12950	65.57978	21.85985	6.99995	1.50	64.50	–1.63
3.50	0.206	0.13737	97.94674	27.98472	7.74992	1.50	96.23	–1.74
4.00	0.211	0.14007	144.55729	36.13926	8.81981	1.58	136.88	–5.31
4.50	0.215	0.14862	200.29495	44.50994	9.69998	1.60	187.53	–6.37
5.00	0.217	0.17713	249.29869	49.85969	9.79993	1.46	249.30	+0.04

A = 21.87 (cal) B = 8.60×10^7 C = 2.50×10^{11} D = 1.46×10^{14}

TABLE-5(A)
DATA AND RESULTS FOR CADMIUM-MIDA-THREONINATE SYSTEM
Threoninate = 0.01, $E_{1/2}[M] = 0.580$ *vs.* SCE

[X] × 10^3	$\Delta E_{1/2}$/V	log I_m/I_c	F_{00} × 10^{-6}	F_{10} × 10^{-9}	F_{20} × 10^{-12}	F_{30} × 10^{-14}	F_{00} × 10^{-6} (cal)	ΔF%
0.50	0.203	0.01194	5.83109	11.65755	3.31510	1.50	5.83	0.00
1.00	0.213	0.04037	13.39306	13.39075	3.39074	1.51	13.39	0.00
1.50	0.220	0.04171	22.96730	15.30999	3.53999	2.00*	22.80	–0.69
2.00	0.225	0.05285	34.56209	17.27988	3.63994	2.00*	34.17	–1.12
2.50	0.229	0.05888	47.61129	19.04359	3.61743	1.51	47.61	0.00
3.00	0.232	0.08308	43.34611	21.11460	3.70486	1.55	63.23	–0.17
3.50	0.235	0.09092	41.16522	23.189403	3.76800	1.51	81.16	0.00
4.00	0.237	0.12150	101.50560	25.37582	3.84395	1.51	101.50	0.00
4.50	0.239	0.14319	124.37125	27.63754	3.91945	1.51	124.47	0.00
5.00	0.241	0.15766	149.87528	29.97459	3.99491	1.51	149.87	0.00

A = 2316 (cal) B = 1.00×10^{10} C = 3.24×10^{12} D = 1.51×10^{14} *May be deleted

TABLE-5(B)
DATA AND RESULTS FOR CADMIUM-MIDA-THREONINATE SYSTEM
Threoninate = 0.001, $E_{1/2}[M] = 0.580$ *vs.* SCE

[X] × 10^3	$\Delta E_{1/2}$/V	log I_m/I_c	F_{00} × 10^{-5}	F_{10} × 10^{-8}	F_{20} × 10^{-11}	F_{30} × 10^{-14}	F_{00} × 10^{-5} (cal)	ΔF%
0.50	0.155	0.01895	1.49899	2.99748	3.97497	1.45	1.49	0.00
1.00	0.172	0.03421	5.71018	5.70993	4.69993	1.45	5.71	0.00
1.50	0.185	0.03755	15.57758	10.38488	6.24992	2.00*	13.72	–11.88
2.00	0.193	0.07056	31.02201	15.51088	7.25044	2.00*	26.62	–14.18
2.50	0.197	0.10376	45.49356	18.19732	6.87493	1.45	45.49	0.00
3.00	0.202	0.13334	71.42989	23.80988	7.59996	1.45	71.43	+0.04
3.50	0.207	0.13643	105.51641	30.14747	8.32499	1.45	105.51	0.00
4.00	0.211	0.15275	148.84012	37.20996	9.04999	1.45	148.84	0.00
4.50	0.214	0.19628	207.04274	46.00940	9.99987	1.50	202.48	–2.20
5.00	0.217	0.21386	271.30013	54.25997	10.64999	1.48	267.55	–1.38

A = 25.05 (cal) B = 1.01×10^8 C = 3.25×10^{11} D = 1.45×10^{14} *May be deleted

TABLE-6(A)
DATA AND RESULTS FOR CADMIUM-MIDA-SERINATE SYSTEM
Serinate = 0.01, $E_{1/2}[M] = 0.580$ *vs.* SCE

$[X] \times 10^3$	$\Delta E_{1/2}/V$	$\log I_m/I_c$	$F_{00} \times 10^{-6}$	$F_{10} \times 10^{-10}$	$F_{20} \times 10^{-12}$	$F_{30} \times 10^{-14}$	$F_{00} \times 10^{-6}$ (cal)	ΔF%
0.50	0.204	0.02567	6.49755	1.29899	3.97991	1.60	6.49	0.00
1.00	0.214	0.05811	15.06225	1.50596	4.05967	1.60	15.05	–0.06
1.50	0.221	0.05887	25.79526	1.71951	4.13008	1.53	25.79	0.00
2.00	0.226	0.07001	38.81771	1.94075	4.20375	1.52	38.81	0.00
2.50	0.230	0.08232	54.25253	2.16999	4.27999	1.52	54.25	0.00
3.00	0.233	0.10666	72.20545	2.40676	4.35587	1.52	72.20	0.00
3.50	0.236	0.11580	92.79402	2.65118	4.43195	1.52	92.79	0.00
4.00	0.238	0.14668	116.12882	2.90315	4.50789	1.52	116.13	+0.08
4.50	0.240	0.16849	142.33789	3.16278	4.58396	1.52	142.32	0.00
5.00	0.242	0.18293	171.50232	3.42999	4.65998	1.52	171.50	0.00

A = 2576 (cal) $B = 1.10 \times 10^{10}$ $C = 3.90 \times 10^{12}$ $D = 1.52 \times 10^{14}$

TABLE-6(B)
DATA AND RESULTS FOR CADMIUM-MIDA-SERINATE SYSTEM
Serinate = 0.001, $E_{1/2}[M] = 0.580$ *vs.* SCE

$[X] \times 10^3$	$\Delta E_{1/2}/V$	$\log I_m/I_c$	$F_{00} \times 10^{-5}$	$F_{10} \times 10^{-8}$	$F_{20} \times 10^{-11}$	$F_{30} \times 10^{-14}$	$F_{00} \times 10^{-5}$ (cal)	ΔF%
0.50	0.156	0.04294	1.71025	3.41995	4.61991	1.44	1.71	0.00
1.00	0.173	0.05386	6.45015	6.44988	5.33988	1.44	6.45	0.00
1.50	0.184	0.06301	15.29995	10.19978	6.06985	1.44	15.30	+0.06
2.00	0.193	0.07962	29.33999	14.66986	6.77993	1.44	29.34	+0.03
2.50	0.198	0.10846	49.65008	19.85992	7.49997	1.44	49.65	0.00
3.00	0.203	0.13442	77.30899	25.76957	8.21985	1.44	77.31	+0.01
3.50	0.208	0.13445	113.39920	32.39969	8.93991	1.44	113.40	+0.01
4.00	0.212	0.15852	152.83959	40.70982	9.89995	1.50	159.00	–2.23
4.50	0.215	0.18343	217.01013	48.22441	10.46986	1.46	215.19	–0.83
5.00	0.218	0.21036	290.54941	58.10982	11.39996	1.50	283.05	–2.57

A = 27.20 (cal) $B = 1.11 \times 10^{8}$ $C = 3.90 \times 10^{11}$ $D = 1.44 \times 10^{14}$

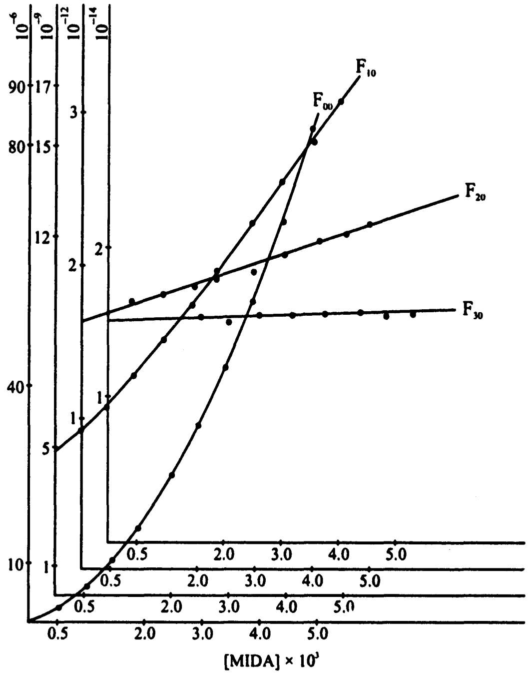


Fig. 1a. Plot of F_{ij} *vs.* [MIDA]: Cd-MIDA-isoluecinate system, [Isolue.] = 0.01 M

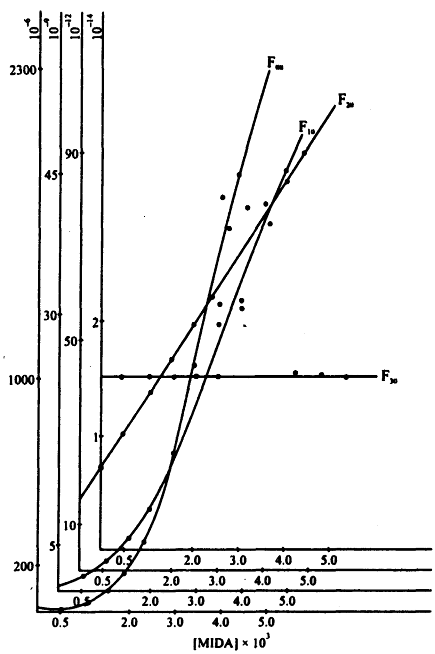


Fig. 1b. Plot of F_{ij} *vs.* [MIDA]: Cd-MIDA-isoluecinate system, [Isolue.] = 0.001 M

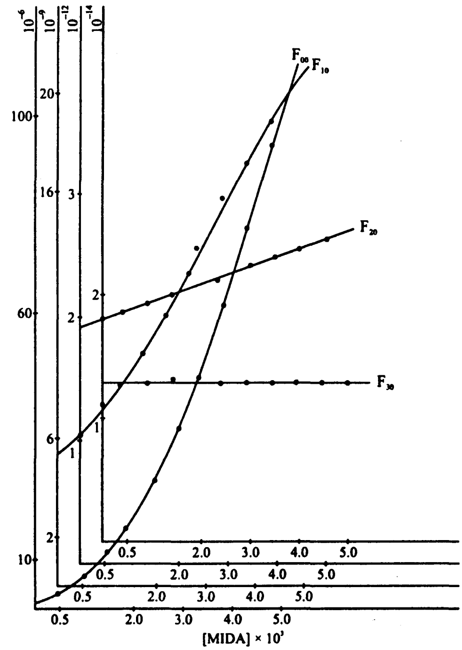


Fig. 2a. Plot of F_{ij} *vs*. [MIDA]: Cd-MIDA-valinate system, [Valin.] = 0.01 M

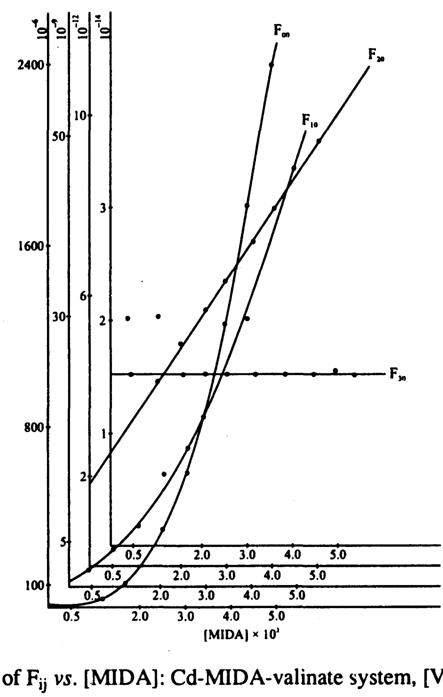


Fig. 2b. Plot of F_{ij} *vs*. [MIDA]: Cd-MIDA-valinate system, [Valin.] = 0.001 M

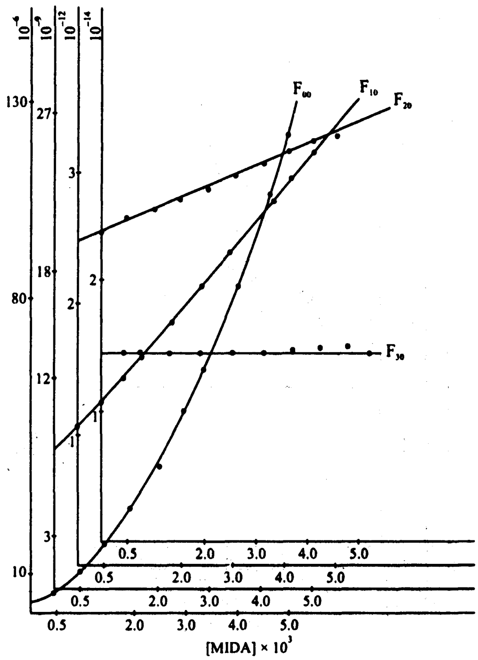


Fig. 3a. Plot of F_{ij} *vs.* [MIDA]: Cd-MIDA-citrulline system, [Cit.] = 0.01 M

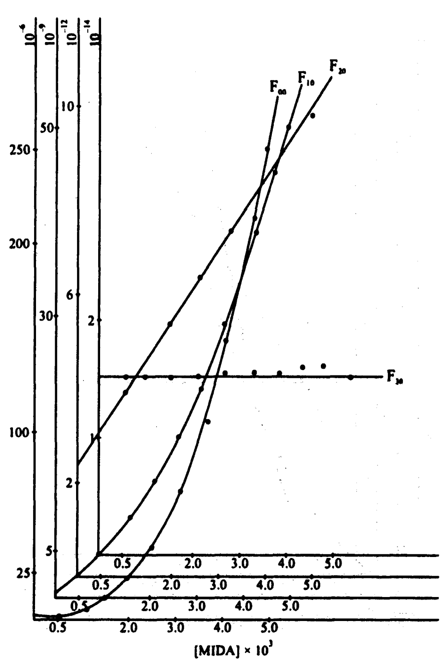


Fig. 3b. Plot of F_{ij} *vs.* [MIDA]: Cd-MIDA-citrulline system, [Cit.] = 0.001 M

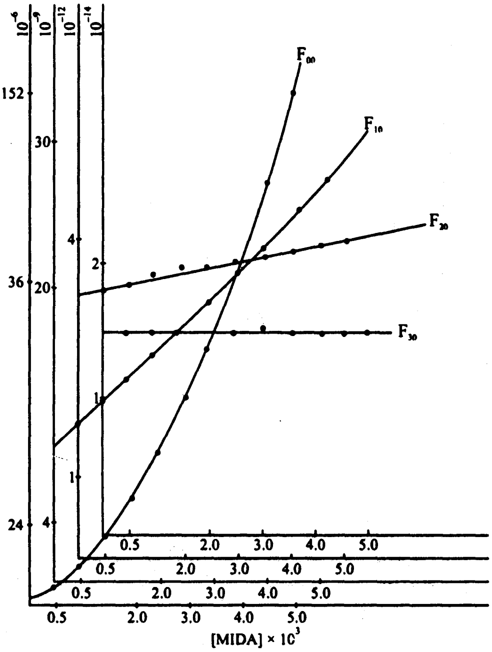


Fig. 4a. Plot of F_{ij} *vs.* [MIDA]: Cd-MIDA-threoninate system, [Threo.] = 0.01 M

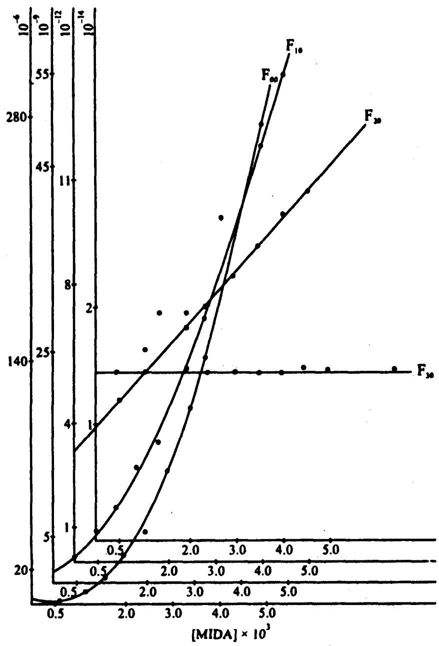


Fig. 4b. Plot of F_{ij} *vs.* [MIDA]: Cd-MIDA-threoninate system, [Threo.] = 0.001 M

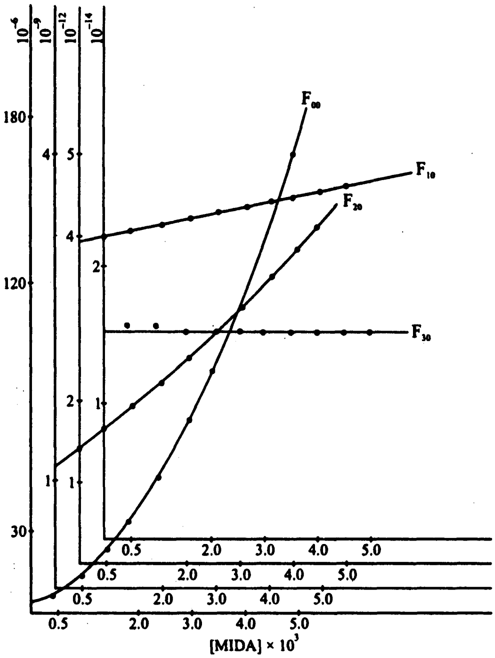


Fig. 5a. Plot of F_{ij} *vs.* [MIDA]: Cd-MIDA-serinate system, [Seri.] = 0.01 M

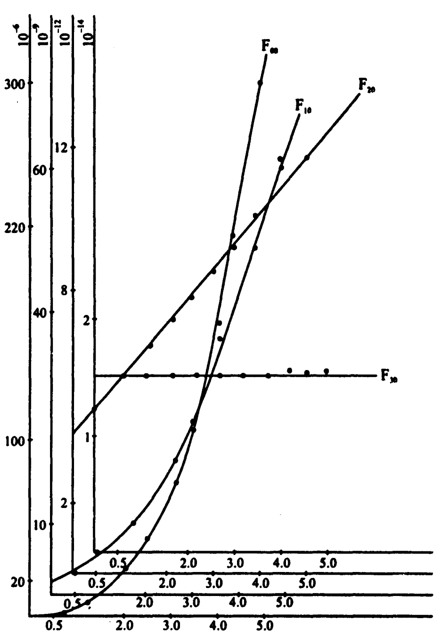


Fig. 5b. Plot of F_{ij} *vs.* [MIDA]: Cd-MIDA-serinate system, [Seri.] = 0.001 M

TABLE-7
STABILITY CONSTANTS OF MIXED LIGAND COMPLEXES WITH Cd-MIDA-AMINO ACIDS SYSTEMS

Systems	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$
Cd-MIDA-Isoleucinate	8.66	13.69	14.20
Cd-MIDA-Valinate	8.66	13.72	14.28
Cd-MIDA-Citrullinate	8.66	13.93	14.40
Cd-MIDA-Threoninate	8.66	14.00	14.21
Cd-MIDA-Serinate	9.14	14.04	14.59

TABLE-8(A)
VALUES OF A, B, C AND D FOR Cd-MIDA-AMINO ACIDS SYSTEMS
Amino acids concentration = 0.01 M

Systems	A	B	C	D
Cd-MIDA-Isoleucinate	1576	49.0×10^{4}	1.60×10^{12}	1.48×10^{14}
Cd-MIDA-Valinate	1531	5.25×10^{9}	1.90×10^{12}	1.49×10^{14}
Cd-MIDA-Citrullinate	1971	8.50×10^{9}	2.50×10^{12}	1.50×10^{14}
Cd-MIDA-Threoninate	2316	1.00×10^{10}	3.24×10^{12}	1.51×10^{14}
Cd-MIDA-Serinate	2576	1.10×10^{10}	3.90×10^{12}	1.52×10^{14}

TABLE-8(B)
VALUES OF A, B, C AND D FOR Cd-MIDA-AMINO ACIDS SYSTEMS
Amino acids concentration = 0.001 M

Systems	A	B	C	D
Cd-MIDA-Isoleucinate	16.12	5.00×10^{7}	1.60×10^{11}	1.48×10^{14}
Cd-MIDA-Valinate	17.24	5.35×10^{7}	1.90×10^{11}	1.47×10^{14}
Cd-MIDA-Citrullinate	21.87	8.60×10^{7}	2.50×10^{11}	1.46×10^{14}
Cd-MIDA-Threoninate	25.05	1.01×10^{8}	3.25×10^{11}	1.45×10^{14}
Cd-MIDA-Serinate	27.20	1.11×10^{8}	3.90×10^{11}	1.44×10^{14}

The knowledge of stability constant is required to obtain optimum dosage to reduce the concentration of metal ion in blood vessels and organs which are accumulated due to the lack of homeostatic mechanism.

Formation of mixed ligand complexes can be explained by considering the

Schemes 1–5. The tendency to add MIDA to Cd[X] and Cd[Y] (here [X] = MIDA and [Y] = amino acids) can be compared. The logarithm of stability constants of the above complexes are (3.24 and 4.76), (3.24 and 4.71), (3.24 and 4.66), (3.24 and 4.60) and (3.24 and 5.04) for Cd-MIDA-isoleucinate, Cd-MIDA-valinate, Cd-MIDA-citrullinate, Cd-MIDA-threoninate and Cd-MIDA-serinate systems, respectively. The largest part of the difference in log K must be attributed to entropy and electrostatic effect, which would favour the formation of charged complex.

The logarithm values of stability constants for the addition of [Y] to Cd[X] and Cd[Y] are (2.85 and 2.90), (2.85 and 2.86), (2.85 and 3.00), (2.85 and 3.00) and (3.33 and 3.00) for all the above systems, respectively, indicating that the mixed ligand complexation is favoured.

The log K values for addition of [X] to $Cd[X]_2$, Cd[XY] and $Cd[Y]_2$ are (5.12, 5.54 and 6.89), (5.12, 5.62 and 6.91), (5.12, 5.74 and 6.93), (5.12, 5.74 and 6.93) and (5.12, 5.55 and 6.94) for all the under studying systems respectively and show that the addition of MIDA is preferred to amino acids.

The log K values for addition of [Y] to $Cd[Y]_2$, Cd[XY] and $Cd[X]_2$ are (2.14, 5.03 and 5.15), (2.09, 5.06 and 5.23), (1.94, 5.27 and 5.35), (1.96, 5.34 and 5.16) and (1.98, 4.90 and 5.54) for Cd-MIDA-isoleucinate, Cd-MIDA-valinate, Cd-MIDA-citrullinate, Cd-MIDA-threoninate and Cd-MIDA-serinate systems, respectively.

The values of β_{21} are higher than β_{30}, so $[Cd(X)_2Y]$ complexes are more stable than $[Cd(X)_3]$ complexes.

Simple and mixed complexes can be easily expressed by calculating the disproportion constant K for the equilibria:

$$2Cd[XY] \rightleftharpoons Cd[X]_2 + Cd[Y]_2$$

The value of log K_D is –0.60 statistically but the observed values are found to be (–1.46, –1.27, –1.21, –2.13, –3.27, –2.01, –1.71 and –1.19) for Cd-MIDA-isoleucinate, Cd-MIDA-valinate, Cd-MIDA-citrullinate, Cd-MIDA-threoninate and Cd-MIDA-sterinate systems respectively. More negative values of log K_D for each equilibrium account for the stability of mixed ligand complexes. For comparing the stabilization of simple and mixed complexes, it is convenient to measure the mixing constants

$$K_m = \frac{\beta_{11}}{\sqrt{(\beta_{02}\beta_{20})}}$$

and stabilization constants, as

$$\log K_s = \log K_m - \log 2$$

The log K_m values are (0.74, 0.73, 0.63, 0.60 and 1.06) and log K_s values are (0.43, 0.42, 0.32, 0.30 and 0.75) for Cd-MIDA-isoleucinate, Cd-MIDA-valinate, Cd-MIDA-citrullinate, Cd-MIDA-threoninate and Cd-MIDA-serinate systems, respectively (Table-9). The positive values of mixing and stabilization constants indicate that the ternary complexes are more stable than the binary complexes.

The tendency to form mixed ligand complexes in solution could be expressed quantitatively in other approach, compares the difference in stability $\Delta \log K$, which is the result from the subtraction of two constants and must therefore, be a constant. This corresponds to:

$$\Delta \log K = \log K^{MA}_{MAB} - \log K^{M}_{MB}$$

TABLE-9
VALUES FOR MIXING CONSTANTS ($\log K_M$) AND STABILIZATION CONSTANTS ($\log K_S$) FOR Cd-MIDA-AMINO ACIDS SYSTEMS

S.No.	Systems	$\log K_M$	$\log K_S$
1.	Cd-MIDA-Isoleucinate	0.74	0.43
2.	Cd-MIDA-Valinate	0.73	0.42
3.	Cd-MIDA-Citrulline	0.63	0.32
4.	Cd-MIDA-Threoninate	0.60	0.30
5.	Cd-MIDA-Serinate	1.06	0.75

Since, more coordination positions are available for bonding of the first ligand [A] to a given multivalent metal ion than for the second ligand [B],

$$\log K^{M}_{MA} > \log K^{MA}_{MA_2}$$

usually holds, *i.e.*, expects to observe negative values for $\Delta \log K$. Another probably more satisfactory manner is to determine statistical values for $\Delta \log K$. The statistical values for regular octahedron is 5/12 and $\Delta \log K_{oh} = -0.4$. For a square-planar (sp) the value of $\Delta \log K_{sp} = -0.6$ and for the distorted octahedron (do) the statistical value, *i.e.*, $\Delta \log K_{do}$ lie between –0.9 and –0.3.

The $\Delta \log K$ values can be obtained using the following equations:

$$\Delta \log X_{11} = \log \beta_{11} - (\log \beta_{10} + \log \beta_{01})$$

$$\Delta \log X_{12} = \log \beta_{12} - (\log \beta_{10} + \log \beta_{02})$$

$$\Delta \log X_{21} = \log \beta_{21} - (\log \beta_{20} + \log \beta_{01})$$

The observed values of the $\Delta \log X_{11}$, $\Delta \log X_{12}$ and $\Delta \log X_{21}$ are (–1.05, 1.08 and 1.25), (–1.10, 1.10 and 1.28), (–1.15, 1.12 and 1.35), (–1.21, 1.13 and 1.10) and (–0.77, 1.13 and 1.44) for systems Cd-MIDA-isoleucinate, Cd-MIDA-valinate, Cd-MIDA-citrullinate, Cd-MIDA-threoninate and Cd-MIDA-serinate respectively. The $\Delta \log K$ values are higher than the statistical values, which again proves that the ternary complexes are more stable than expected from statistical reasons.

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