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Polarographic Study of Mixed Ligand Complexes of Cd(II) in Khetri Ore Sample with Cadaverine and Dicarboxylic Acid in Aqueous Medium

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In present work the polarographic study of mixed ligand complexes of Cd(II) in Khetri one sample with cadaverine and various dicarboxylic acids such as adipic acid, malonic acid, maleic acid, succinic acid or phthalic acid are reported.

INTRODUCTION

From the survey of literature it appears that no polarographic study has been reported so far in regard to the mixed ligand complex of Cd(II) in the ore soil samples of the Khetri Copper Complex with the diamine (cadaverine) and dicarboxylic acid. Hence the title study has been undertaken on the mixed ligand system involving cadaverine as the primary ligand and some dicarboxylic acid, *viz.*, adipic, malonic, maleic, succinic and phthalic acid as the secondary ligands. The possible mixed species for Cd(II) are greater in number than those with copper, as the configuration of Cu(II) can easily move from tetrahedral to octahedral geometry depending upon the nature of bond-ligands. Cd(II) is considered as an extra coordinated metal ion and three theoretical mixed complexes $Cd(XY)_1$, $Cd(XY)_2$ and $Cd(X_2Y)$ are expected with the two X and Y bidentate ligands. Stability constants of mixed ligand complexes of Cd(II) with different Carboxylate ions have been determined by various workers[1–4] and Jadhav *et al.*[5–7] Many organic acids[8–10] have been used as complexing agents, the concentration of which may not be necessarily the same. We have picked up ore soil samples from eight different sites in the vicinity of Khetri Copper Project. Rajasthan and picked up one sample which has patented cadmium content Jasrapur for this polarographic study in the aqueous medium.

TABLE-1
SAMPLES COLLECTED FROM VARIOUS SITES AND THEIR Cd-CONTENT

	Sites	Cd (%)
1.	Name Wali Bawari	1.260
2.	Discharge from Copper plant (Main Gate)	3.000
3.	Chawara river incoming	0.229
4.	Koti Ki Dhani	0.145
5.	Modi Wali Bagichi	1.190
6.	Mishra Wali Dhani	2.240
7.	Jasrapur	3.160
8.	Rojata Village	0.790

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EXPERIMENTAL

All the chemicals used were of analytical reagent grade and their stock solutions were prepared in double distilled water. The concentration of Cd(II) was maintained constant at 1×10^{-3} M. Polarographs of the deaerated solution were obtained using manually operated polarograph (Osaw slide wire potentiometer and galvanometer AJCO, model No. P-GI, Sr. No P 71049) having sensitivity of 3.71×10^{-2} ua/div and H-type well saturated with sodium chloride agar-agar bridge at constant ionic strength $\mu = 1.0$ M using sodium perchlorate solution in all the systems and pH was maintained at 7.5 in the presence of tritone-x-100 $= 2.0 \times 10^{-3}$% (at 25 ±0.1°C). The DME has following characteristics in 1.0 M sodium perchlorate open circuit: $m = 2.20$ mg s^{-1}, $t = 2.5$ sec, $m^{2.3}$, $t^{1.6} = 1.197$ $mg^{2.3}$, $S^{-1.2}$ and $h_{corr} = 51.2$ cm. The pK value of the ligands were determined by the method of Elebert and Serjeant[13]. The determined pK values of the ligands are incorporated in Table-2.

TABLE-2
pK VALUE OF THE LIGANDS AT 25°C

S.No.	Ligand	pK_1	pK_2
1.	Cadaverine	11.85	10.76
2.	Adipic acid	4.35	5.30
3.	Malonic acid	2.13	5.69
4.	Maleic acid	2.00	6.26
5.	Succinic acid	4.15	5.44
6.	Phthalic acid	2.92	5.43

The method of Schaap and McMasters[14] was used to evaluate the stability constants of mixed ligand complexes of Cd(II)-cdv-adipate, Cd(II)-cdv-malonate, Cd(II)-cdv-maleate, Cd(II)-cdv-succinate and Cd(II)-cdv-phthalate system. The values of equilibrium constants are correlated in terms of factors, like statistical concentration, charge neutralisation and size of metal chelate ring, etc.

RESULTS AND DISCUSSION

Cd(II) gives a well defined wave in the presence of increasing concentration of cadaverine. This is true for both the simple and mixed systems. The plots of i_d *vs.* $h_{corr}^{1/2}$ are linear and pass through the origin confirming the diffusion controlled nature of the waves. The slope values of the linear plots of $\log i_d/(i_d - i)$ *vs.* $E_{de.}$ lie in the range of 30–32 mV at 25°C, thereby showing the reversible nature of Cd(II) electrode process involving two electrons in the presence of single as well as in mixed ligands under study. Identical conditions were maintained in both simple and mixed systems. Representative data are incorporated in Table-3.

TABLE-3
POLAROGRAPHIC CHARACTERISTICS AND $F_j(x)$ FUNCTIONS OF Cd(II)-cdv-SYSTEM

$[Cd(II)] = 1.0 \times 10^{-3}$ M, $\mu = 1.0$ M ($NaClO_4$), pH = 7.5, Temp. = 25 ± 0.1°C,
[Triton X-100] = 2.0×10^{-3}%, $[E_{1/2}]$ s = +0.014 V (S.C.E.), i_d = 7.05 uA

$[Cdv]_t$	$[Cdv]_f$	i_d	$-E_{1/2}$ (V)	Slope (mV)	$F_0(x) \cdot 10^{-7}$	$F_1(x) \cdot 10^{-12}$	$F_2(x) \cdot 10^{-18}$
0.01	1.5	8.91	0.221	31	5.89	6.12	3.42
0.02	2.6	8.76	0.246	32	16.64	7.89	3.51
0.03	3.8	8.55	0.259	30	35.12	12.26	3.49
0.04	4.9	8.48	0.271	30	62.71	15.13	3.48
0.06	6.6	8.36	0.276	31	134.15	26.17	3.42
0.08	9.2	8.28	0.288	33	210.11	31.89	3.52
0.10	10.8	8.01	0.292	32	355.79	37.24	3.90

$(E_{1.2})_s$ is simple Cd ion concentration.
$(Cdv)_t$ is total analytical concentration of cadaverine.
$(Cdv)_f$ is free ligand concentration.of cadaverine.

The plot of $E_{1/2}$ *vs.* log [cdv] is a smooth curve shows the formation of successive complex. The composition and stability constants of the complex have been determined by DeFord-Hume's method[15]. The half wave potential of Cd(II) shifts to move –ve value of increasing the free ligand conc. Showing the complex formation, the plots of $E^{1/2}$ *vs.* (–)log [free ligand conc.] were smooth curves confirming the formation of two more complex species. The plots of $F_0(x)$, $F_t(x)$ and $F_2(x)$ *vs.* [x], where x = ligand, *i.e.*, cadaverine, K give the value of overall stability constants. In this case the plots of $F_2(x)$ *vs.* [x] resulted in a line originating in x-axis indicating the formation of 1 : 1, 1 : 2 complexes with Cd(II).

$$\log K_1 = \log b_1, \quad \log k_2 = \log b_2 - \log b_t \quad \text{and} \quad \log K_3 = \log b_3 - \log b_2$$

TABLE-4
OVERALL STABILITY CONSTANTS OF Cd(II) COMPLEXES

System	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
Cd(II)-Cdv.	3.98	5.85	6.71
Cd(II)-Adp.	2.13	2.45	3.82
Cd(II)-Malo.	2.59	4.06	5.19
Cd(II)-Mal.	2.54	3.30	4.66
Cd(II)-Succ.	2.27	3.10	4.79
Cd(II)-Phth.	2.80	4.30	5.91

In all systems the order is $k_1 > k_2 > k_3$.

The stability constant of the mixed complex which characterises the following equilibrium (charges omitted):

$$M + iX + jX = MX_iY_j \tag{1}$$

is given by

$$\beta_{ij} = \frac{[MX_iY_i]}{[M][X]^i[Y]^j} \tag{2}$$

The mixed constant [K_m] correlates the stability of mixed complex species to that of the parent complexes and can be defined[16] as the equilibrium constant of the reaction.

$$(i/m)MX_m = (j/m)My_m = Mx_iY_j \quad (3)$$

by the expression,

$$K_m = \frac{[Mx_iY_j]}{[MX_m]^{i/m}[MY_m]^{j/m}} \quad (4)$$

or

$$K_m = B_{ij} \cdot B_{mo}^{-i/m} \cdot Bo_m^{-j/m} \quad (5)$$

It is obvious[17] that a major contribution of K^m will arise from statistical factors. Hence Marcus and Elizeer[18] defined another parameter called the stabilization constant which for ligands of equal density is given by

$$\log K_s = \log K_m - \log (n/i \cdot j) \quad (6)$$

where $n = i + j$.

The stabilisation constant, therefore gives a measure of the extra stability of mixed complex due to electrostatic forces, geometrical forces and solvent effect etc. in addition to the statistical effect. The values of K_m and K_s have been calculated from eqns. (5) and (6) respectively and are listed in Table-5.

TABLE-5
COMPLEX FORMATION CONSTANT FOR THE MIXED LIGAND COMPLEX AT 25°C AND μ = 1.0 ($NaClO_4$)

Mixed species	log K_m	log K_s
Cd(II)-cdv-Adp.	1.18	0.89
Cd(II)-cdv-Malo.	0.84	0.51
Cd(II)-cdv-Mal.	1.16	0.92
Cd(II)-cdv-Succ.	0.88	0.79
Cd(II)-cdv.Phth.	0.85	0.55

A perusal of Table-5 shows that the log values of K_m and K_s are positive showing that mixed complexes are relatively more stable than the binary complexes.

Mixed complexes system: Mixed-ligand complexes of Cd(II) with cadaverine, adipic, malonic, maleic, succinic and phthalic acid have been studied polarographically with a different approach since free ligand concentration has been determined for the purpose of evaluating overall formation constants. Since the coordination number of Cd(II) is six, hence three different mixed complex species would be expected with two different bidentate ligands. These are [Cd(XY)], $[Cd(XY_2)]^{-2}$ and $[Cd(X_2Y)]$, where X = cadaverine, Y = carboxylic acid such as adipic acid, malonic acid, maleic acid, succinic acid or phthalic acid.

We have made use of ligand displacement technique in which a much stronger complexing agent species is added to a mixture of metal ions with a weaker complexing species. In the present investigation carboxylic acids serve the purpose of weaker ligand while cadaverine acts as stronger ligand. The two fixed concentrations of weaker ligand (carboxylic acids) were so chosen that at the lower value, 1 : 1 species and at higher value, 1 : 2 species predominate in the simple system. The two fixed concentrations chosen of weaker ligands are 0.20 M and 0.25 M for adipate, malonate, maleate, succinate and phthalate (Table-6).

TABLE-6
MIXED STABILITY CONSTANTS [PARAMETERS FOR MIXED COMPLEXES AT 25°C, $\mu = 1.0$ ($NaClO_4$)

Sl. No.	[X]	[Y]	Concentration of [Y] ligand	A ($\times 10^2$)	B ($\times 10^5$)	C ($\times 10^6$)	D_{av} ($\times 10^9$)	β_{30} ($\times 10^8$)
1.	Cadaverine	Adipic acid	0.20 M	00.68	1.71	9.11	3.144	8.016
			0.25 M	01.16	2.79	10.15	4.773	—
2.	Cadaverine	Malonic acid	0.20 M	01.39	3.15	11.02	1.85	8.016
			0.25 M	02.14	4.02	12.77	1.914	—
3.	Cadaverine	Maleic acid	0.20 M	02.88	4.85	13.83	2.863	8.016
			0.25M	03.79	5.91	14.11	2.796	—
4.	Cadaverine	Succinic acid	0.20 M	04.06	6.67	16.79	1.323	8.016
			0.25 M	10.76	7.35	19.76	1.589	—
5.	Cadaverine	Phthalic acid	0.20 M	14.86	7.89	20.18	4.733	8.016
			0.25 M	15.24	8.14	21.22	5.012	—

The concentration of strong ligand cadaverine was varied over a wide range (0.02 M to 0.20 M). Care was taken in choosing pH for these mixed ligand systems and they were kept at least two units more than the pK_2 value of corresponding weaker ligand, thereby at these pH, the corresponding weaker ligands (*viz*., carboxylic acid) are almost completely dissociated.

The pH for ternary system was kept for adp-cdv, malo-cdv, mal-cdv, succ-cdv, and phth-cdv systems. However for malo-cdv and mal-cdv system, it was kept at 7.7 and 8.5 so that the total concentrations of sodium adipate, sodium malonate, sodium maleate, sodium succinate and sodium phthalate serve as the measure of the concentrations of the respective ligands. The corresponding binary systems were also studied under identical pH values and experimental conditions. The equilibrium concentration of stronger ligand cadaverine was determined from pH of the solution and pK values determined.

Two series of polarograms were taken at 25°C with solution containing 1 mM Cd(II). Fixed concentrations of weaker ligand and varying concentration of stronger ligand. $E_{1/2}$ of Cd(II) at $\mu = 1$ ($NaClO_4$) was found to be −0.5950 V *vs*. S.C.E. The reduction of Cd(II) was found to be diffusion controlled and reversible involving two electrons in each case. The values of A, B, C and D were computed by the graphical extrapolation method as proposed by Leden[19].

The values of $E_{1/2}$, log I_s/I_c and F_{10} functions for the system under investigations are given in Table-7.

The function $F_{10}(X, Y)$ *vs*. concentration of variable ligand ion [X] have been plotted and shown in Fig. 1, where X = cadaverine.

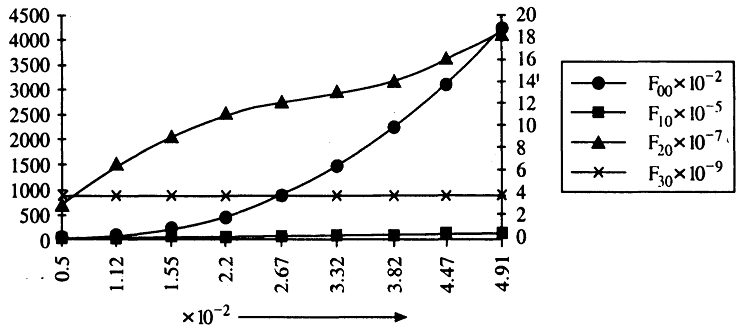

Fig. 1. Cd(II)-cadaverine-adipate system at 25°C

The values of A were calculated from the previously determined stability constant of Cd(II-Y species) where Y denotes adipic, malonic, maleic, succinic or phthalic acid using the relation

$$A = 1 + \beta_{01}[\gamma] + \beta_{02}[\gamma]^2 + \beta_{03}[\gamma]^3.$$

TABLE-7
Cd(II)-CADAVERINE-ADIPATE SYSTEM

$E^{1/2}$ [Cd(II)] = 0.5542 V *vs.* S.C.E., Conc. of ligand Y [adipate] = 0.20 M, I_s = 4.755 μ.A

S.No.	$[X] \cdot 10^2$	Log I_s/I_c	$E_{1/2}$	$F_{00} \times 10^{-2}$	$F_{10} \times 10^{-5}$	$F_{20} \times 10^{-7}$	$F_{30} \times 10^{-9}$
1.	0.496	0.0216	0.1010	17.224	2.914	3.001	3.761
2.	1.116	0.0331	0.1128	65.224	6.189	6.662	3.842
3.	1.545	0.0428	0.1265	210.186	14.115	9.015	3.779
4.	2.197	0.0519	0.1379	435.390	24.163	11.297	3.857
5.	2.665	0.0528	0.1471	862.786	37.289	12.168	3.849
6.	3.318	0.0546	0.1252	1428.105	46.145	13.224	3.821
7.	3.824	0.0575	0.1586	2286.161	51.156	14.000	3.791
8.	4.469	0.0632	0.1639	3130.579	82.802	16.194	3.808
9.	4.910	0.0751	16.9400	4285.366	93.161	18.510	3.801

$A_{cal} = 0.68 \times 10^2$, $B = 1.656 \times 10^5$, $D_{av} = 3.794 \times 10^9$, $C = 8.31 \times 10^6$

The intercepts at X = 0 of the plots of $F_{00}[XY]$, $F_{10}[XY]$, $F_{20}[XY]$ and $F_{30}[XY]$ *vs.* [X] give the respective values of A, B, C and D. The value of A obtained graphically are identical to the calculated values. The values of A, B, C and D_{av} for these ternary systems are summarised in Table-7 and the values of β_{11} and β_{12} were calculated from the two values of using the relation.

$$B = \beta_{10} + \beta_{11}[\gamma] + \beta_{12}[\gamma]^2$$

Further, $C = \beta_{20} + \beta_{21}[\gamma]$; the two values of C yield two values of β_{21} which are almost identical from the theory. The value of D should be equal to β_{30} which is indeed found to be so.

Value of log β_{11}, log β_{12} and log β_{21} for the ternary system under present investigation are shown in Table-8. The stability of these mixed complexes as seen from their overall formation constants follows the order

$$[Cd(XY)] < [Cd(XY_2)]^{-2} < [Cd(X_2Y)]$$

TABLE-8
OVERALL STABILITY CONSTANT OF MIXED LIGAND SPECIES

System	log β_{11}	log β_{12}	log β_{21}
Cd(II)-cdv-adp.	5.88	6.45	7.39
Cd(II)-cdv-malo.	5.94	7.02	7.63
Cd(II)-cdv-mal.	6.01	6.88	7.73
Cd(II)-cdv-succ.	5.13	6.32	7.11
Cd(II)-cdv-phth.	6.38	6.99	7.76

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