Polarographic Investigation of mixed ligand complex formation of Cd(II) Oxalate-Valinate System and determination of thermodynamic parameters of complexes formed.

SAROJ BHATIA

Principal LCHL Mahavidyalaya, 285 001 KarsanOrai(Jalaun), India

Abstract –

The binary &ternary complexes of Cd(II) with oxalate &valinate ions were studied by their reduction at Dropping Mercury electrode & their formation constants were determined by the Method of Deford& Hume's along with Schaap& McMasters method at two different temperatures.An attempt was made to interpret the results in the light of statistical, steric and electrostatic factors.

Preface

Mixed complexes in which metal ion is bonded to two or more different complexing species, are formed when solution of a metal ion contains more than one kind of complexing ligand. The importance of mixed ligand complexes in which one of the ligand is an amino acid has increase over the years (valinate ion from amino acid valine). In polarographic analysis Cd(II) is one of the most extensively used metal ions as far as simple & mixed complexes are concerned. It is because Cd(II) behaves reversibly& in a diffusion controlled manner in the presence of almost all the ligands.

In 1961, Schaap& McMasters formulated an excellent method to study mixed ligand complex formation i.e. step equilibria between the metal ion & two or more different types of ligands. Their method was a logical extension of Deford& Hume's method for simple complexes.

A survey of literature reveals that the mixed halide complexes of Cd(II) have been reported by M. Zangen (1969). The mixed ligand complex formation by Cd(II) with oxalate ion & ethylene diamine has been investigated by Fridmann (1963). Variation of half wave potential is the non-aqueous media has been investigated by Schaap& McMasters.

Mixed ligand complex formation of Cd(II) with some amino acids & drug efavirenz have been studied by Ramesh L. ware et. al. (2013). Cd(II) & Zn(II) complexes of the Tetradentate Schiff Base ligand was studied by Lotf A. Saghatforoush, et. al. (2008). Mixed ligand Cd (II) & Zn (II) complexes with alkyl xanthates & 2,2'-bipyridyl have been studied by K Hussain Reddy etals (2001).

Experimental

All reagents used were of analytical purity grade. Potassium salts of acid were used as complexing agents. KNO_3 was used as supporting electrolyte to maintain the ionic strength constant at 1.5M. 0.004% gelatin in final solution is used to suppress the maxima observed. All solutions were made in conductivity water. The temperature was maintained constant at 300^0K & 310^0K throughout the investigations. The test solution was placed in H-cell coupled with saturated calomel electrode through an agar saturated KCl salt-bridge. Pure N_2 was streamed through test solution for 10 minutes to remove dissolved O_2. The current variation as a function of applied potential was recorded as 'polarogram'.

Result & Discussion

A negative shift in half wave potential, with increase in valinate ions is observed. The values of $E_{1/2}$ at 0.15 M Concentration of oxalate ions are more negative than those for the simple Cd-valinate system. This is significant. This indicates mixed ligand complex formation by oxalate &valinate ions with Cd(II). Foi(x,y) functions were calculated from Schaap& McMasters treatment & values of A,B, C &

D computed by the graphical extrapolation Method proposed by Leden. The half wave potentials, log IM/IC, slopes of Ede Vs log i / id-i& corresponding Foi function were derived (in Table 1). Foi function is shown in Figure 1.
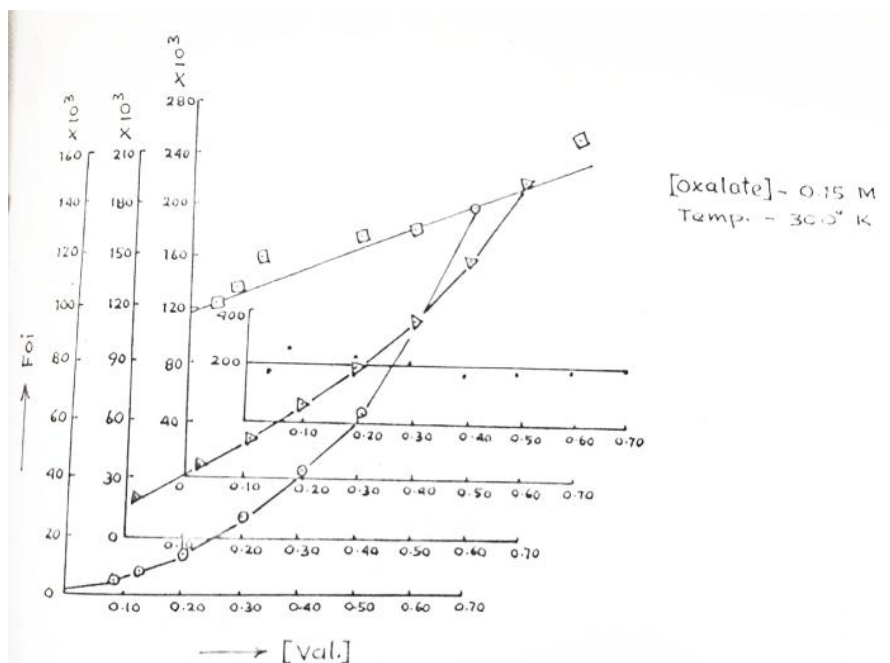
Table 1. Derived polarographic functions for Cd-Oxalate-valinate System at 300^0K

$[Cd^{++}]= 6 \times 10^{-4}$ M; $\mu = 1.5$ M; temperature 300^0K, $E^{1/2}_{Cd} = 0.5830$; [Oxalate]= 0.15 M

[Val] (M)	$E^{1/2}$ versus SCE (V)	Lg (IM/IC)	Slopes of log plots (mV)	F_{00}	F_{01} $(\times 10^3)$	F_{02} $(\times 10^3)$	F_{03} $(\times 10^3)$
0.04	0.105	0.0648	29	3920	23	125	175
0.08	0.108	0.0939	29	5285	29	138	250
0.12	0.112	0.1112	29	7495	37	158	-
0.20	0.119	0.1242	30	13259	51	-	-
0.30	0.126	0.1562	30	24569	72	190	207
0.40	0.132	0.1656	30	36967	92	185	168
0.50	0.137	0.1972	31	63248	121	206	176
0.60	0.141	0.2450	31	90220	155	223	183
0.70	0.146	0.2569	31	145575	204	266	211

$A= 3 \times 10^3$, $B= 18 \times 10^3$; $C = 118 \times 10^3$; $D = 170 \times 10^3$.

Figure 1: Plot of FoiVs [Val]:Cd (Oxalate)(Val) System

Keeping the oxalate ion concentration constant at 0.30 M, the above procedure was repeated under identical conditions & the results are presented in table 2 & figure 2.

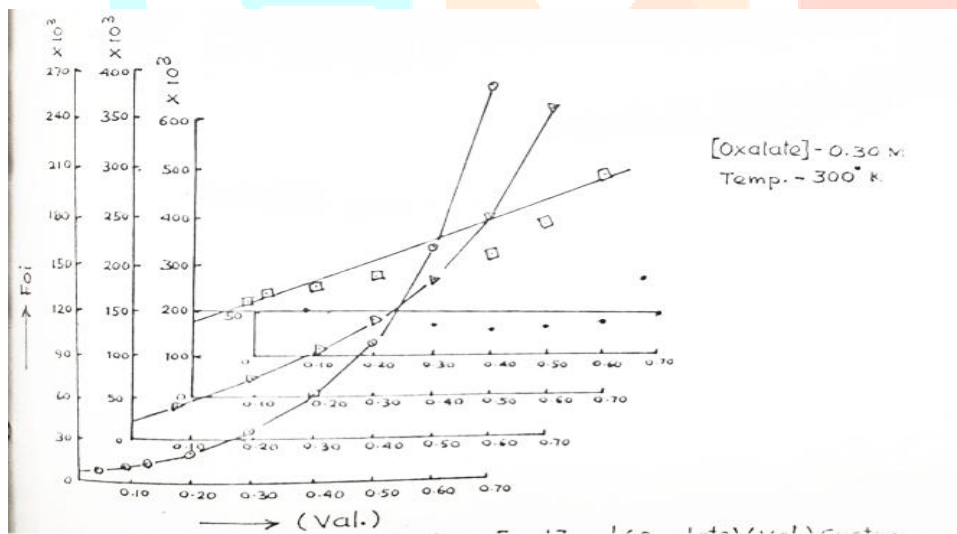**Table 2. Derived polarographic functions for Cd-Oxalate-valinate System at 300^0K**

$[Cd^{++}]= 6 \times 10^{-4}$ M; $\mu = 7.5$ M; temperature 300^0K, $E^{1/2}_{Cd} = 0.5830$ V; [Oxalate]= 0.30 M

[Val] (M)	$E^{1/2}$versus SCE (V)	Lg (IM/IC)	Slopes of log plots (mV)	F_{00}	F_{01} ($\times 10^3$)	F_{02} ($\times 10^3$)	F_{03} ($\times 10^3$)
0.04	0.114	0.0646	29	7862	34	-	-
0.08	0.116	0.0964	29	9975	42	213	475
0.12	0.119	0.1100	29	12852	53	233	483
0.20	0.125	0.1299	30	21399	75	250	375
0.30	0.132	0.1500	30	39532	107	273	327

0.40	0.139	0.1612	30	62900	141	290	288
0.50	0.143	0.1969	31	100525	188	326	302
0.60	0.148	0.2444	31	165157	264	398	372
0.70	0.154	0.2552	31	269355	376	501	466

A= 6500, B= 25×10^3; C = 175×10^3; D = 475×10^3.

Figure 2: Plot of FoiVs [Val]:Cd (Oxalate)(Val) System

The effect of increase in valinate ion concentration was also studied at 310^0K. The relevant data is summarized in table 3, 4& depicted in figure 3 & 4.

Table 3. Derived polarographic functions for Cd-Oxalate-valinate System at 310^0K

$[Cd^{++}]= 6 \times 10^{-4}$ M; $\mu = 1.5$ M; temperature 300^0K, $E^{1/2}_{Cd} = 0.5790$; [Oxalate]= 0.15 M

[Val] (M)	$E^{1/2}$versus SCE (V)	Lg (IM/IC)	Slopes of log plots (mV)	F_{00}	F_{01} $(\times 10^3)$	F_{02} $(\times 10^3)$	F_{03} $(\times 10^3)$
0.04	0.102	0.0632	29	2401	10	25	50
0.08	0.104	0.0940	29	2993	12	-	-
0.12	0.106	0.1102	29	3609	13	33	83
0.20	0.111	0.1200	30	5368	16	35	60
0.30	0.116	0.1514	30	8391	21	40	57
0.40	0.121	0.1668	30	12642	29	45	55
0.50	0.127	0.1934	31	21063	39	58	70
0.60	0.133	0.2454	31	37209	59	83	100
0.70	0.139	0.2552	31	59645	82	104	116

A= 2000, B= 9×10^3; C = 23×10^3; D = 60×10^3.

Table 4. Derived polarographic functions for Cd-Oxalate-valinate System at 300^0K

$[Cd^{++}]= 6 \times 10^{-4}$ M; $\mu = 7.5$ M; temperature 310^0K, $E^{1/2}_{Cd} = 0.5830$ V; [Oxalate]= 0.30 M

[Val] (M)	$E^{1/2}$versus SCE (V)	Lg (IM/IC)	Slopes of log plots (mV)	F_{00}	F_{01} $(\times 10^3)$	F_{02} $(\times 10^3)$	F_{03} $(\times 10^3)$
0.04	0.109	0.0600	29	4024	22	-	-
0.08	0.111	0.0998	29	5124	24	75	188
0.12	0.114	0.1136	29	6585	28	83	192

0.20	0.120	0.1200	30	10531	36	90	150
0.30	0.126	0.1302	30	17693	48	100	133
0.40	0.131	0.1616	30	26413	58	-	-
0.50	0.136	0.1972	31	41668	77	118	116
0.60	0.142	0.2456	31	73036	116	163	172
0.70	0.148	0.2568	31	117452	163	207	210

A= 3200, B= 16×10^3; C = 60×10^3; D = 190×10^3.

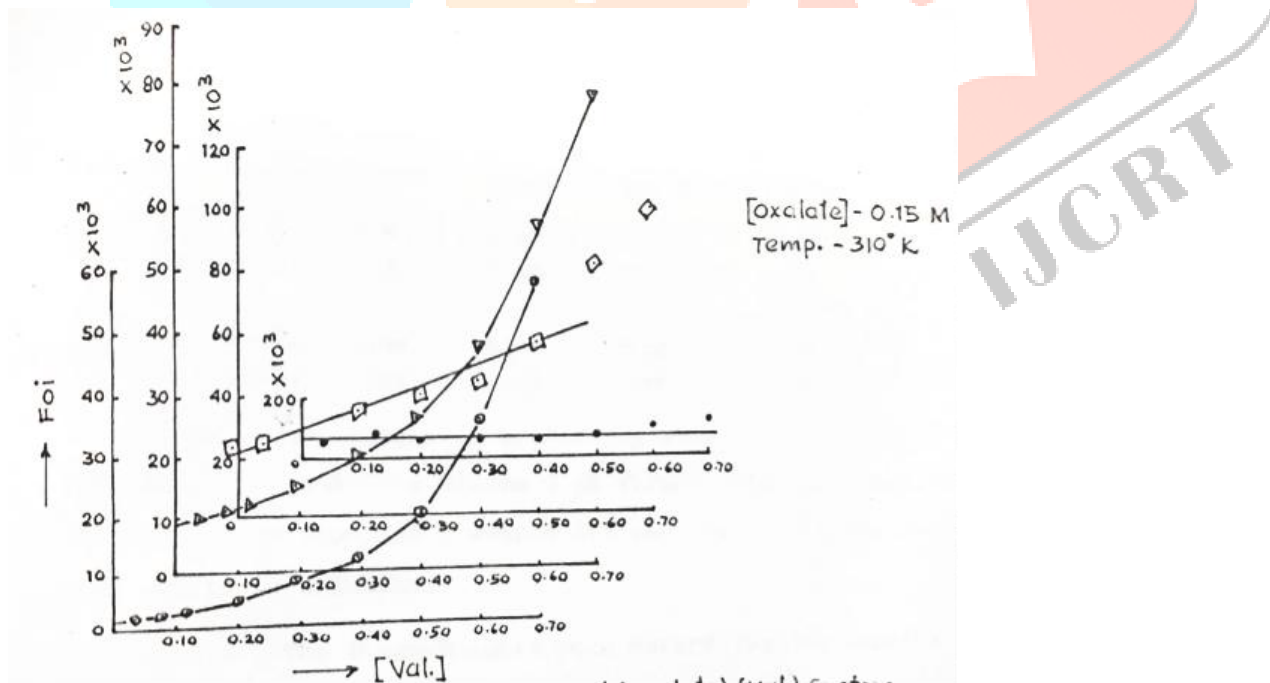Figure 3: Plot of FoiVs [Val]:Cd (Oxalate)(Val) System
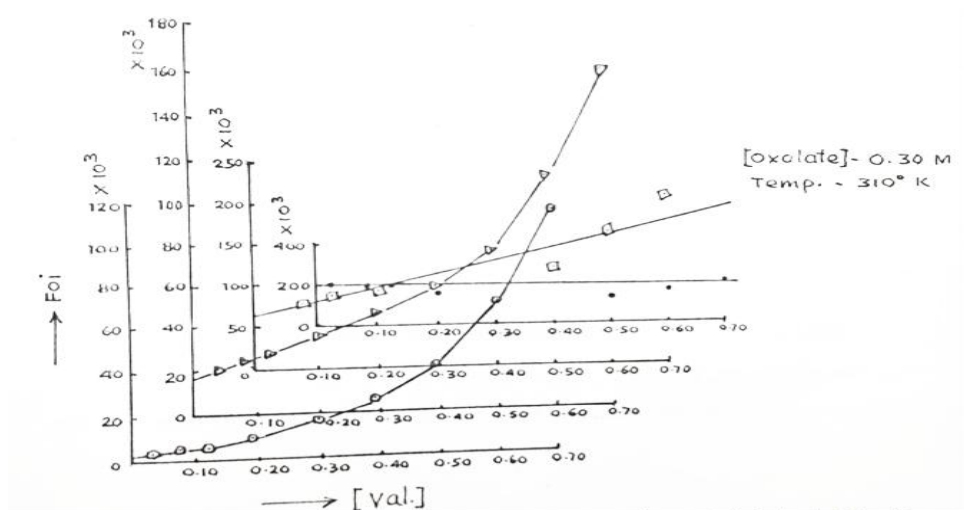
Figure 4: Plot of FoiVs [Val]:Cd (Oxalate)(Val) System

Table 5.Values of A, B, C and D at 300 and 310 K.

Oxalate		log A	log B	log C	log D
0.15 M	AT 300^0K	3.48	4.26	5.07	5.23
	AT 310^0K	3.30	3.95	4.36	4.78
0.30M	AT 300^0K	3.81	4.40	5.24	5.68
	AT 310^0K	3.51	4.20	4.78	5.28

The values of D Coincidewith values of β_{O3} (For Cd-valinate system) as finally simple 1:3 Cd-Valinate complex exists in solution.

Another invariable trend observed in mixed ligand complex formation for a system at two temperatures is that at higher temperature the value of PKs constant is smaller. The reason is obvious but at the higher temperature there is great dissociation of complexes leading to smaller values of formation constant.

Table 6. PK$_s$ Values of Cd(II)-oxalate-valinate at 300 and 310 K

Cd(II)-oxalate-valinate	At 300^0 K	At 310^0 K
(P K$_s$ Values)	2.06	1.80

$-\Delta S$ values of 1:1:1 complexes at two temperatures exhibit little change. This is because when we raise the temperature, dissociation takes place resulting no change in number of particles present in the solution. As the number of particles in a system determines its degree of disorder & entropy, there is virtually no change when the temperature is raised.

At higher temp, there is variably a positive shift in the $-\Delta G$ value. It means lesser stability at the higher temperatureresulting in increase of its free energy.

Negative value of ΔH implies that the heat complex of the system is decreased due to mixed ligand complex formation in which initially weaker ligand metal bonds have replaced by stronger ligand to metal bond.

The thermodynamic parameters for the Cd-oxalate-valinate system at two temperatures are as:

Table 7. Thermodynamic parameters for Cd(II) oxalate-valinate system

Temp. (^{0}K)	$\log\beta_{11}$	$-\Delta G$ (KJ)	$-\Delta H$ (KJ)	$-\Delta S$ (KJ/DEGREE)
300^0K	5.17	29.70165	69.4551	0.1325115
310^0K	4.78	28.37408		0.1325194

We have obtained a negative value of β_{12}(formation constant for 1:2 complex). These negative values are quantitatively insignificant because they have been obtained by solving two simultaneous equations with as many unknowns (Table 7).

Table 8. Mixed complex formation constants

System	log of mean β_{21} at		log of mean β_{11} at		log of mean β_{12} at	
	300 K	310 K	300 K	310 K	300 K	310 K
Cd(II)oxalate– valinate	5.82	5.35	5.17	4.78	-	-

β_{21} : is formation constant of 2:1 complex.

The significance of negative values lies in the fact that due to the much greater co-ordinating ability the third valinate ion hurries to enter the co-ordination sphere to the exclusion of the formation of 1:1:2 complex.

REFERENCES

1- Ramesh L. ware & et al, Topic-Mixed ligand complex formation of Cd(II) with same amino acids & drug efavirenz, Journal of Chemical & Pharmaceutical research, 2013, 5(8): 59-63.

2- Lotf A. Saghatforoush&etal,Prep. of Cd(II) & Zn(II) complexes of the Tetradentate Schiff base Ligand, Molecules 2008, 13, 804-811.

3- K. Hussain Reddy & et.al, Mixed ligand Cd(II) & Zn (II) complexes with alkyl xanthates& 2,2'-bipyridyl,Indian Journal of chemistry Vol. 40A, October 2001. pp 1118-1120

4- J. Heyrovsky, Principles of polarography, Czechoslovak Academy of Sciences, Prague, 61-63, (1965)

5- W.B. Schaap& D.L. McMasters , J. Am. Chem. Soc., 83, 4699 (1961)

6- Y.D. Fridman, R.A., veresova , N.V. Dolgasheva& R.I. Sorochan, Zh. Neorg. Khim., 8, 676 (1963).

7- M.Zangen, Proc. 5th intern, Conf. SoluExtr. Chem. Wiley inter science, New Yord, N.Y. (1969)