Polarographic Study of Cd(II)-Triazole-Malonate Mixed System

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Cd(II)-triazole-malonate system has been investigated polarographically at constant pH 6 and ionic strength $\mu=2$ (NaNO$_3$) in aqueous medium at $25\pm0.1°$. The reduction of the simple and mixed complexes is reversible and diffusion-controlled. The application of Schaap and McMasters method leads to the formation of the mixed complex species, [Cd(Tr)$_2$(Mal)], (Tr=1,2,4-triazole; Mal=malonate) with log $\beta_{21}=3.46$ at 25°.

THE extension of polarographic method of DeFord and Hume[1] by Schaap and McMasters[2] to the study of mixed complexes has opened new vista in the field of coordination chemistry. Since then, mixed complexes of metal ions with nitrogen containing ligands and polycarboxylate ions have been studied[3-16] polarographically. A survey of literature reveals that though Cd(II)-malonate system has already been studied[17], yet no study on Cd(II)-triazole-malonate mixed system has been reported so far. This paper reports the results of investigation on this system.

Experimental

All the chemicals used were of analytical reagent grade and their solutions were prepared in conductivity water. The ionic strength was maintained constant at $\mu=2.0$ M using NaNO$_3$ as supporting electrolyte. 1,2,4-Triazole and potassium malonate were used as ligands. The concentration of Cd(II) was kept constant at 1×10^{-3} M. Polarograms of the solutions were obtained by means of a manual polarograph (Toshniwal, CLO2) in conjunction with Toshniwal polyflex galvanometer (PL, 50). Purified hydrogen was used for removing the dissolved oxygen and all measurements were made at $25\pm0.1°$. Saturated calomel electrode (SCE) was used as a reference electrode. The d.m.e. had the following characteristics (in 0.1 M NaNO$_3$, open circuit) m=3.98 mg/sec, t=2.2 sec, m$^{2/3}$ t$^{1/6}$=2.9 mg$^{2/3}$ sec$^{-1/2}$, h$_{corr}$=39 cm.

Results and Discussion

The stability constants of simple complexes of Cd(II)-triazole and Cd(II)-malonate systems were studied separately prior to the study of the mixed ligand system. Identical conditions were maintained in both the simple and the mixed systems.

Cd(II)-triazole system :

A series of polarograms were obtained with increasing concentrations of 1,2,4-triazole (0 to 0.6 M) at constant ionic strength $\mu=2$ (NaNO$_3$) and at constant pH 6. In each case a single well-defined and diffusion-controlled wave appeared. The slope values indicated that the reduction of Cd(II)-triazole system is reversible. A plot of $E_{1/2}$ vs log [Tr] was a straight line thereby showing the formation of a single complex. Lingane[18] method was used to determine the stability constant of the complex. This gave the coordination number equal to 2 and therefore the composition of the complex is [Cd(Tr)$_2$]$^{2+}$ and the stability constant log $\beta_{20}=$ 2.50.

Cd(II)-malonate system :

A series of polarograms were obtained in presence of increasing concentrations of malonate at constant pH 6 and at constant ionic strength $\mu=2$. In each case a single well-defined and diffusion-controlled wave appeared. The slope values (Table 1) of the log plots indicate that the reduction of Cd(II) in presence of increasing concentrations of malonate is reversible. A plot of $E_{1/2}$ vs log [Mal^{2-}] was a smooth curve thereby showing the formation of successive complexes. DeFord and Hume's[1] method was used for the determination of composition and stability constants of the complexes. An analysis of $F_j[X]$ functions (Table 1 and Fig. 1) reveals the formation of three successive complexes, viz., [Cd(Mal)], [Cd(Mal)$_2$]$^{2-}$ and [Cd(Mal)$_3$]$^{4-}$ with stability constants, log $\beta_{01}=1.38$, log $\beta_{02}=2.47$ and log $\beta_{03}=3.23$.

TABLE 1—POLAROGRAPHIC CHARACTERISTICS AND $F_j[X]$ FUNCTIONS FOR Cd(II)-MALONATE SYSTEM

[Cd^{2+}]=1×10^{-3} M ; $\mu=2.0$ (NaNO$_3$); pH=6 ; Temp.=$25\pm0.1°$

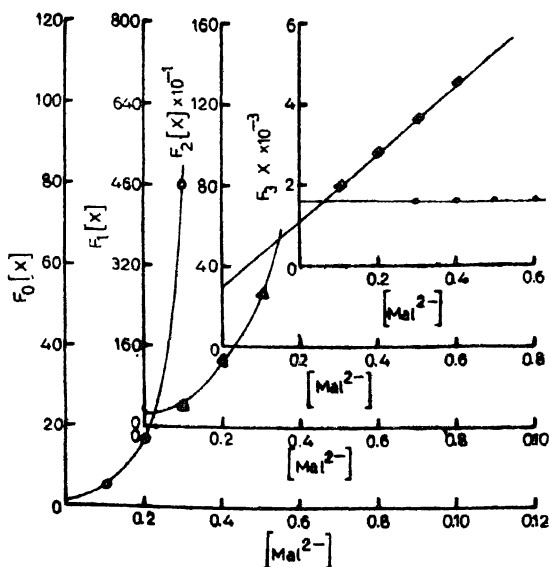| [Mal^{-2}]	$-E_{1/2}$ V vs SCE	i_d (μA)	Slope (mV)	$F_0[X]$	$F_1[X]$	$F_2[X]$ $\times10^{-1}$	$F_3[X]$ $\times10^{-2}$
0	0.570	11.4	33	—	—	—	—
0.1	0.590	11.0	33	4.91	39.20	—	—
0.2	0.612	11.0	33	27.23	131.20	53.6	—
0.3	0.626	11.0	32	80.97	266.60	80.87	1.70
0.4	0.634	10.0	32	165.27	410.68	96.90	1.67
0.5	0.641	9.9	31	288.93	575.81	110.37	1.61
0.6	0.648	9.9	30	498.00	829.04	134.17	1.74

Fig. 1. Plot of $F_j[X]$ vs $[Mal^{2-}]$ for Cd(II)-Mal^{2-} system.

Cd(II)-triazole-malonate system :

This system has been investigated at constant pH 6 and at constant ionic strength $\mu = 2$. The concentration of triazole was varied from 0 to 0.6 M keeping the malonate concentration constant at 0.2 M. In each case the waves were well-defined and diffusion-controlled. $E_{1/2}$ values were more negative than those obtained in the absence of malonate thereby showing the formation of mixed complex. A perusal of slope values (Table 2) shows that the reduction of Cd(II) remains reversible in the mixed system.

On keeping [Tr] constant and varying $[Mal^{2-}]$ no tangible shift in $E_{1/2}$, as compared to that in the absence of triazole, was perceptible. This shows that triazole is a stronger ligand than the malonate.

The Schaap and McMasters[2] method has been used for the determination of composition and stability constant of mixed ligand system. Since triazole is a monodentate ligand and malonate is a bidentate one, the possible mixed complexes are $[Cd(Tr)_2(Mal)]$ and $[Cd(Tr)_2(Mal)_2]^{2-}$. But the formation of $[Cd(Tr)_2(Mal)_2]^{2-}$ complex species is ruled out as the plot of $F_{20}[X, Y]$ was a straight line parallel to X axis. Thus, only one mixed complex species, i.e., $[Cd(Tr)_2(Mal)]$ should be

formed. This has actually been established from the analysis of $F_{ij}[X, Y]$ data as detailed further.

An analysis of $F_{ij}[X, Y]$ functions (Table 2 and Fig. 2) gives the following values of the constants: log A = 1.48 (calculated value 1.49), log B = 2.70, log C = 2.95 and log D = 4.08. The stability constant of the mixed complex has been calculated using these constants. One mixed complex viz., $[Cd(Tr)_2(Mal)]$ with log $\beta_{21} = 3.46$ is formed.
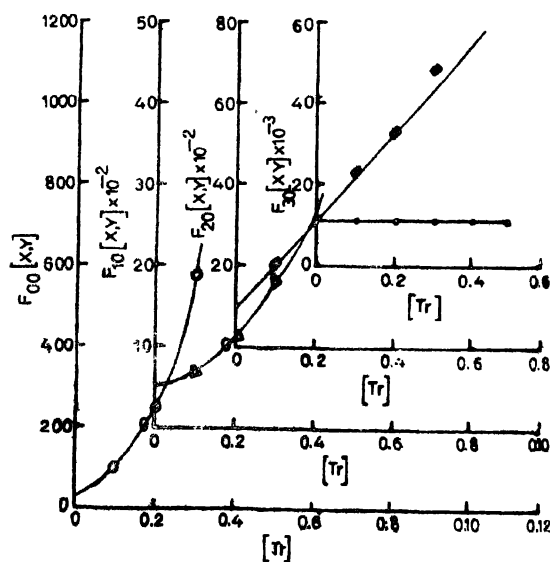

Fig. 2. Plot of $F_{ij}(X,Y)$ vs [Tr] for Cd(II)-Tr-Mal^{2-} system.

The results of the present study are conveniently summarized in the following diagram where the numerical values shown are the logarithms of equilibrium constants for the reactions indicated :
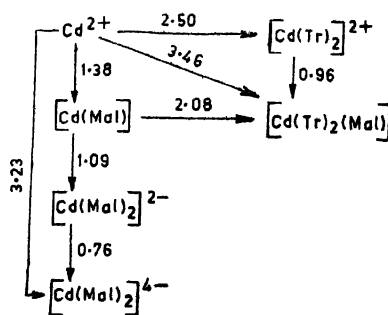
TABLE 2—POLAROGRAPHIC CHARACTERISTICS AND $F_{ij}[X, Y]$ FUNCTIONS FOR Cd(II)-TRIAZOLE-MALONATE MIXED SYSTEM

$[Mal^{2-}] = 0.2\ M$ (Fixed) ; $\mu = 2.0$ (NaNO$_3$) ; $pH = 6$; Temp. $= 25 \pm 0.1°$; $(E_{1/2})_S = -0.57$ V (SCE)

[Tr] M	$-E_{1/2}$ V vs (SCE)	i_d (μA)	Slope (mV)	$F_{00}[X, Y]$	$F_{10}[X, Y]$ $\times 10^{-2}$	$F_{20}[X, Y]$ $\times 10^{-2}$	$F_{30}[X, Y]$ $\times 10^{-3}$
0.1	0.628	10.3	33	101.0	7.10	21.00	12.00
0.2	0.640	10.3	32	157.0	11.35	31.75	11.88
0.3	0.650	10.0	33	575.4	18.18	43.93	11.64
0.4	0.658	10.0	33	1072.5	26.00	52.65	10.91
0.5	0.666	10.0	33	1998.9	39.37	68.76	11.95
0.6	0.672	9.9	34	3227.0	53.28	80.47	11.91

A = 30, B = 5×10^2,; C = 9×10^2, D = 19×10^2

As Cd(II) is hexa-coordinated, the various complex species existing in the solution have the following equilibria. The equilibrium constant (log value) has been indicated for each equilibrium :

1. $Cd^{2+}+2Tr+Mal^{2-}\rightleftharpoons[Cd(Tr)_2(Mal)]$ 3.46

2. $[Cd(Tr)_2]^{2+}+Mal^{2-}\rightleftharpoons[Cd(Tr)_2(Mal)]$ 0.96

3. $[Cd(Mal)]+2Tr\rightleftharpoons[Cd(Tr)_2(Mal)]$ 2.08

4. $[Cd(Mal)_2]^{2-}+2Tr\rightleftharpoons[Cd(Tr)_2(Mal)]+Mal^{2-}$ 0.99

5. $[Cd(Mal)_3]^{4-}+2Tr\rightleftharpoons[Cd(Tr)_2(Mal)]+2Mal^{2-}$-0.26

From the above equilibrium constant (K) values, the tendency of a ligand to add to a complex and to substitute another ligand may be compared. The relative tendencies of Mal^{2-} and Tr to add to $[Cd(Tr)_2]$ and $[Cd(Mal)]$ (equilibria 2 and 3), respectively can be compared. It is seen that Tr can add more easily than does Mal^{2-}.

The mixing constants (K_m) for the reactions

$[Cd(Tr)_2]^{2+}+[Cd(Mal)]\rightleftharpoons[Cd(Tr)_2(Mal)]+Cd^{2+}$
... (1)

$[Cd(Tr)_2]^{2+}+\frac{1}{2}[Cd(Mal)_2]^{2-}$
$\rightleftharpoons[Cd(Tr)_2(Mal)]+\frac{1}{2}Cd^{2+}$ ... (2)
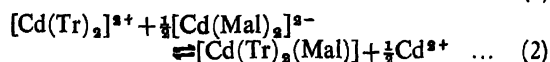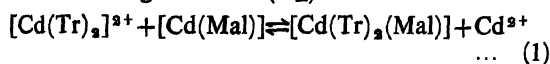
are given by the expressions :

$\log K_{m(1)}=\log \beta_{21}-(\log \beta_{20}+\log \beta_{01})$

$\log K_{m(2)}=\log \beta_{21}-(\log \beta_{20}+\frac{1}{2}\log \beta_{02})$

These work out to be -0.42 and -0.27, respectively. The negative log values of K_m show that the mixed complex $[Cd(Tr)_2(Mal)]$ is less stable than the simple $[Cd(Tr)_2]^{2+}$, $[Cd(Mal)]$ and $[Cd(Mal)_2]^{2-}$ complexes.

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