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Studies on Mixed-Ligand Complexes of Cadmium with 2,2′-Bipyridyl and Some Dicarboxylic Acids in Dioxane Medium

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The mixed-ligand complexes of cadmium with 2,2′-bipyridyl and dicarboxylic acids (tartaric, succinic, maleic, malonic, and malic) were studied polarographically in the 50% dioxane medium. The stability constants of simple systems were calculated by Deford and Hume[1] method, and the values of stability constants of mixed-ligand complexes have been determined by the method of Schaap and McMasters.[2] The overall stability constants have been evaluated with the help of Leden's[3] graphical extrapolation method and the values of β_{11}, β_{12}, and β_{21} are (5.24, 5.80, and 8.19) for Cd-bpy-tartarate system (5.62, 6.15, and 8.34) for Cd-bpy-succinate system (5.48, 6.10, and 8.32) for Cd-bpy-maleate system (5.57, 6.15, and 8.37) for Cd-bpy-malonate system, and (5.57, 6.15, and 8.34) for Cd-bpy-malate system.

Polarography has been widely used in complex chemistry. Recently, a large number of mixed-ligand complexes have been studied by this technique. The mixed-ligand complexes of Cd have been studied in our laboratory.[4,6] The present communication is a part of our programme. The metal complexes of 2,2′-bipyridyl have been studied by many workers.[7,8] The spectrochemical studies of bipyridyl with cadmium and other metals have been reported in the literature.[9] The mixed-ligand complexes of 2,2′-bipyridyl with malonate, amino acids, and copper have been carried out by potentiometry[10] and by electrode process.[11] But the literature is quite silent about the polarographic studies of mixed-ligand complexes of cadmium with 2,2′-bipyridyl and dicarboxylates. Hence the present investigations have been undertaken to study their stability constants polarographically.

Theoretical

For a complexation reaction

$$\mathrm{M} + i\mathrm{X} + j\mathrm{Y} \rightleftharpoons \mathrm{MX}_i\mathrm{Y}_j, \tag{1}$$

where i, j are stoichiometry numbers, X and Y are two different ligands and charges have been ignored for simplicity.

The overall stability constants β_{ij} for the above reaction is given by

$$\beta_{ij} = \frac{\mathrm{MX}_i\mathrm{Y}_j}{\mathrm{M}[\mathrm{X}]^i[\mathrm{Y}]^j}. \tag{2}$$

According to Schaap and McMasters mixed-ligand complex formation should be preferred over simple complexes whenever the concentration of the ligands involved are such that the products of the formation constants for the simple complexes and the concentration of the ligand raised to the appropriate power are approximately equal, *i.e.*

$$\beta_{\mathrm{MX}_i}[\mathrm{X}]^i = \beta_{\mathrm{MY}_j}[\mathrm{Y}]^j = \cdots\text{''}. \tag{3}$$

$F_0[\mathrm{X}]$ function of the Deford and Hume method may be extended to give a new function.

$$F_{00}[\mathrm{X},\mathrm{Y}] = \mathrm{antilog}\left[\frac{0.4343\,nF}{RT}E_{1/2} + \log\frac{I_\mathrm{M}}{I_\mathrm{C}}\right], \tag{4}$$

where n, F, R, and T have the same meaning as in the Nernst equation, I_M and I_C are the diffusion current constants of the uncomplexed and complexed metal ion respectively.

This expression can be written in the form (assuming three bidentate ligands)

$$\begin{aligned} F_{00}[\mathrm{X},\mathrm{Y}] = {} & \{\beta_{00}+\beta_{01}[\mathrm{Y}]+\beta_{02}[\mathrm{Y}]^2+\beta_{03}[\mathrm{Y}]^3\}[\mathrm{X}]^0 \\ & + \{\beta_{10}+\beta_{11}[\mathrm{Y}]+\beta_{12}[\mathrm{Y}]^2\}[\mathrm{X}] \\ & + \{\beta_{20}+\beta_{21}[\mathrm{Y}]\}[\mathrm{X}]^2 \\ & + \{\beta_{30}\}[\mathrm{X}]^3 \end{aligned} \tag{5}$$

or

$$F_{00}[\mathrm{X},\mathrm{Y}] = A + B[\mathrm{X}] + C[\mathrm{X}]^2 + D[\mathrm{X}]^3. \tag{6}$$

Where for a given value of [Y], A, B, C, and D are constant having values defined in equation (5).

The concentration of one ligand is kept constant while that of the other is varied. In practice [Y] is kept constant and [X] is varied. The other functions were

$$F_{10}[\mathrm{X},\mathrm{Y}] = \frac{F_{00}-A}{[\mathrm{X}]} = B + C[\mathrm{X}] + D[\mathrm{X}]^2,$$

$$F_{20}[\mathrm{X},\mathrm{Y}] = \frac{F_{10}-B}{[\mathrm{X}]} = C + D[\mathrm{X}],$$

and

$$F_{30}[\mathrm{X},\mathrm{Y}] = \frac{F_{20}-C}{[\mathrm{X}]} = D.$$

With the help of two values of B at two concentrations the overall stability constants β_{11}, β_{12}, and β_{21} may be calculated.

Experimental

The DME used in recording polarographic waves manually, had the following characteristics, m=1.96 mg s^{-1}, t=4.05 sec drop^{-1}, h_corr=40 cm (at 303±1 K in 0.1 M $\mathrm{NaClO_4}$ in open circuit (1 M=1 mol dm^{-3})).

The chemicals used were of AnalaR grade. 2,2′-bipyridyl and dicarboxylic acids were used as complexing agents. Potassium nitrate was used as supporting electrolyte to maintain the ionic strenght constant at 1.5 M. The presence of 0.004 % gelatin in final solution sufficed to suppress the maxima observed. All the investigations were carried out at constant temperature of 303±1 K and in the 50% dioxane medium. The experimental technique was the same as described earlier.[12]

Results

The pK values, calculated by the method of Albert and Sergeant[13] and the values of stability constants of simple systems are tabulated in Table 1. All the systems were studied by keeping the concentration of weaker ligands (dicarboxylic acids) constant while varying that of bipyridyl. In all the systems a single well-defined wave was found. The plots of $-E_{de}$ *vs.* log $(i/(i_d-i))$ were linear with a slope of 30±2 mV showing that two electron reduction is reversible. The reduction is diffusion-controlled as evident by the direct proportionality of the diffusion current to the square root of the effective height of mercury column.

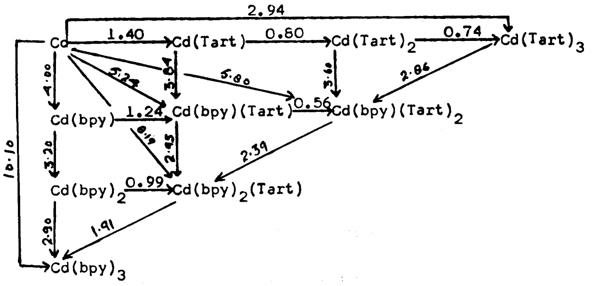
The overall stability constants β_{11}, β_{12}, and β_{21} as calculated by the method of Schaap and McMasters are tabulated in Table 2, and are summarised in Schemes (1—5), where the numerical values indicate the logarithms of the equilibrium constants, The values of F_{ij} function for all the systems are not given in the paper to avoid the length of the paper.

TABLE 1.

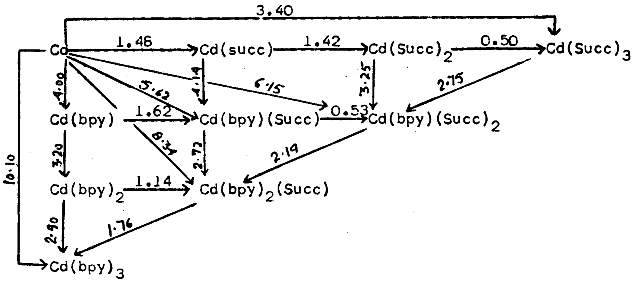
	Log β_{01}	Log β_{02}	Log β_{03}
bpy	4.00	7.20	10.10
Tart.	1.40	2.20	2.94
Succ.	1.48	2.90	3.40
Male.	1.70	2.65	3.32
Malo.	1.70	2.75	3.48
Mal.	1.90	2.80	3.46

TABLE 2. MIXED-LIGAND COMPLEXES OF Cd-bpy-DICARBOXYLIC ACIDS

Systems	Log β_{11}	Log β_{12}	Log β_{21}
Cd-bpy-Tart.	5.24	5.80	8.19
Cd-bpy-Succ.	5.62	6.15	8.34
Cd-bpy-Male.	5.48	6.10	8.32
Cd-bpy-Malo.	5.57	6.15	8.37
Cd-bpy-Mal.	5.57	6.15	8.34



Scheme 1. Cd-bpy-Tartrate system.

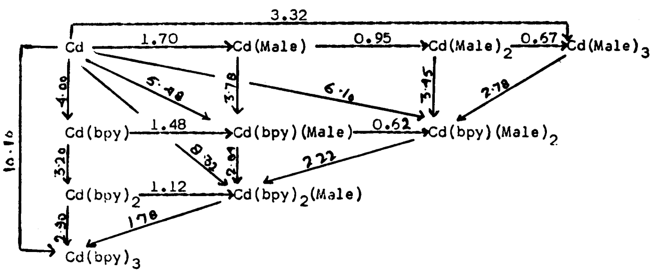


Scheme 2. Cd-bpy-succinate system.

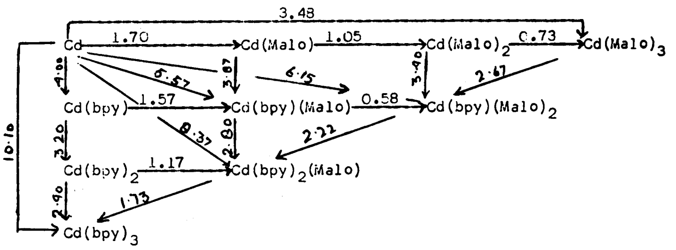
Discussion

By considering the schemes (1—5), the formation of β_{11}, β_{12}, and β_{21} may be explained in a good manner. The tendency to add dicarboxylate to Cd(dicarboxylate), Cd(Bipyridyl) can be compared. The log K values are (0.80, 1.24), (1.42, 1.62), (0.95, 1.48), (1.05, 1.57), and (0.90, 1.57) for Cd-bpy-tartrate, Cd-bpy-succinate, Cd-bpy-maleate, Cd-bpy-malonate, and Cd-bpy-malate 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 a charged complex. The addition of bipyridyl to Cd(dicarboxylate) and Cd(bpy) can also be confirmed, the mixed-ligand complex formation. The log K values are (3.84, 3.20), (4.14, 3.20), (3.78, 3.20), (3.87, 3.20), and (3.67, 3.20) for the Cd-bpy-tartrate, Cd-bpy-succinate, Cd-bpy-maleate, Cd-bpy-malonate, and Cd-bpy-malate systems respectively.

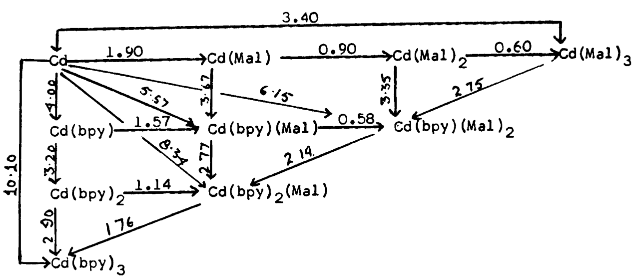
For the addition of dicarboxylate as a second ligand to [Cd(bpy)dicarboxylate)][Cd(dicarboxylate)$_2$] and [Cd(bpy)$_2$]. The log K values are (0.56, 0.74, and 0.99), (0.53, 0.50, and 1.14), (0.62, 0.67, and 1.12),



Scheme 3. Cd-bpy-Maleate system.



Scheme 4. Cd-bpy-Malonate system.



Scheme 5. Cd-bpy-Malate system.

TABLE 3. VALUES OF STABILITY CONSTANTS OF MIXED-LIGAND OF Cd(II) WITH 2,2′-BIPYRIDYL AND DICARBOXYLIC ACIDS BY WATTERS AND DEWITT EQUATIONS

Systems	Log β_{11}	Log β_{12}	Log β_{21}
Cd-bpy-Tart.	5.12	5.80	8.19
Cd-bpy-Succ.	5.28	6.11	8.34
Cd-bpy-Male.	5.25	6.06	8.32
Cd-bpy-Malo.	5.30	6.16	8.37
Cd-qpy-Mal.	5.28	6.11	8.34

(0.58, 0.73, and 1.17), and (0.58, 0.60, and 1.14) for the Cd-bpy-tartrate, Cd-bpy-succinate, Cd-bpy-maleate, Cd-bpy-malonate, and Cd-bpy-malate systems respectively.

The higher log K values in the addition of dicarboxylate ion to $[\mathrm{Cd(bpy)_2}]$ suggest that the addition or the substitution of dicarboxylate occurs easier to $[\mathrm{Cd(bpy)_2}]$ than that to [Cd(dicarboxylate)(bpy)] or to [Cd(dicarboxylate)].

The log K values for the addition of bpy as a second ligand to [Cd(bpy)(dicarboxylate)], $[\mathrm{Cd(dicarboxylate)_2}]$, and $[\mathrm{Cd(bpy)_2}]$ are (2.95, 3.60, and 2.90), (2.72, 3.25, and 2.90), (2.84, 3.45, and 2.90), (2.80, 3.40, and 2.90), and (2.77, 3.55, and 2.90) respectively.

The higher log K values for the addition of bipyridyl to [Cd(dicarboxylate)] suggest that the formation of mixed-ligand complexes is favoured in the presence of weaker ligand.

According to Watters and Dewitt equations, the formation of mixed-ligand complexes may be speculated on the basis of thermodynamical considerations. The values of stability constants calculated on these equations are given in Table 3.

By comparing these values with the observed ones, it may be suggested that $\mathrm{MX_2Y}$ complexes are formed in an equilibrium state thermodynamically.

If we assume the following equilibria:

$$[\mathrm{2Cd(bpy)(dicarboxylate)}] \rightleftharpoons [\mathrm{Cd(bpy)_2}] + [\mathrm{Cd(dicarboxylate)_2}]$$

then thermodynamically the value of log K^{D} is expected to be -0.60 but the observed values were -1.08, -1.14, -1.11, -1.19, and -1.14 for the Cd–bpy–tartrate, Cd–bpy–succinate, Cd–bpy–maleate, Cd–bpy–malonate, and Cd–bpy–malate systems respectively.

If we assume that the two equilibria of the disproportionation reactions, cited below should occur in dioxane medium,

$$[\mathrm{3Cd(bpy)(dicarboxylate)_2}] \rightleftharpoons [\mathrm{Cd(bpy)_3}] + [\mathrm{2Cd(dicarboxylate)_3}]$$

and

$$[\mathrm{3Cd(bpy)_2(dicarboxylate)}] \rightleftharpoons [\mathrm{2Cd(bpy)_3}] + [\mathrm{Cd(dicarboxylate)_3}],$$

then, the values of the disproportionation constant are calculated to be (1.42, 1.55, 1.56, 1.39, and 1.55) and (1.43, 1.42, 1.44, 1.43, and 1.42) respectively for both the equilibria of the corresponding Cd–bpy–dicarboxylate systems.

These results suggest that these mixed ligand complexes may exist more stably than those with a single ligand in an equilibrium state of 50% dioxane medium thermodynamically.

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