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Polarographic Studies On Mixed Ligand Complexes Of Cadmium-1-Methylimidazole-Oxalate System.

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ABSTRACT:

The over-all formation constants of the mixed ligand complexes of 1-methylimidazole (1-MeIm) and oxalate (Oxal) with cadmium (II) have been studied polarographically at constant ionic strength, $\mu = 2.0$, ($NaNO_3$) and pH 8 at $25 \pm 0.1^{\circ}C$. The reduction of the complexes at a dropping mercury electrode, DME, is reversible and diffusion controlled. The constants for three mixed complexes of Cd(II) are log $\beta_{11} = 4.0$ for Cd(1-MeIm)(Oxal), log $\beta_{12} = 4.4$ for $Cd(1\text{-}MeIm)(Oxal)_2$ and log $\beta_{21} = 5.9$ for $Cd(1\text{-}MeIm)_2(Oxal)$. The tendency of a ligand to add to a complex and to substitute another ligand was compared.

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Introduction:

Studies on mixed-ligand complexes, particularly those of biological significance have become of interest during the past decade. Studies of the over-all formation constants of cadmium complexes of imidazole have been the subject of several investigations(1-11). Tanford(1) has shown that in the combination of cadmium with serum albumin, the principal binding sites are imidazole groups of the histadine residues of the protein molecule, These complexes were investigated potentiometrically. Norman et al.(12) have studied polarographically, the over-all formation constant of cadmium and copper complexes of imidazole and 1-methylimidazole. The formation constants of 1-methylimidazole complexes of cadmium and copper were of the same order as those of the imidazole complexes. These results indicated that the site of binding in the imidazole molecule was the "pyridine" nitrogen rather than the "pyrrole" nitrogen . Li et al.(13) have studied polarographically the compositions and stability constants of simple complexes of Cd(II) with imidazole in aqueous and alcoholic media. Although the plot of $E_{1/2}$ vs $\log[\mathrm{Im}]$ was a curve it was interpreted as a composite of three straight lines revealing the formation of three complexes. However, the method employed by Li et al. was not accurate(14). Khurana et al.(15) has been found that the cathodic reduction of the mixed cadmium-oxalte-tartarate complex involve a two electron, reversible and diffusion controlled

step. A survey of data cited in literature revealed that further studies are required. Also, no study has been reported on mixed-ligand complexes of cadmium-1-methylimidazole-oxalate system. The present work is devoted to an investigation of the composition and stability constants of simple and mixed-ligand complexes of the above mentioned system at the DME.

Experimental:

Polarographic measurements were carried out using a PAR Model 174A Polarographic Analyser in conjugation with a three electrode cell system, having a saturated Ag/AgCl as reference, platinum as the counter electrode and a dropping mercury electrode (DME) as working electrode.

The polarograms were recorded on a Houston Omnigraphic Model RE 0074 X-Y recorder, De-aeration was done with a purified nitrogen stream through a teflon tube. The gas was purified by passing through an acidic vanadous chloride solution, and by passing over hot copper wool. During polarographic measurements the solution was kept oxygen free by passing nitrogen over the solution surface. All chemicals were reagent grade (BDH) and their stock solutions were prepared in double distilled water. The ligand 1-methyimidazole (Sigma) was used without further purification. The ionic strength was maintained constant at $\mu = 2.0$ using $NaNO_3$ as supporting electrolyte. The concentration of Cd(II) was kept at 1×10^{-3} M. The studies were carried out at pH 8. All measurements of pH were made with a PYE-UNICAM extended scale digital pH-meter with readings to ±0.005 pH unit.

The pH-meter was calibrated with saturated buffer solutions (Burroughs Wellcome and Co. England).

Results and Discussion:

The stability constants for simple complexes of Cd(II) with 1-methylimidazole and oxalate system were determined prior to the study of the mixed-ligand system. Identical conditions were maintained in both the simple and mixed ligand systems. The reduction of Cd(II) in 1-methylimidazole and oxalate media was found to be reversible and diffusion-controlled. The same was true for mixed system, the slopes of linear plots of $-E_{d.e.}$ vs $\log i/i_d-i$ were of the order of 33 ±1 mV(16) in all cases and the plots of i_d versus $h^{1/2}$ were linear and passed through the origin.

Cadmium (II)-1-methylimidazole system

A plot of $E_{\frac{1}{2}}$ versus log [1-MeIm] was a smooth curve, suggesting the formation of successive complexes. DeFord and Hume's(17) method was applied to determine the stability constants of successive complexes. Four complexes were formed, namely $[Cd(1\text{-}MeIm)]^{+2}$, $[Cd(1\text{-}MeIm)_2]^{+2}$, $[Cd(1\text{-}MeIm)_3]^{+2}$ and $[Cd(1\text{-}MeIm)_4]^{+2}$ with stability constants $\log \beta_{10} = 2.7$, $\log \beta_{20} = 4.0$, $\log \beta_{30} = 5.3$ and $\log \beta_{40} = 7.0$, respectively.

The values are in close agreement with the published values(12).

Cadmium (II)-oxalate system

A plot of $E_{1/2}$ versus log $[oxal,^{-2}]$ gave a smooth curve thereby suggesting the formation of successive complexes. DeFord and Hume's(17) method was applied to determine the stability constants of successive complexes. The stability constants for three complexes of Cd(II) are $\log \beta_{01} = 1.0$ for $[Cd(Oxal)]$, $\log \beta_{02} = 2.6$ for $[Cd(Oxal)_2]^{-2}$ and $\log \beta_{03} = 3.6$ for $[Cd(Oxal)_3]^{-4}$. The values are in less agreement with the published values(15).

Cadmium (II)-1-methylimidazole-oxalate-mixed system

The 1-methylimidazole concentration was varied from 0.02 to 0.16 M and that of oxalate was kept constant at 0.10 M. The half-wave potential values were more negative than those obtained in the absence of oxalate thereby showing the formation of mixed complexes. The process was repeated at another concentration of oxalate (0.20 M). To determine the values of the stability constants of mixed ligand complexes, the method of Schaap and McMasters(18) was applied.

The logarithmic value of the stability constant of the mixed-ligand complexes ($\log \beta_{XY}$) was calculated from the analysis of $F_{ij}[XY]$ functions (figs 1 and 2) in which i, j are stoichiometry and X, Y two different ligand species.

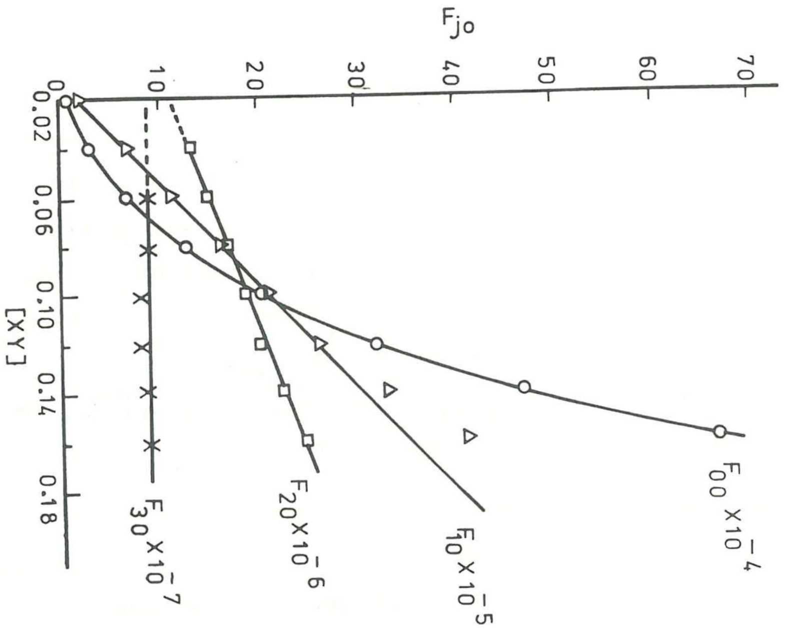

Fig.(1) Plot F_{jo} vs. [XY] for cadmium -1- methylimidazole oxalate system at $[oxal^{-2}] = 0.1$ M

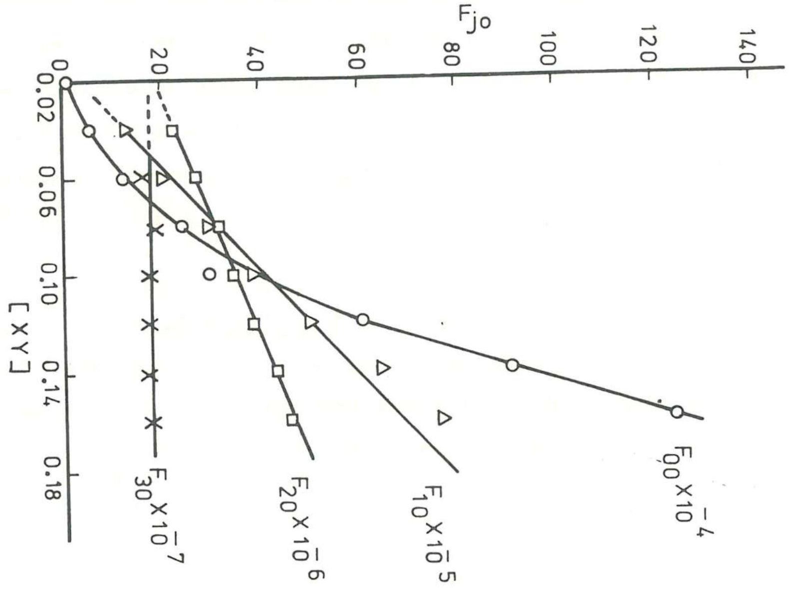

Fig.(2) Plot F_{jo} vs. [XY] for cadmium -1- methylimidazole oxalate system at $[oxal^{-2}] = 0.2$ M

The values are reproducible to ±5 %. Three mixed complexes as noted below are formed:

$[Cd(1\text{-}MeIm)(Oxal)]$ log $\beta_{11} = 4.0$

$[Cd(1\text{-}MeIm)(Oxal)_2]^{-2}$ log $\beta_{12} = 4.4$

$[Cd(1\text{-}MeIm)_2(Oxal)]$ log $\beta_{21} = 5.9$

The mixed constant K_M (equilibrium constant) for the reactions:

$$\tfrac{1}{2}[Cd(1\text{-}MeIm)_2]^{+2} + \tfrac{1}{2}[Cd(Oxal)_2]^{-2} \rightleftharpoons [Cd(1\text{-}MeIm)(Oxal)] \qquad (1)$$

$$\tfrac{1}{2}[Cd(1\text{-}MeIm)_4]^{+2} + \tfrac{1}{2}[Cd(Oxal)_2]^{-2} \rightleftharpoons [Cd(1\text{-}MeIm)_2(Oxal)] \qquad (2)$$

indicates the relative stability of mixed complexes in solution as compared to parent binary complexes. This is given by the following relations(19,20);

$$K_M = \beta_{11}/\sqrt{(\beta_{20}\ \beta_{02}} \qquad (3)$$

$$K_M = \beta_{21}/\sqrt{(\beta_{40}\ \beta_{02}} \qquad (4)$$

These yield +1.4 and +0.9 for reactions 1 and 2, respectively. The positive value of the mixed constant thus shows that, their formation is thermodynamically possible, because the concentration of a certain species depends on the equilibrium constants and on the free concentration of their components. Three mixed complexes existing in solution have the equilibria listed in Table 1.

Table 1: Equilibria Involved in three Mixed Complexes and Equilibria Constant (K) Values.

	Equilibrium			$\log K$ at 25 °C
1.	$\mathrm{Cd^{+2} + 1\text{-}MeIm + Oxal^{-2}}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)(Oxal)]}$	4.0
2.	$\mathrm{Cd^{+2} + 1\text{-}MeIm + 2Oxal^{-2}}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)(Oxal)_2]^{-2}}$	4.4
3.	$\mathrm{Cd^{+2} + 2(1\text{-}MeIm) + Oxal^{-2}}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)_2(Oxal)]^{-2}}$	5.9
4.	$\mathrm{[Cd(1\text{-}MeIm)(Oxal)] + 1\text{-}MeIm}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)_2(Oxal)]}$	1.9
5.	$\mathrm{[Cd(1\text{-}MeIm)(Oxal)_2]^{-2} + 1\text{-}MeIm}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)_2(Oxal)] + Oxal^{-2}}$	1.5
6.	$\mathrm{[Cd(1\text{-}MeIm)]^{+2} + Oxal^{-2}}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)(Oxal)]}$	1.3
7.	$\mathrm{[Cd(1\text{-}MeIm)_2]^{+2} + Oxal^{-2}}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)_2(Oxal)]}$	1.9
8.	$\mathrm{[Cd(1\text{-}MeIm)]^{+2} + 2Oxal^{-2}}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)(Oxal)_2]^{-2}}$	1.7
9.	$\mathrm{[Cd(Oxal)] + 1\text{-}MeIm}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)(Oxal)]}$	2.2
10.	$\mathrm{[Cd(Oxal)_2]^{-2} + 1\text{-}MeIm}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)(Oxal)_2]^{-2}}$	1.8
11.	$\mathrm{[Cd(Oxal)] + 2(1\text{-}MeIm)}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)_2(Oxal)]}$	4.1
12.	$\mathrm{[Cd(Oxal)_2]^{-2} + 2(1\text{-}MeIm)}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)_2(Oxal)_2] + Oxal^{-2}}$	3.3
13.	$\mathrm{[Cd(Oxal)_3]^{-4} + 1\text{-}MeIm}$	$\rightleftharpoons$	$\mathrm{[Cd(1\text{-}MeIm)(Oxal)_2]^{-2} + Oxal^{-2}}$	1.8

The equilibrium constant (log values) are given for each. From these values the tendency of a ligand to add to complex and the substitute another ligand may be compared. It is seen that "1-MeIm" adds to $\mathrm{[Cd(1\text{-}MeIm)(Oxal)]}$ readily. The ligand "1-MeIm" can replace "$\mathrm{Oxal^{-2}}$" in the complex $\mathrm{[Cd(Oxal)_3]^{-4}}$. Equilibria 10, 11 and 12 favour mixed complexations over the simple ones.

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