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Electrochemical Studies on Mixed Ligand Complexs of Lead Ion with DL-3(3,4-Dihydroxy Phenyl) Alanine and Some Dicarboxylic Acids

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Stability constants of the mixed ligand complexes with Pb(II), *viz.*, Pb(DOPA)(dicarboxylate), Pb(DOPA)(dicarboxylate)$_2$ and Pb(DOPA)$_2$ (dicarboxylate) have been determined electrochemically at 30 ± 1°C and ionic strength of 1.0 M. DOPA = 3(3,4-dihydroxy phenyl) alanine. For the comparison of the stability of simple and mixed complexes, the mixing constant (K_m) and the stabilization constant show that the ternary complexes are more stable than the binary complexes.

Keywords: stability constant, mixed-ligand complexes, polarography, lead-DOPA-dicarboxylate complexes.

INTRODUCTION

Mixed ligand complexes are important in analytical, biochemical and pharmaceutical fields[1–3]. A large number of such complexes have been studied electrochemically[4, 5]. The mixed-ligand complexes of Cd(II), Pb(II), Cu(II) and other metals with various ligands have been studied by many workers[6–8]. Complexation behaviour of some metal ions with DL-3(3,4-dihydroxy phenyl) alanine (DL-DOPA) have been carried out potentiometrically[9, 10]. Mixed ligand complexes of Cd(II) with DL-DOPA and some dicarboxylic acids have been studied in our laboratory[11]. However, electrochemical studies on the simple complexes of Pb(II) with DL-DOPA and its mixed complexes with dicarboxylic acids have not been reported so far and hence the present work has been undertaken. This communication deals with the study of simple and mixed ligand complexes of lead with DL-DOPA and dicarboxylic acids.

EXPERIMENTAL

The reagents, DL-DOPA, oxalic acid and malic acid (dicarboxylic acids), were of AnalaR grade and were used as complexing agents. The solutions were prepared in double distilled water. Potassium nitrate was used as supporting electrolyte to maintain the ionic strength at 1.0 M and 0.004% gelatin in the final solution sufficed to suppress the maxima observed. The temperature was maintained constant at 30 ± 1°C. The polarograms of the simple and mixed systems were taken using a manual polarograph. Saturated calomel electrode was used as a reference electrode. The capillary had the following characteristics, m = 1.96 mg s^{-1}, t = 4.05 s per drop, h ≈ 40.0 cm.

The experimental technique was the same as described earlier[12].

RESULTS AND DISCUSSION

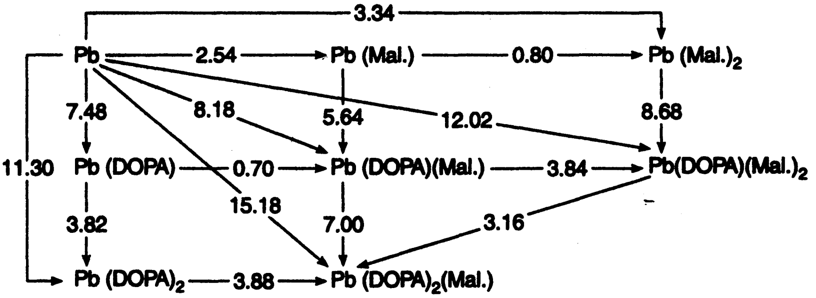
Simple System: The formation constants of simple systems of Pb-DOPA and Pb-dicarboxylate were calculated with the help of Deford and Hume's[13] method, before the study of mixed-ligand systems. The results of Pb-dicarboxylate are in good agreement with the literature[14, 15]. The formation constants of Pb-DOPA were not reported earlier in literature and were studied first time in the present communication. The values of formation constants of simple systems log β_1 and log β_2 are (7.48 and 11.30), (2.54 and 3.34) and (3.25 and 4.90) for Pb-DOPA, Pb-malate and Pb-oxalate systems respectively. The condition used corresponded as closely as possible to those for the mixed system *i.e.*, 1.0 M potassium nitrate and 30 ± 1°C.

Mixed Systems: The mixed systems of lead-DOPA-malate and lead-DOPA-oxalate were studied by keeping the concentration of weaker ligand (malic acid and oxalic acid) constant at two values (0.02 M and 0.2 M), while varying the concentration of the second ligand DL-DOPA in each case.

At fixed concentration of malate and oxalate ions with varying concentration of DL-DOPA, the slope of the straight line for the plot of E_{de} *vs.* log $i/(i_d - i)$ was 31 ± 1mV showing that two-electron reduction is reversible. The direct proportionality of the diffusion current to the square root of effective height of mercury column indicated that the reduction is entirely diffusion controlled.

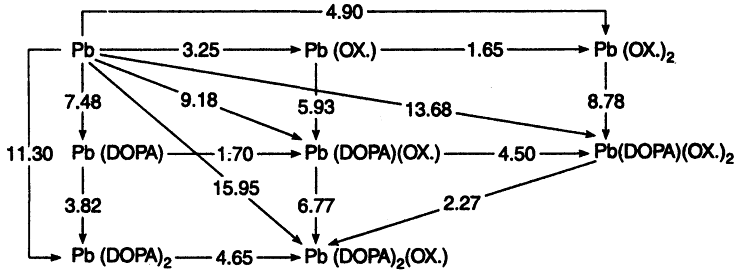
A shift in half wave potential to more negative side with increase in DL-DOPA concentration was observed. This shift in half-wave potential is greater in presence of the weaker ligands (malic acid and oxalic acid) than in its absence. It signified mixed ligand formation. The extended Schaap and McMaster's treatment was applied to the $E_{1/2}$ data and $F_{10}(XY)$ function and Leden's graphical extrapolation method to calculate A, B and C.

The stability constants β_{11} and β_{12} were evaluated from two values of B, and two values of C gave two values of β_{21} in good agreement with each other. Values of the stability constants (β_{11}, β_{12} and β_{21}) of mixed ligand complexes of lead(II) with dicarboxylic acids (malic acid and oxalic acid) are (8.18, 12.02 and 15.18) and (9.18, 13.68 and 15.95) for the lead-DOPA-malate and lead-DOPA-oxalate systems respectively.



Scheme-I. [Pb-DOPA-malate system]

The results are summarised in the form of Schemes I and II, where the numerical values indicate the log of the equilibrium constant.



Scheme-II. [Pb-DOPA-oxalate system]

The mixed ligand complex formation may be explained by considering Schemes I and II. The tendency to add X [X = DOPA] to PbX and PbY [Y = malate and oxalate] can be compared. The logarithms of stability constants of the above complexes are (3.82 and 5.64) and (3.82 and 5.93) for lead-DOPA-malate and lead-DOPA-oxalate 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 tendency to add Y to PbX and PbY can also be compared. The log K values are (0.70 and 0.80) and (1.70 and 1.65) for lead-DOPA-malate and lead-DOPA-oxalate respectively. This shows that the mixed complex formation is effected by statistical factors. The log K values for the addition of X to Pb(XY) and $Pb(Y)_2$ are (7.00 and 8.68) and (6.77 and 8.78) for lead-DOPA-malate and lead-DOPA-oxalate respectively and shows that the addition of amino acid is preferred to a weaker ligand.

The log K values for the addition of Y to Pb(XY) and $Pb(X)_2$ are (3.84 and 3.88) and (4.50 and 4.65) for lead-DOPA-malate and lead-DOPA-oxalate respectively, indicates that the addition of dicarboxylate ions is preferred to [Pb(dicarboxylate)DOPA] as compared to $Pb(dicarboxylate)_2$ and $Pb(DOPA)_2$.

The tendency of formation of the simple and mixed complexes can be expressed by calculating the disproportionation constant K for the equilibrium.

$$2Pb(XY) \Leftrightarrow Pb(X)_2 + Pb(Y)_2$$

The value of log K^D is –0.60 statistically but the observed values are found to be –1.72 and –2.16 for the Pb-DOPA-malate and Pb-DOPA-oxalate systems respectively. More negative values of log K^D for each equilibrium account for the stability of the mixed ligand complexes.

For comparing the stabilities of simple and mixed complexes, it is convenient to measure the mixing constants.

$$K_m = \beta_{11}/\sqrt{(\beta_{02}\,\beta_{20})}$$

and stabilization constants,

$$\log K_s = \log K_m - \log 2$$

The log K_m values are 1.33 and 1.10 and log K_s values are 1.03 and 0.80 for lead-DOPA-malate and lead-DOPA-oxalate systems respectively. The positive values of mixing and stabilization constants show that the ternary complexes are more stable than the binary complexes.

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