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Polarographic Studies on Mixed-Ligand Complexes of Lead(II) with DL-3-(3,4-Dihydroxy Phenyl) Alanine and Some Dicarboxylic Acids

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The polarographic reduction of lead(II) in the aqueous solution of DL-3-(3,4-dihydroxy phenyl) alanine (DL-DOPA) and some dicarboxylic acids (maleate and succinate) has been carried out. The stability constants have been determined for the simple Pb-DOPA system first, and then the mixed-ligand complexes of lead with DOPA and dicarboxylic acids (maleate and succinate) have been studied polarographically. The stability constant of mixed-ligand complexes have been determined by the method of Schaap and McMasters at 303 ± 3 K and ionic strength of 1.0 M. For the comparison of the stability of simple and mixed complexes, the mixing constant (K_m) and stabilization constant (K_s) have been measured. The positive values of the mixing constants and stabilization constants show that the ternary complexes are more stable than the binary complexes.

INTRODUCTION

The importance of amines and their derivatives has been widely recognized in the biochemical, analytical and pharmaceutical fields[1–3]. A large number of such complexes have been studied polarographically during the last decade[4, 5]. These complexes therefore attract wide attention in different areas of research. 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]. Potentiometric investigations of the complexation behaviour of some metal ions with DL-3(3,4-dihydroxy phenyl alanine) (DOPA) have been carried out by Rajan, Schan and others[9, 10]. Mixed-ligand complexes of Cd(II) with DOPA and some dicarboxylic acids have been studied in our laboratory[11]. However, there is not a single reference about the polarographic studies of Pb(II) with DOPA and its mixed-ligand complexes with dicarboxylic acids. Hence the title study has been undertaken. This communication deals with the study of mixed ligand complexes of lead(II) with DOPA and dicarboxylic acids.

EXPERIMENTAL

Polarograms were recorded on a manual polarograph using a saturated calomel electrode as the reference electrode. The capillary had the following characteristics: ṃ = 1.96 mg/s, t = 4.10 sec/drop and h ≈ 40.0 cm. The reagents, DOPA and dicarboxylic acids were of AR grade and were used as complexing agents. The solution was prepared in double distilled water. Potassium nitrate was used as a 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 303 ± 3 K. The experimental technique was the same as described earlier[12].

RESULTS AND DISCUSSION

Simple Systems: Before the study of the mixed-ligand complexes, the formation constants of the complexes of lead(II) with DOPA and lead(II) wth dicarboxylate (maleate and succinate) were determined by the method of Deford and Hume[13]. The results of lead-bicarboxylate are in good agreement with the literature[14, 15]. The formation constants of lead-DOPA were not reported earlier in literature and were studied first time in the present communication. The values of formation constant of simple systems log β_1 and log β_2 are (7.48 and 11.30), (2.25 and 3.00) and (2.36 and 3.10) for the Pb-DOPA, Pb-maleate and Pb-succinate systems respectively. The conditions used corresponded as closely as possible to those for the mixed system, *i.e.*, 1.0 M potassium nitrate as supporting electrode and temperature was maintained constant at 303 ± 3 K.

Mixed Systems: The concentration of the weaker ligands (maleate and succinate) was kept constant (0.02 M and 0.2 M), while varying the concentration of the second ligand DOPA in each case. In all the systems, solutions containing 0.5×10^{-3} M Pb(II), 1.0 M potassium nitrate, 0.04% gelatin in final solution sufficed; the maxima were polarographed at varying concentrations of DOPA.

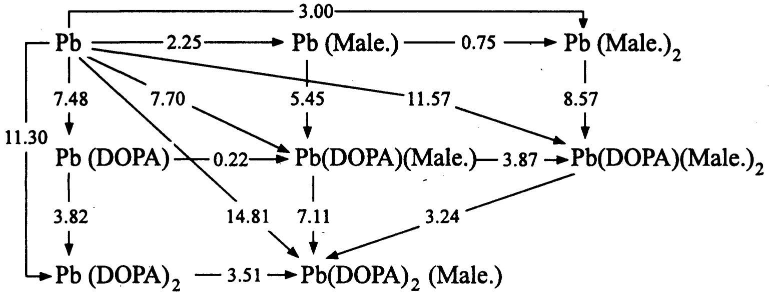
In each case, a single well-defined wave was obtained. The plots of Ede *vs.* log $i/(i_d - i)$ were linear with a slope of 30 ± 2 mV, showing that the two-electron reduction was reversible. The direct proportionality of the diffusion current to the mercury column indicated that the reduction was entirely diffusion controlled.

A shift in half wave potential to more negative side with increase in DOPA concentration was observed. This shift in half wave potential is greater in presence of the weaker ligands (maleate and succinate) than in its absence. It signified mixed ligand formation. The extended Schaap and McMasters treatment was applied to the $E_{1/2}$ data and $F_{10}(XY)$ function and Leden's graphical extrapolation method to calculate the values of A, B and C. The stability constants β_{11} and β_{12} were evaluated from the two values of B, and the two values of C gave two values of β_{21} in good agreement with each other. Value of the stability constants (β_{11}, β_{12} and β_{21}) of mixed ligand complexes of Pb(II) with DOPA and dicarboxylic acids (maleate and succinate) are (7.70, 11.57 and 14.81) and (7.70, 11.74 and 14.96) for the Pb-DOPA-maleate and Pb-DOPA-succinate systems respectively.

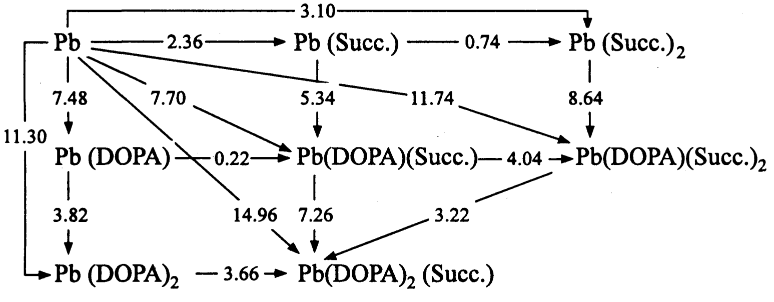
The results are summarized in the form of Schemes I and II, where the numerical values indicate the log of the equilibrium constants.

RESULTS AND DISCUSSION

The mixed ligand complex formation may also be explained by considering Schemes I and II. The tendency to add X (X = DOPA) to PbX and PbY (Y = maleate and succinate) can be compared. The logarithmic value of stability constants of the above complexes are (3.82 and 5.45) and (3.82 and 5.34) for lead-DOPA-maleate and lead-DOPA-succinate 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 tendency to add Y to PbX and PbY can be compared. The log K values are (0.22 and 0.75) and (0.22 and 0.74) for Lead-DOPA-Maleate and Lead-DOPA-Succinate systems respectively, indicating that the mixed ligand complexation is favoured.



Scheme (I): Pb–DOPA–Maleate system



Scheme (II): Pb–DOPA–Succinate system

The log K values for the addition of X to Pb(XY) and $Pb(Y)_2$ are (7.11 and 8.57) and (7.26 and 8.57) for lead-DOPA-maleate and Pb-DOPA-succinate systems respectively and show 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 (3.87 and 3.51) and (4.04 and 3.66) for lead-DOPA-maleate and lead-DOPA-succinate systems respectivley, indicating 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^D 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 –1.10 and –1.00 for lead-DOPA-maleate and lead-DOPA-succinate 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 the stabilization contants,

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

The log K_m values are +0.55 and +0.50 and log K_s values are +0.51 and +0.46 for lead-DOPA-maleate and lead-DOPA-succinate systems respectively. The positive values of mixing and stabilization constants show that the ternary complexes are more stable than the binary complexes.

The tendency to form mixed complexes in solution could be expressed quantitatively in another approach which compares the difference in stability Δ log K, which is the result from the subtraction of two constants, and must, therefore, also be a constant. This corresponds to

$$\Delta \log K = \log K^{MA}_{MAB} - \log K^{M}_{MB}$$

Since more coordination positions are available for bonding of the first ligand (A) to a given multivalent metal ion than for the second ligand (B),

$$\log K^{M}_{MA} > \log K^{MA}_{MA_2}$$

usually holds, *i.e.*, one expects to observe negative values for A log K. Another, probably more satisfactory, manner is to determine statistical values for Δ log K. The statistical values for regular octahedron (oh) is 5/12 and $\Delta \log K_{oh} = -0.4$. For a square plane (sp) the value of $\Delta \log K_{sp} = -0.6$ and for the distorted octahedron (do) the statistical values, *i.e.*, $\Delta \log K_{do}$ lie between –0.9 to –0.3.

The Δ log K values can be obtained using the following equations.

$$\Delta \log K_{11} = \log \beta_{11} - (\log \beta_{10} + \log \beta_{01})$$

$$\Delta \log K_{12} = \log \beta_{12} - (\log \beta_{10} + \log \beta_{02})$$

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

The observed values of $\Delta \log K_{11}$, $\Delta \log K_{12}$ and $\Delta \log K_{21}$ are [–2.03, +1.09 and +1.26] and [–2.14, +1.16 and +1.30] for the Pb-DOPA-maleate and Pb-DOPA-succinate systems respectively.

The Δ log K values are higher than statistical values, which again proves that the ternary complexes are more stable than expected from statistical reasons.

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REFERENCES

1. R.N. Patel,, H.C. Pandey nad K.B. Pandeya, *Bull. Electrochem.*, **12,** 612 (1996).
2. B.K. Singh, C.L. Jain and R.S. Sindhu, *Trans. SAEST*, **30,** 04 (1995).
3. R. Rodriguez-Amaro, M. Sanchez, E. Munoz, J.J. Ruiz and L. Camcho, *J. Electrochemical Soc.*, **143,** 2132 (A) (1996).
4. P. Rajeswari, R. Thamilarasi and S. Rajeswari, *Trans. SAEST*, **31,** 3 (1996).
5. K.B. Chaudhary, Ph.D. Thesis, BARC, Bombay (1981).
6. S. Mohanty, S. Anand and P. Mohanty, *Trans. SAEST*, **34,** 19 (1999).
7. J. Dei and P. Mohanty, *J. Indian Chem. Soc.*, **73,** 608 (1996).
8. A. Zaidi and F. Khan, *Bull. Electrochem.*, **16,** 119 (2000).
9. K.S. Rajan, S. Mainer and J.M. Danis, *Bio. Inorg. Chem.*, **9,** 187 (1978).
10. N.P. Sachan, C.P.S. Chandel and C.M. Gupta, *Chem. Scr.*, **20,** 111 (1982).
11. Nishi Gupta, C.P.S. Chandel, P.C. Gupta and C.M. Gupta, *Bull. Chem. Soc. Japan*, **56,** 3138 (1983).
12. C.P.S. Chandel, C.M. Gupta and N.P. Schan, *Chem. Scr.*, **20,** 229 (1982).
13. D.D. Deford and D.N. Hume, *J. Am. Chem. Soc.*, **73,** 5321 (1951).
14. S.C. Khurana, Ph.D. Thesis, University of Rajasthan, Jaipur (1973).
15. S.K. Shah, Pn.D. Thesis, University of Rajasthan, Jaipur (1980).

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