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Study of reduction of lead with some amino acids and thiodiglycolic acid (TDGA) at Dropping mercury electrode (DME)

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ABSTRACT

The reduction of Pb(II) in the aqueous solution with some amino acid (glycine and valine) and thiodiglycolic acid (TDGA) have been investigated at dropping mercury electrode first by the method of Deford and Humes and that of Pb-amino acids-TDGA have been studied by the method of Shaap and McMasters. The reduction of all the complexes has been found to be reversible and diffusion controlled, involving two electrons in each case. Three types of mixed complexes MXY, MX_2Y and MX_2Y have been determinedand found to be more stable than that of the simple ones. With the help of these data statistical and electrostatic have been considered.

Key words: Thiodiglycolic acid, aminoacids, reduction.

INTRODUCTION

The studies of mixed ligand complexes play an important role in biological processes[1]. Biological active complexes with amino acids are important in analytical, biochemical and pharmaceutical field[2-7]. Aminoacids form stable complexes have analytical importance in separation of transition metals and rare earth[8-9]. A study of these complexes is also important in biological chemistry, in that the accumulation of sufficient data on amino acids complexes with metal ion may contribute to a better understanding of the type linkages involved in metal protein interaction. Mixed ligand complexes of cadmium ion with some amino acids and L-Asperginate have been reported[10]. However there is no single reference about the mixed ligand complex of Pb(II) with amino acids (Glycine and Valine) and TDGA. Hence, the present work has been undertaken for study.

EXPERIMENTAL

All polarograms were recorded of ELICO CL 375 DC Polarograph using a saturated calomel electrode (SCE) as the reference electrode and platinum (Pt) electrode as counter electrode. The capillary had the following characteristics m=1.96 mg/s, t=4.10 sec/dro and h=40cm. The reagents TDGA and amino acids were of AR grade and were used as complexsing agents. KCL was used as supporting electrolyte to maintain the ionic strength at 1M. Triton X-100 of 0.001% in the final solution have been used as maximum suppressor. The temperature was maintained constant at 303K. A glass cell is used as electrolytic cell in which all the three electrodes are immersed in test solution. N_2 is used to remove the dissolved oxygen. Then increasing voltage was applied to record the current by the help of the plot between current-voltage (polarogram) the value of $E_{½}$ is calculated.

RESULTS

Simple systems

Before the studies of mixed ligand complexes, the formation constants of the complexes of lead with TDGA and lead with amino acids (Glycine and Valine) were determined by the method of Before and Hume[11]. The results are in good agreement with the literature. The values of formation constant of simple systems are presented in Table 1 The condition using corresponded as closely as possible to those for the mixed system.

The half wave potential of Pb(II) for each series ranged between -0.389 and -0.391 volts v/s SCE.

Mixes systems

In all the systems solution containing 2.5×10^{-3}M Pb(II), 1M KCl and 0.001% Triton X-100 was used. The concentration of waker ligand (TDGA) was kept constant (0.001M and 0.01M) while varying the concentration of second ligand (amino acids) in each case.

In each case, a single well-defined wave was obtained. The plots of E_{de} v/s log I/i_d-I were linear with a slope of 30±2m V, showing that the two electrons reduction was revisable. 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 amino acid concentration was observed. This shift in half wave potential is greater in the presence of the weaker ligand that its absence. It sifnified mixed ligand in the presence of the weaker ligand than its absence. It signified mixed ligand formation. The extended Shaap and McMasters[12] treatment was applied and Leden's[13] graphical extrapolation method to calculate the value of A, B, C and D. Details of calculation are given in table 2.

The stability constant β_{11} and β_{12} were evaluated from the two values of B. From the values of C two values of β_{21} were obtained which are in good agreement with each other. β_{30} is almost equal to D. The results are presented in table 4. The results are summarized in the form of schemes 1 and 2 where the numerical values indicate the log of the equilibrium constants.

Table 1: Stability constant for simple system

Systems	log β_1	log β_2	log β_3
Pb-TDGA	2.93	3.48	5.51
Pb-Glycine	5.15	7.43	10.69
Pb-Valine	5.00	7.25	10.32

Table 2: Values of A,B, C and D for Pb (II)-TDGA-Amino acids systems TGDA concentration = 0.01M

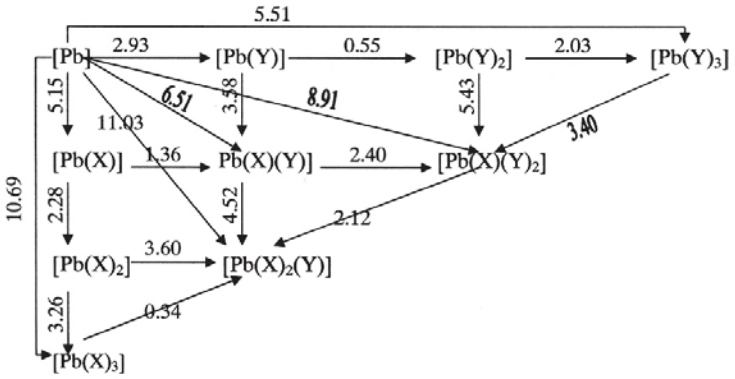
Systems	A	B	C	D
Pb-TDGA-Glycine	1.32	5.40	9.04	10.71
PB-TDGA-Valine	1.21	5.18	8.96	10.33

Table 3: Values of A,B, C and D for Pb (II)-TDGA-Amino acids systems TGDA concentration = 0.001M

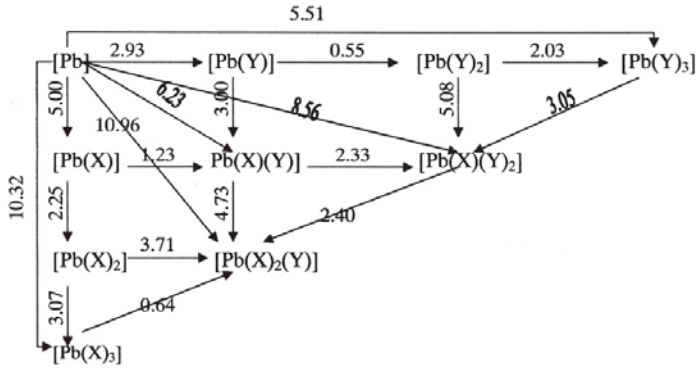
Systems	A	B	C	D
Pb-TDGA-Glycine	1.30	5.16	8.12	10.71
PB-TDGA-Valine	1.19	5.00	8.03	10.32

Table 4: Formation constants of mixed systems

Systems	log β_{11}	log β_{12}	log β_{21}
Pb-TDGA-Glycine	6.51	8.91	11.03
PB-TDGA-Valine	6.23	8.56	10.96



Scheme 1: Pb(II) - TDGA-Glycine system



Scheme 2: Pb(II) - TDGA-Valine system

DISCUSSION

The mixed ligand complex formation may also be explained with the help of schemes 1-2. The tredency to add X (X=amino acids) to PbX and PbY (Y=TDGA) can be compared. The logarithm value of stability constant of the above complexes are (2.28, 3.58) and (2.25, 3.30) for Tb-TDGA-Glycine and Pb-TDGA-Valine systems respectively.

The tendency to add Y to PbX and PbY can also be compared. The log K values are (1.36, 0.55) (1.23, 0.55) for Pb-TDGA-Glycine and Pb-TDGA-Valine respectively. This indicates that the addition of TDGA preferred to Pb(amino acids) as compared to Pb(TDGA).

The log K values for the addition of X to Pb[XY] and $Pb[Y]_2$ are (4.52, 5.43) and (4.73, 5.08) for Pb - TDGA-Clycine and Pb-TDGA-Valine system respectively. This indicates that addition for TDGA is preferred to Pb $[X]_2$ over Pb [XY].

The log K values for the addition of X to Pb [XY] and $Pb[Y]_2$ are (2.40, 3.60) and (2.33, 3.71) for Pb-TDGA-Glycine and Pb-TDGA-Valine systems respectively. This indicates that addition of TDGA is preferred to Pb $[X]_2$ over Pb [XY].

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

$$km = \frac{\beta_{11}}{\sqrt{\beta_{02} \times \beta_{20}}}$$

and the stabilization constants.

$\log K_s = \log K_m$ - log2

The log Km values are 1.055 and 0.865 and log Ks values are 0.754 and 0.564 for Pb-TDGA-Glycine and Pb-TDGA-Valine system respectively. The positive values of mixing and stablisation 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 other approach compares the difference in stability (Δ log K), which is the result from the substraction of two constants and must therefore, be a constant. This corresponds to:

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

Since more coordination position are available for the bonding of the 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 Δ 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 Δ log Koh = -0.4 for a square planer (sp), the value of Δ log K = -0.6 and for the distorted octahedron (do), the statistical value i.e. Δ log K =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 $\Delta \log K_{11}$, $\Delta \log_{12}$ and $\Delta \log K_{21}$ are (-1.57, 0.28, 0.67) and (-1.70, 0.08, 0.78) for Pb-TDGA-Glycine and Pb-TDGA-Valine systems respectively.

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

CONCLUSION

From the above investigation it is found that Pb makes three types of ternary stable complexes with amino acids and TDGA i.e. MXY, MXY_2 and MX_2Y. The Δ log K values of these systems are higher than staistical values, which again prove that these complexes are stable.

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