STABILITY CONSTANTS OF Pb(II) COMPLEXES WITH MERCAPTOSUCCINIC ACID AND SOME AMINO ACIDS: A POLAROGRAPHIC STUDY

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ABSTRACT

The reduction of Pb(II) in the aqueous solution with some amino acids (glycine and valine) and mercaptosuccinic acid (MSA) have been investigated at dropping mercury electrode (DME) .The stability constants of Pb-MSA and Pb-amino acids were measured first by the method of Deford and Humes and that of Pb-amino acids-MSA 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 ststistical and electrostatic effects have been considered.

Keywords: *Mercaptosuccinic acid, Aminoacids, Reduction*
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INTRODUCTION

Polarography plays very important role in the identification of mixed ligand complexes of different metals. Biological active metal complexes with amino acids are important in analytical, biochemical and pharmaceutical have been studied by many coworkers[1-7]. Polarographic study of mixed ligand complexes of Cadmium with L-amino acids and VitaminB_5 have been studied by Khan[8] et al. The Polarographic studies on the complexes of Copper and oxalate are reported in the literature[9-10]. A survey of literature shows that ternary complexes of Pb(II) with amino acids and MSA have not been studied so far. The present communication reports the formation of mixed ligand complexes of Pb(II) with amino acids as primary ligands and MSA as secondary ligand, studied by polarographic technique.

EXPERIMENTAL

All polarograms were recorded on ELICO CL 375 DC Polarograph using a saturated calomel electrode (SCE) as the reference electrode and a platinum (Pt) electrode as counter electrode. The capillary had the following characteristics m=1.96 mg/s, t = 4.10 sec/drop and h = 40 cm. The reagents MSA and amino acids were of AR grade and were used as complexing 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 suppresser. The temperature was maintained constant at 303 K. 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 $E_{1/2}$ is calculated.

RESULTS AND DISCUSSION

Simple systems:

Before the studies of mixed ligand complexes, the formation constants of the complexes of lead with MSA and lead with amino acids (Glycine and Valine) were determined by the method of Deford 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 was ranged between –0.389 and –0.391 volt v/s SCE.

Table-1: Stability constants for simple system

Systems	log β_1	log β_2	log β_3
Pb-MSA	3.07	3.63	5.73
Pb-Glycine	5.15	7.43	10.69
Pb-Valine	5.00	7.25	10.32

Mixed Systems:

In all the systems solution containing 2.5 x 10^{-3} M Pb(II), 1M KCl and 0.001% Triton X-100 was used. The concentration of weaker ligand (MSA) 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±2mV, showing that the two electrons 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 amino acid concentration was observed. This shift in half wave potential is greater 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.

Table-2: Values of A, B, C and D for Pb(II) – MSA- Amino acids systems

MSA concentration = 0.01M

System	A	B	C	D
Pb-MSA-Glycine	1.35	5.46	9.17	10.71
PB-MSA-Valine	1.24	5.26	9.07	10.33

Table-3: Values of A, B, C and D for Pb(II) – MSA- Amino acids systems

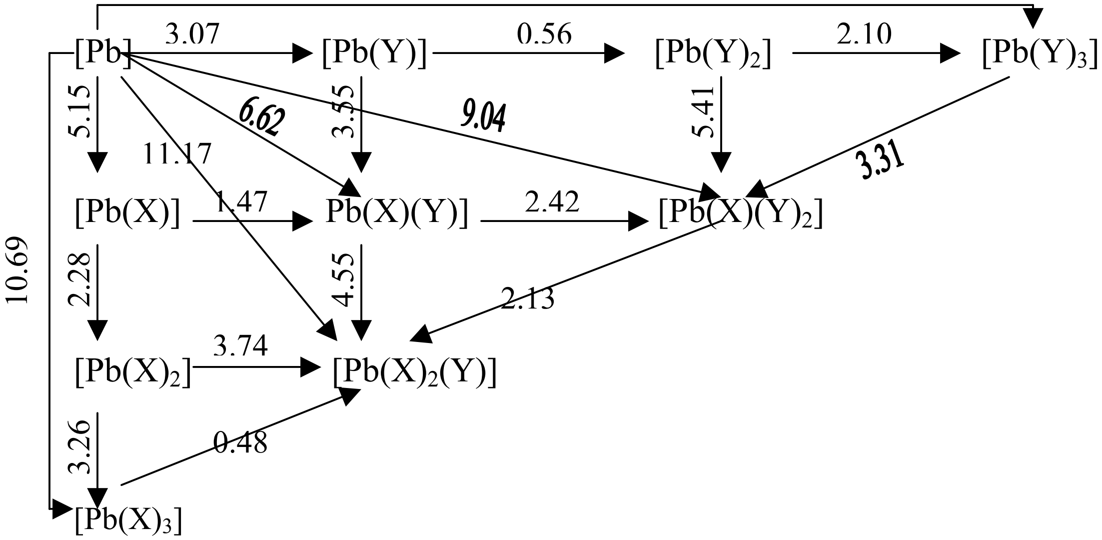
MSA concentration = 0.001M

System	A	B	C	D
Pb-MSA-Glycine	1.32	5.16	8.24	10.71
PB-MSA-Valine	1.21	5.01	8.13	10.32

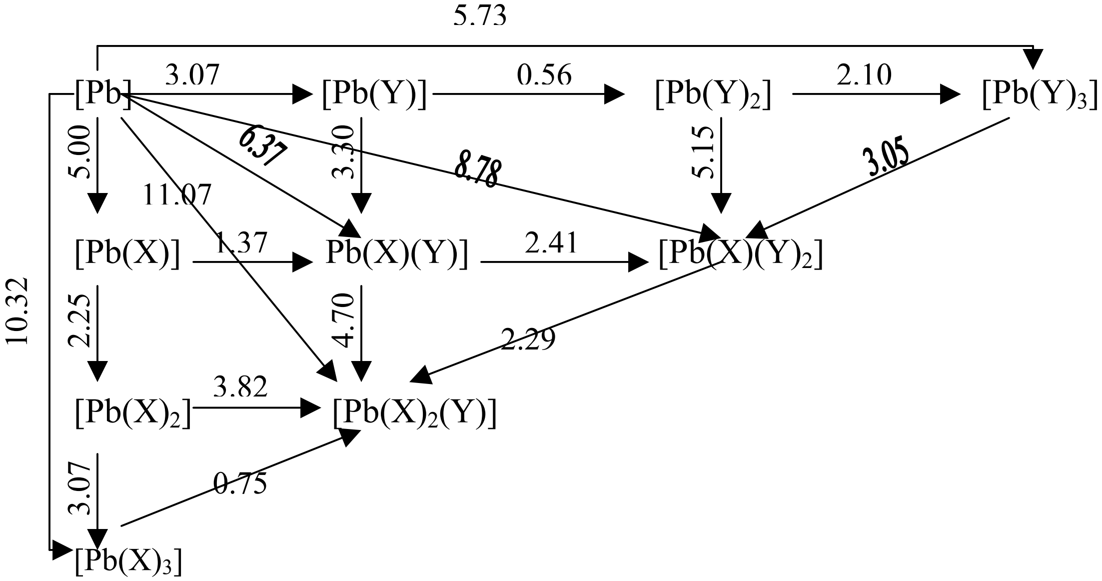
The stability constants β_{11} and β_{12} were evaluated from the two values of B. From the values of C two values of β_{21} were obtained which are in good agreement with each other. β_{30} is almost equal to D. The results are presented in table 4. The results are summarized in the form of schemes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

Table-4: Formation Constants of Mixed Systems

Systems	log β_{11}	log β_{12}	log β_{21}
Pb-MSA-Glycine	6.62	9.04	11.17
PB-MSA-Valine	6.37	8.78	11.07



Scheme-1: Pb(II)-MSA-Glycine System



Scheme-2: Pb(II)-MSA-Valine System

The mixed ligand complex formation may also be explained with the help of schemes 1-2. The tendency to add X (X= amino acids) to PbX and PbY (Y=MSA) can be compared. The logarithm value of stability constants of the above complexes are (2.28, 3.55) and (2.25, 3.30) for Pb-MSA-Glycine and Pb-MSA-Valine systems respectively.

The tendency to add Y to PbX and PbY can also be compared. The log K values are (1.47, 0.56) and (1.37, 0.56) for Pb-MSA-Glycine and Pb-MSA-Valine respectively. This indicates that the addition of MSA is preferred to Pb (amino acids) as compared to Pb(MSA).

The log K values for the addition of X to Pb[XY] and $Pb[Y]_2$ are (4.55, 5.41) and (4.70, 5.15) for Pb-MSA-Glycine and Pb-MSA-Valine systems respectively. This indicates that the mixed ligand complexation is favoured.

The log K values for the addition of Y to Pb[XY] and $Pb[X]_2$ are (2.42, 3.74) and (2.41, 3.82) for Pb-MSA-Glycine and Pb-MSA-Valine systems respectively. This indicates that addition of MSA 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.

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

and the stabilization constants.

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

The log Km values are 1.09 and 0.93 and log Ks values are 0.78 and 0.62 for Pb-MSA-Glycine and Pb-MSA-Valine systems 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 subtraction 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 positions 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 squar planer(sp), the value of Δ log K = -0.6 and for the distorted octahedron (do), the statistical values 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 Δ log K_{11}, Δ log K_{12} and Δ log K_{21} are (-1.60, 0.26, 0.67) and (-1.70, 0.15, 0.75) for Pb-MSA-Glycine and Pb-MSA-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 MSA i.e. MXY, MXY_2 and MX_2Y. The Δ log K values of these systems are higher than statistical values, which again prove that these complexes are stable.

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