Asian Journal of Chemistry Vol. 21, No. 6 (2009), 4658-4662

Determination of Stability Constants of Ternary Complexes of Lead With Vitamin B_5 and Amino Acids (L-Citrulline and Valine) Polarographycally

MEENA and O.D. GUPTA*
Department of Chemistry, University of Rajasthan, Jaipur-302 004, India
E-mail: meenu_aadi @rediffmail.com

The reduction of Pb(II) in the aqueous solution with amino acids (L-citrulline and valine, vitamin B_5) have been investigated at dropping mercury electrode (DME) .The stability constants of Pb-vitamine B_5 and Pb-amino acids were measured first by the method of Deford and Humes and that of Pb-amino acids-vitamine B_5 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, MXY_2 and MX_2Y have been determined and found to be more stable than that of the simple ones. With the help of these data statistical and electrostatic effects have been considered.

Key Words: Ternary complexes, Lead(II), Vitamin B_5, Amino acids, Reduction.

INTRODUCTION

Mixed ligand complexes play important roles in biological processes. Amino acids with biologically active complexes are important in various fields like pharmaceutical, biochemical and analytical[1,2]. Dicarboxylic acids and amino acids are used for the separation of transition metals and earth metals[3-5]. Study of ternary complexes of Cd(II) with β-picoline and some hydroxy acids have been studied by Verma *et al.*[6]. Copper(II) complexes with β-picoline, malic acid and tartaric acid are also reported Durrani *et al.*[7] investigated the behaviour of Cu(II) complexes with picolinic acid and some amino acids. Cadmium(II) complexes with L-amino acids and vitamin B_5 have been studied[8] but Pb(II) with L-citrulline and valine have not been studied. The present communition reports the formation of mixed-ligand complexes as primary ligands and vitamin B_5 as secondary ligand.

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 s/drop and h = 40 cm. The reagents vitamin B_5 and amino acids were of AR grade and were used as complexing agents. Potassium chloride was used as supporting electrolyte to maintain the ionic strength at 1 M. Triton-X-100 of 0.001 % in the final solution has 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. Nitrogen 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 AND DISCUSSION

Simple systems: Before the studies of mixed ligand complexes, the formation constants of the complexes of lead(II) with vitamin B_5 and with amino acids (L-citrulline and valine) were determined by the method of Deford and Hume[9]. 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 *vs.* SCE.

TABLE-1
STABILITY CONSTANTS FOR SIMPLE SYSTEM

Systems	log β_1	log β_2	log β_3
Pb-Vitamin B_5	2.85	3.23	5.34
Pb-L-Citrulline	5.21	7.59	10.89
Pb-Valine	5.00	7.25	10.32

Mixed systems: In all the systems solution containing 2.5×10^{-3} M Pb(II), 1 M KCl and 0.001 % Triton-X-100 was used. The concentration of weaker ligand (vitamin B_5) was kept constant (0.001 M and 0.01 M) 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} *vs.* log I/i_d-I were linear with a slope of 30 ± 2 mV, 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[10].

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[10] treatment was applied and Leden's[11] 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)–VITAMIN B_5-AMINO ACIDS
SYSTEMS VITAMIN B_5 CONCENTRATION = 0.01 M

System	A	B	C	D
Pb-Vitamin B_5 –L-citrulline	1.28	5.37	9.04	10.91
Pb-Vitamin B_5 -Valine	1.17	5.16	8.89	10.35

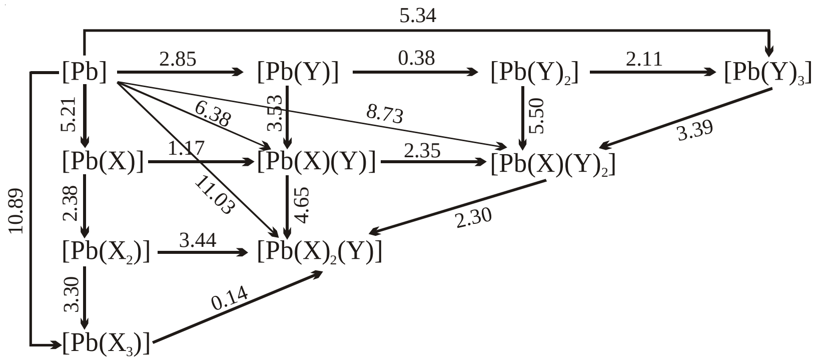
TABLE-3
VALUES OF A, B, C AND D FOR Pb(II) – VITAMIN B_5 - AMINO ACIDS SYSTEMS VITAMIN B_5 CONCENTRATION = 0.001 M

System	A	B	C	D
Pb- Vitamin B_5 -L-Citrulline	1.27	5.21	8.16	10.90
PB- Vitamin B_5 -Valine	1.16	5.00	7.97	10.33

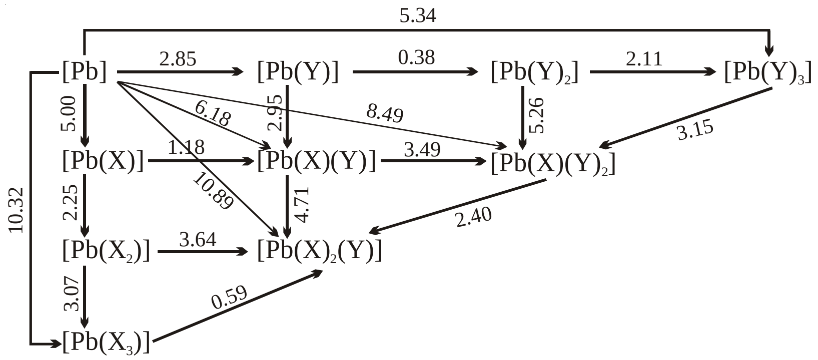
The stability constants β_{11} and β_{12} were evaluated from the two values of B. From the values of C two values of β_{21} were obtained which are in good agreement with each other. β_{30} is almost equal to D. The results are presented in Table-4. The results are summarized in the form of **Schemes I-II** 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- Vitamin B_5 -L-Citrulline	6.38	8.73	11.03
Pb- Vitamin B_5 -Valine	6.18	8.49	10.89



Scheme-I: Pb(II)-vitamin B_5-L-citrulline system



Scheme-II: Pb(II)-vitamin B_5-valine system

The mixed ligand complex formation may also be explained with the help of **Schemes I-II**. The tendency to add X (X = amino acids) to PbX and PbY (Y = vitamin B_5) can be compared. The logarithm value of stability constants of the above complexes are (2.38, 3.53) and (2.25, 2.95) for Pb-vitamin B_5-L-citrulline and Pb-vitamin B_5 - valine systems, respectively.

The tendency to add Y to PbX and PbY can also be compared. The log K values are (1.17, 0.38) and (1.18, 0.38) for Pb-vitamin B_5 - L-citrulline and Pb-vitamin B_5 -valine, respectively. This indicates that the addition of vitamin B_5 is preferred to Pb(amino acids) as compared to Pb(vitamin B_5).

The log K values for the addition of X to Pb[XY] and $Pb[Y]_2$ are (4.65, 5.50) and (4.71, 5.26) for Pb-vitamin B_5-L-citrulline and Pb-vitamin B_5-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 (2.35, 3.44) and (3.49, 3.64) for Pb-vitamin B_5-L-citrulline and Pb-vitamin B_5-valine systems, respectively. This indicates that addition of vitamin B_5 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 K_m values are 0.97 and 0.94 and log K_s values are 0.669 and 0.639 for Pb-vitamin B_5-L-citrulline and Pb-vitamin B_5-valine 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 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 (o_h) 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 (d-o_h), 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 $\Delta \log K_{11}$, $\Delta \log K_{12}$ and $\Delta \log K_{21}$ are (-1.68, 0.29, 0.59) and (-1.67, 0.26, 0.79) for Pb-vitamin B_5 - L-citrulline and Pb-vitamin B_5 -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 3 types of ternary stable complexes with amino acids and vitamin B_5 *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.

ACKNOWLEDGEMENTS

One of the authors (Meena) is thankful to Head, Department of Chemistry, University of Rajasthan, Jaipur for providing the necessary laboratory facilities.

REFERENCES

1. F. Khan and L. Tantuvay, *J. Pharm. Biomed. Anal.*, **27**, 933 (2002).
2. K.R. Jangid and C.P.S. Chandel, *J. Ultrasci. Phys. Sci.*, **19**, 167 (2007).
3. M.A. Shakoor and S. Hussain, *Asian J. Chem.*, **19**, 311 (2007).
4. F.D.S. Pabreja, K.P. Patel and S.C. Parikh, *Asian J. Chem.*, **20**, 963 (2008).
5. T.K. Yadav and S. Singh. *Asian J. Chem.*, **20**, 870 (2002).
6. P.K.S. Chauhan, A. Verma and R.K. Paliwal, *Orient. J. Chem.*, **20** (2003).
7. A. Durrani, M. Farooqui, S. Pakhare, S. Nausheen and A. Zaheer, *Asian J. Chem.*, **18**, 3114 (2006).
8. A.K. Khan and F. Khan, *J. Indian Chem. Soc.*,**75**, 31 (1998).
9. D.D. Deford and D.N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
10. Lenden, *J. Phys. Chem.*, **188**, 160 (1941).
11. W.B. Schaap and D.L. McMasters, *J. Am. Chem. Soc.*, **83**, 4699 (1961).

(*Received*: 1 August 2008; *Accepted*: 25 March 2009) AJC-7379