

Potentiometric Studies on Some Ternary Complexes of Uranyl Ion with Pyridine Carboxylic Acids and Some Amino Acids

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The proton ligand stability constants and stability constants of simple and mixed ligand chelates of uranyl ion with glycine, glycyl-glycine, mercaptopropionyl glycine, α -alanine, β -alanine, aspartic acid, glutamic acid, picolinic, nicotinic and isonicotinic acids have been studied potentiometrically at $25 \pm 0.5^\circ\text{C}$ and $\mu = 0.1 \text{ M}$ (NaClO_4) in aqueous medium. Uranyl forms 1 : 1 and 1 : 2 complexes with all the chelating agents except in aspartic acid. The mixed ligand chelates are shown to have formed in simultaneous equilibria. The lower values of stability constants of mixed ligand chelates than the sum of the individual log stability constants of the first and second ligand are discussed. The values of the log K_{MLA} for the systems nicotinic/isonicotinic-amino acids have been ascribed to their differences in the position of the carboxylic group to the pyridine ring, steric hindrance between the ions, size of the chelating agent and electron density of the ring.

INTRODUCTION

Recently there has been considerable interest in the study of binary, ternary and quaternary complexes by pH metric method.¹⁻⁴ Data on the number of systems involving uranyl ion and some other bivalent metal ions with pyridine carboxylic acids, dicarboxylic amino acids, phenolic acids and few biologically important compounds has already appeared.⁵⁻¹¹ Mixed ligand complexes of uranyl ion with amino acids and carboxylic acids or monocarboxylates have been published recently by many workers⁸⁻¹¹ each stating relatively strong bond formation between uranyl ion and oxygen donors. It is also known that a maximum of three bidentate ligand molecules are being quite sufficient to coordinate with UO_2^{2+} to reach the specified coordination number, as a maximum coordination number of eight has been suggested for uranium ion.¹² However, although several studies of mixed ligand complexes of UO_2^{2+} ion with pyridine carboxylic acids and amino acids have been published, no data on the title investigation is available systematically. It, therefore, seemed desirable to evaluate the stability constants of the mixed ligand complexes of uranyl ion and to obtain some information about the complexing ability of the amino acids with

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1:1 UO_2^{2+} -pyridine carboxylate complexes particularly from the standpoint of metal-ligand interactions.

EXPERIMENTAL

The ligands picolinic, nicotinic, isonicotinic, glycine, α -alanine, glutamic acid, aspartic acid and 2-mercapto propionyl glycine were of BDH AnalaR grade and were used as such. Uranyl nitrate BDH AR grade, sodium hydroxide BDH, sodium perchlorate and perchloric acid of AnalaR quality were of E. Merck, Germany. All solutions were prepared in air-free conductivity water.

The pH-metric measurements were carried out by using Elico digital pH meter model L-120 with glass and calomel electrodes with an accuracy of ± 0.01 of pH unit at 25°C . The pH-meter was standardized against 0.05 M potassium hydrogen phthalate for pH 4.0. The ionic strength was maintained at $\mu = 0.1$ M (NaClO_4). The pHs were plotted against moles of base added per mole of metal ion/ligand.

Calculations

The acid dissociation constants of the ligands and stability constants of the simple metal complexes were calculated by the method of Irving and Rossotti.^{13, 14} The accurate values of $\log K_1$ and $\log K_2$ were calculated by the method of least squares and are compared with the literature values. These are presented in Table-1. The formation constants for the determination of stability constants, the concentration of total (first and second) free ligand and the value of X were calculated by the following expressions obtained by modification of Thompson and Lora's method¹⁵ and Ramamoorthy and Santappa's method.^{16, 17}

TABLE-1
DISSOCIATION CONSTANTS OF THE LIGANDS AND STABILITY CONSTANTS OF
 UO_2^{2+} COMPLEXES OF BINARY AND TERNARY SYSTEMS

Temp. = $25 \pm 0.5^\circ\text{C}$ $\mu = 0.1$ M (NaClO_4)

Ligand/Acid	Dissociation constants		Stability constants	
	pK ₁	pK ₂	log K ₁	log K ₂
Picolinic	1.66 (1.66)	5.24 (5.23)	4.46 (4.46)	3.75 (3.75)
Nicotinic	2.04 (2.05)	4.74 (4.70)	2.60 —	1.81 —
Isonicotinic	1.83 (1.81)	4.92 (4.87)	3.17 —	3.05 —
Glycine	2.42 (2.43)	9.67 (9.68)	7.50 (7.53)	7.13 (7.15)
2-Mercapto-propionylglycine	3.59 (3.59)	8.88 (8.87)	—	—
Glycyl-glycine	3.12 (3.12)	8.18 (8.17)	—	—
DL- α -alanine	2.53 (2.53)	9.59 (9.59)	7.33 (7.33)	7.64 (7.64)
β -alanine	3.62 (3.62)	10.22 (10.21)	7.81 (7.78)	7.60 (7.53)
Aspartic	3.91 (3.87)	9.89 (9.89)	8.80 (8.71)	—
Glutamic	4.12 (4.07)	9.58 (9.54)	8.48 (8.43)	6.35

$$X = 1 + \frac{2[\text{H}]^2}{K_1K_2 + K'_1K'_2} + \frac{[\text{H}]}{K_2 + K'_2}$$

and

$$A = \frac{2T_L + 2T_A - T_{\text{OH}} - [\text{H}^+]}{\frac{4[\text{H}]^2}{(K_1K_2) + (K'_1 + K'_2)} + \frac{2\text{H}^+}{(K_2 + K'_2)}}$$

where T_L and T_A represent the concentration of first and second ligand, $T_{\text{OH}} = [\text{NaOH}]$, $[K_1K_2$ and $K'_1K'_2$ are the first and second dissociation constants of the two ligands. The value of stability constants of the mixed complexes is given by]

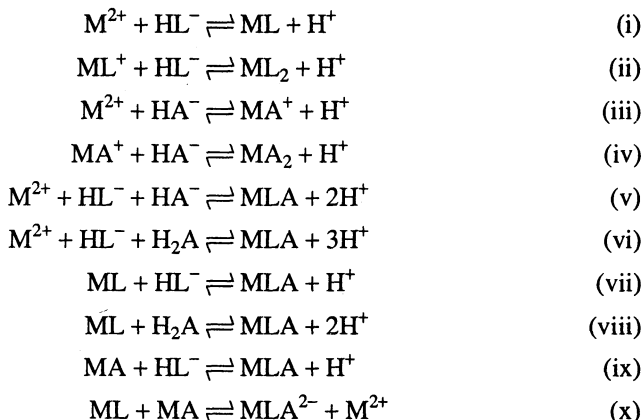
$$\log K_{\text{MLA}} = \frac{[T_M - \frac{1}{2}A - X]}{\frac{1}{2}[A]^3 X}$$

The free energies of formation are calculated by using ref. 18 which are recorded in Table-1.

RESULTS AND DISCUSSION

In the present work uranyl forms 1 : 1 and 1 : 2 complexes with all the ligands except in aspartic acid. Since the mixed ligand curve did not coincide with either of the individual metal titration curves in all the segments, the formation of 1 : 1 : 1 complex by a simultaneous equilibrium was inferred.

The possible equilibria for the simple and mixed complexes are:



The values of stability constants of binary systems have been evaluated in order to get their data under identical experimental conditions maintained for the mixed systems and also to conform the effect of substitution in the pyridine ring and amino acids. The values of proton ligand stability constants for all the ligands studied are tabulated in Table-1. There was a good agreement between the values obtained in the present investigation and reported by other workers. The log K values in case of DL- α -alanine and β -alanine were found to be higher than glycine which was on expected lines because of the higher basicity of alanines. The

polarographic evaluation of stability constants of binary and ternary complexes of uranyl and cadmium ions¹⁹⁻²¹ with amino acids and nicotinamide has already appeared in the literature from our laboratory. In order to establish further support in connection with the effect of substitution in pyridine ring in uranyl complexes, the present work was undertaken.

From the curves of the nicotinic and isonicotinic acids with uranyl ion, it was observed that the formation of the positive charge over N starts in the pH range of 2.5–3.0 above which the formation of mixed ligand complexes starts in all the systems, *i.e.*, the pK_1 of nicotinic and isonicotinic acids were 1.80 and 1.43 respectively. From this it was inferred that the chelation occurs through the carboxylic oxygen in both the ligands. The pH of formation of precipitate was noted down for the individual complexes and compared to the pH of formation of precipitate for the mixed complexes. From this it was observed that the pH of hydrolysis of all the mixed ligand complexes was lower than the pH of hydrolysis of the individual complexes, and hence a complex less resistant to hydrolysis was produced when both the ligands were mixed. The formation of mixed ligand complexes was inferred primarily from the qualitative evidence and further supported by drawing a composite curve (by adopting the procedure as usual) which was found to be slightly above the experimental curve with some exceptions of isonicotinic glycine, isonicotinic- α -alanine and nicotinic aspartic acid where the composite curve was found to be below the experimental curve. The non-superimposable nature of the curves of the experimental curve to either of the curves of the individual complexes and absence of any solid phase during the titration give additional support to the formation of soluble and stable 1:1:1 mixed ligand complexes.

In the systems nicotinic- α -alanine, nicotinic-glycine and isonicotinic-aspartic acid, the composite curve was found to be below the mixed ligand curve. This may probably be due to the back donation of the charge from the carboxylic group to the nitrogen which is in the form of N^+ . The $\log K_{\text{MLA}}$ value in case of uranyl-nicotinic-aspartic system was found to be higher than glutamic acid which is expected because of the size of the molecule and the tendency to form mixed ligand complexes with nicotinic acid. However, in case of nicotinic-glycine the values of $\log K_{\text{MLA}}$ are nearly identical.

The $\log K_{\text{MLA}}$ values for all the systems were tabulated in Table-2 along with the free energy of formation values ΔG° . It has been observed that the position 4 in pyridine ring tend to pull electrons from the metal ion into the ring thereby forming a double bond as in case of isonicotinic acid and hence the values of stability constants of binary and ternary complexes of uranyl isonicotinic, uranyl-isonicotinic- β -alanine systems ought to be higher than that of uranyl-nicotinic and uranyl-nicotinic- β -alanine systems respectively. The values of stability constants of the mixed ligand complexes were found to be lower than would be predicted from the sum of the individual parent 1:1 complexes. This can be explained on the basis of electrostatic forces, space available for the second incoming ligand, size of the chelating agent and simultaneous π bonding between the metal ion and the ligands.

TABLE-2
STABILITY CONSTANTS OF MIXED LIGAND COMPLEXES

Systems	log K_{MLA}	log $K_{ML} + \log K_M$	$\Delta \log K_{MLA}$	ΔG° kcal/deg/mol
Nicotinic-glycine	9.68	9.57	-0.11	13.33
Nicotinic- α -alanine	9.12	10.92	1.80	12.55
Nicotinic- β -alanine	8.82	9.81	0.99	12.15
Nicotinic-aspartic acid	8.24	10.12	1.88	11.35
Nicotinic-glutamic acid	10.65	8.35	-2.30	14.67
Isonicotinic- β -alanine	10.58	10.38	-0.20	14.46

The values given in the parenthesis are the literature values.

The log K_1 and log K_2 were calculated by the method of least squares.

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