

A Potentiometric Study of Ternary Complexes of some Transition metals with Pyridine-2,6-dicarboxylic acid and 2-hydroxy benzalidine-anthranilic acid

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Abstract- Mixed ligand complexes of some transition metals [Cu(II), Ni(II), Co(II) and Zn(II)] have been investigated Potentiometrically with Pyridine-2,6-dicarboxylic acid (PDA) and 2-hydroxy benzalidine-anthranilic acid (HBAA) in aqueous solution at 298.15 K and 313.15 K. The ionic strength of 0.1 mol dm⁻³ was kept constant using KNO₃. The stability constants of these 1:1:1 ternary complex have been evaluated by the computational methods. The relative order of stability has been observed in accordance with the increasing (ϕ) = charge/ radius ratio. The changes in thermodynamic parameters (ΔG^0 , ΔH^0 , ΔS^0) have also been calculated under the same conditions.

Index Terms- Potentiometric Study, Ternary Complexes, Transition metals, HBAA, PDA

respectively(27,28).The study of the formation stabilities and reactivities of mixed ligand complexes have been adopted by many research workers(29-31). There are various papers appeared in last few decades regarding ternary complexes of transition and non-transition metals(32-43).Recently there has been considerable interest in the study of binary, ternary and quaternary complexes by pH metric method(17,44-46). In the present study mixed ligand complexes of some transition metals [Cu^(II), Ni^(II), Co^(II) and Zn^(II)] have been investigated Potentiometrically with Pyridine-2,6-dicarboxylic acid (PDA) and 2-hydroxy benzalidine-anthranilic acid (HBAA) in aqueous solution at 298.15 K and 313.15 K. The changes in thermodynamic parameters (ΔG^0 , ΔH^0 , ΔS^0) have also been calculated under the same conditions.

I. INTRODUCTION

Metal coordination complexes have been extensively used in clinical applications as enzyme inhibitors (1), anti bacterial (2-3), antiviral (4-6) and anti cancerous (7-9). The complexes of metal ions are common in analytical and Biological systems (10-12). The metal ions in presence of organic and inorganic ligands are playing a crucial role in the field of analytical chemistry (13-15), catalysis (14-16), biology (14,17), medicine (18-21), chemical protection of radiation(22,23) in the study of metalloproteins and metalloenzymes (24,25). Different kinds of metals have been employed in these complexes including Platinum, Gold, Vanadium, Iron, Cobalt, Tin, Copper and many others (8). Ligands play two prominent roles in complex formation. First, they act as electron pair donors to a single cation. The other important function of ligands is to act as bridging groups. The complex formation depends on the affinity of the metal ion towards the various ligands present and the relative concentrations thereof. Carboxylic pyridine and hydroxyl anthranilic acid structures provide selective and effective ligational site for metal ion binding through oxygen and nitrogen. Presence of carbonyl group, ring structure, -OH and C=N make ligands fascinating for tailoring the electron releasing and resonating ability on coordination with various metal ion at different pH conditions. The ligands have been chosen because of their ability to forming complex with metal ions (26).The transition metals are attraction for complex studies due to their high charge and tendency to exhibit large and variable coordination number. In case of ternary complexes two different type of ligands are coordinate to the central metal ion

II. EXPERIMENTAL

All chemicals used in this study were of AR grade obtained from BDH. Double distilled water was used for the preparation of solutions. The solution of transition metal nitrates were prepared and standardized by the oxalate method (47). Pyridine-2, 6-dicarboxylic acid was used and prepared in calculated volume of KOH. The solution of PDA, HBAA, KNO₃ and potassium hydrogen phthalate were prepared by direct weighing method and solution of KOH was prepared by standardization method. pH-metric titration were carried out by ELICO(LI-613) pH-meter fitted with a combined glass-calomel electrodes assembly having an accuracy of ± 0.01 pH unit. The instrument was standardized against potassium hydrogen phthalate solution (0.05M) for pH-4 and standard buffer tablets solution (pH-9). Each titration was repeated at least twice against 0.1 mole dm⁻³(KNO₃) and total volume (50ml) kept constant in the beginning of each titration.

III. RESULT AND DISCUSSION

The dissociation constants of PDA, HBAA were calculated by the method of Chaberck and Martel (48) and recorded in Table-1. The values were calculated from titration curves by the direct algebraic method for mono and dibasic ligands.

$$K = \frac{[H^+][a_{CA} + [H^+] - [OH^-]]}{CA - [a_{CA} + [H^+] - [OH^-]}}$$

$$K_1 = \frac{[H^+][a_{CA} + [H^+]]}{CA - [a_{CA} + [H^+]]} \quad \text{For mono basic ligand}$$

$$K_2 = \frac{[H^+](a-1)CA - [OH^-]}{CA - (a-1)CA - [OH^-]} \quad \text{For dibasic ligand}$$

Where K_1 and K_2 are the first and second dissociation constants, CA = Total concentration for ligands, a = number of moles of alkali added per mole of ligand.

The stability constants ($\log K_{MLL'}$) for ternary mixed ligand complexes were calculated as suggested by Ramamoorthy and Santappa (49) for simultaneous complexation of ligand to the metal ion. The stability constants for the ternary system were calculated by the following expression

$$(K_{MLL'}) = \frac{T_M - \frac{1}{2}[A]X}{\left(\frac{1}{2}\right)^3 [A]^3 X}$$

$$A = \frac{3T_M - T_{OH} - [H^+]}{\frac{2[H^+]}{K_1 + K'_2} + \frac{2[H^+]^2}{K_1 K'_2}}$$

Where,

$$X = 1 + \frac{2[H^+]}{K_1 + K'_2} + \frac{[H^+]^2}{K_1 \cdot K'_2}$$

Where T_M = Total metal ion concentration; K_1 and K_2 = the first and second dissociation constants of ligand (L'); K_1 = the dissociation constant of the ligand (L)

The calculated values of stability constants are summarised in Table-2. The relative order of stability has been

found as $Ni(II) > Cu(II) > Co(II) > Zn(II)$. It can be correlated in terms of increasing ionic potential (ϕ) of the metal ion (50). It was reported that (51) the stability of ternary complexes depends on several factors such as a double bond present in a ligand increases stability of the complex due to exocyclic conjugation, the OH group present in the ligand increases stability due to electron withdrawing nature, if the ring form is bigger, the stability will be low.

The average ($\log K_{MLL'}$) values were used to calculate the free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) from the Van't Hoff's isotherm., The values of free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) change of the resulting ternary complexes are shown in the table-3, the calculated ΔG^0 has been found to be negative in all the systems indicating spontaneity of the complex formation. Calculated positive values of entropy (ΔS^0) indicate the formation of ternary complexes in the solution. The negative enthalpy (ΔH^0) values indicate the exothermic nature of the reaction.

IV. CONCLUSION

On the basis of above study the stability of various ternary complexes has been found in the following order $Ni(II) > Cu(II) > Co(II) > Zn(II)$. The observed order of stability of complexes may be correlated in terms of increasing polarisability of metal ion due to their decrease in size and increase in ionic potential (ϕ).

TABLE: 1 Dissociation Constants of PDA and HBAA at experimental temperatures

Ligand	PK ₁		PK ₂	
	298.15K	313.15K	298.15K	313.15K
PDA	2.57	2.63	4.33	4.38
HBAA	4.37	4.77	8.36	8.45

TABLE:2 Stability Constants for M(II)-PDA-HBAA, Ternary System [$\mu=0.1 \text{ mol dm}^{-3}(\text{KNO}_3)$, $\text{KOH}=0.1\text{M}$] at temperatures 298.15 and 313.15K

S.No.	m	Cu(II)-PDA-HBAA		Ni(II)-PDA-HBAA		Zn(II)-PDA-HBAA		Co(II)-PDA-HBAA	
		298.15K	313.15K	298.15K	313.15K	298.15K	313.15K	298.15K	313.15K
1	0.2	11.92	11.65	12.05	11.92	11.11	11.03	11.13	11.05
2	0.3	11.63	11.56	11.68	11.63	10.74	10.74	10.77	10.69
3	0.4	11.51	11.35	11.47	11.42	10.53	10.53	10.56	10.48
4	0.5	11.42	11.12	11.24	11.19	10.30	10.30	10.33	10.25
5	0.6	11.21	10.89	11.02	10.97	10.08	10.08	10.11	10.03
6	0.7	10.97	10.81	10.93	10.88	9.99	9.99	10.02	9.98

TABLE: 3 Free energy (ΔG^0), Enthalpy (ΔH^0) and Entropy (ΔS^0) changes of ternary complexes [$\mu=0.1 \text{ moldm}^{-3}(\text{KNO}_3)$] at temperatures 298.15 and 313.15K

S.No.	Systems, 1:1:1	Mean Value $\log K_{MLL'}$		- ΔH (k.cal/Mole)	- ΔG (k.cal/Mole)		+ ΔS (Cal/Mole/degree)	
		298.15K	313.15K		298.15K	313.15K	298.15K	313.15K
1	Cu(II)-PDA-	10.82	10.61	5.97	14.75	15.19	29.46	29.45

	HBAA							
2	Ni(II)- PDA- HBAA	10.87	10.82	1.42	14.82	15.49	44.96	44.95
3	Zn(II)- PDA- HBAA	9.94	9.83	3.13	13.55	14.07	34.96	34.95
4	Co(II)- PDA- HBAA	9.97	9.89	2.56	13.59	14.16	37.01	37.06

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