



# POTENTIOMETRIC STUDIES OF SOME MIXED LIGAND TRANSITION METAL TERNARY COMPLEXES WITH PYRIDINE DICARBOXYLIC ACID AS PRIMARY AND 3-NICOTINIC ACID AS SECONDARY LIGAND

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**Abstract:** The stability complexes of Pyridine dicarboxylic acid and Nicotinic acid with transition metal ions Cu<sup>(II)</sup>, Ni<sup>(II)</sup>, Zn<sup>(II)</sup> and Co<sup>(II)</sup> were determined pH metrically at temperature 25<sup>o</sup>C and 40<sup>o</sup>C at an ionic strength 0.1 mole dm<sup>-3</sup> KNO<sub>3</sub>. The stability constant for ternary complex were calculated. The thermodynamic parameters free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were also calculated using the average stability constants.

**Index Terms:** Stability Constant, Ternary Complexes, Transition Metals.

## INTRODUCTION:

The formation of ternary complexes primarily depends upon the availability of two bonding electrons of the ligands the vacant d-orbitals and ionic radius of the metal ion. Thus, on the nature of the metal ligand bond i.e., Pi ( $\pi$ ) and Sigma ( $\sigma$ ) bond, the possibility of coordination of the secondary ligand with the metal primary ligand complex is there only if enough space is available with the metal ion to accept the lone pairs of electrons from secondary ligand. The probability of formation of the ternary species is therefore enhanced because the de-stabilization caused by the ligand-ligand repulsion is much less in the ternary species rather than in the parent binary complexes. In case of ternary complexes two different types of ligands are co-ordinate to the central metal ion respectively<sup>1-2</sup>. On the other hand, if metal of d-electrons interacts with vacant ligand orbitals forming a Pi ( $\pi$ ) bond occurs lowering of electronic concentration near the central metal ion takes place. The formation of the ternary species takes place if both the ligands have either Sigma ( $\sigma$ ) or Pi ( $\pi$ ) bonding. The tendency of  $\pi$ -bonding ligand results in the formation of less stable ternary complexes. A significant amount of study of the formation stabilities and their activities of mixed ligand complexes has been adapted by many research workers<sup>3-8</sup>. The formation of metal chelates with nitrogen containing ligands have been found more biologically active<sup>9-11</sup>. It has been found that the other important function of ligands is to act as bridging groups. It has found that their corresponding metal chelates leads very active against some gram-positive, gram-negative bacteria and in different fungi. The transition metals are attraction of complex studies due to their high charge and tendency to exhibit large and variable coordination numbers. In huge progress in the coordination chemistry of metals has taken on account of the wide application of metal complexes almost every sphere of chemistry generally in analytical, pharmaceutical, clinical, biological, toxicological and industrial particular<sup>12-17</sup>. Recently there has been considerable interest in the study of binary, ternary and quaternary metal complexes by pH metric method<sup>18-19</sup>. The coordination chemistry of metal ions of aqueous solution has been subjected to numerous investigations. This field is still being explored focusing on the influence of the presence of donor atoms in the complexation behaviour and stability. Hence investigation on stability of mixed ligand complexes is increasingly becoming more important and will give an idea about the role of metal ions in biological system.

The Metal complexes can be used as therapeutic drugs to treat human disease, a study stated that Nicotinic acid may also act as a neutral ligand ligating the metal ion through its "N" atom<sup>20-21</sup>. The interaction of cobalt, zinc, nickel, copper with Nicotinic acid and Pyridine dicarboxylic acid has been studied by the pH metric technique at 0.1 mole. dm<sup>-3</sup> (KNO<sub>3</sub>) ionic strength at 298.15 K and 313.15 K. The changes in thermodynamic parameters ( $\Delta G^0$ ,  $\Delta H^0$ ,  $\Delta S^0$ ) have also been calculated under the same conditions. The wide spread studies reported up to now on complexation between biologically important trivalent and divalent metal ions and biological oxygen/nitrogen donor ligands Nicotinic acid in solution mainly aimed at unfolding the role of metal ligands equilibria in the proceeding of metabolic reactions. They have possible application in medicine if these therapeutic bio-ligands and other ligands are combined in one compound. There are various papers appeared in last few decades regarding ternary complexes of transition and non-transition metals<sup>22-29</sup>.

The present study deals with the systematic pH metric study on the formation and stability of mixed ligand complexes of Ni Cu, Zn, Co with Pyridine dicarboxylic acid (PDA) and Nicotinic acid (NICO) as ligand.

### EXPERIMENTAL:

All the reagents used were of AR, BDH grade. The solution of all the chemicals were prepared in doubly distilled water. The solution of transition metal nitrates was prepared and standardized by the oxalic acid<sup>30</sup>. PDA was used in its mono protonated form and prepared in calculated volume of KOH. The solution of NICO, KNO<sub>3</sub> and potassium hydrogen phthalate were prepared by direct weighing method and solution of KOH was prepared by standardization method.

pH-metric titration was carried out by ELICO (LI-613) pH-meter fitted with a combined glass calomel electrodes assembly, used for entire pH, range (0 to 14) having an accuracy of  $\pm 0.01$  pH unit. The instrument was standardized against potassium hydrogen phthalate solution (0.05 M) for pH-4 and standard buffer tablets solution (pH-9). Each titration was repeated at least twice against (0.1 M) KOH solution at temp.  $25 \pm 1^\circ\text{C}$  and  $40 \pm 1^\circ\text{C}$  to ensure the reproducibility of result, keeping the ionic strength at 0.1 mole  $\text{dm}^{-3}$  (KNO<sub>3</sub>) and total volume (50 ml) constant in the beginning of each titration.

### RESULTS AND DISCUSSION:

The dissociation constants (Table-1) of PDA and NICO were calculated by the method of Chaberck and Martell<sup>31</sup>. The values were calculated from titration curves by the direct algebraic method for mono and dibasic ligands.

For mono basic ligands

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

For dibasic ligands

$$K_1 = \frac{[H^+][a_{CA} + [H^+]]}{C_A - [a_{CA} + [H^+]}}$$

$$K_2 = \frac{[H^+][(a-1)C_A - [OH^-]]}{C_A - [(a-1)C_A - [OH^-]}}$$

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

The stability constants ( $\log K_{MLL'}$ ) for ternary mixed ligand complexes were calculated by method. Remamoorthy and Santappa<sup>32</sup> for simultaneous complication of ligand to the metal ion. The stability constants for the ternary system were calculated in the following expression.

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

Where

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

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

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 average ( $\log K_{MLL'}$ ) values were used to calculate the free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) from the van't Hoff's isotherm using following relations-  
The free energy of formation

$$\Delta G^\circ = -RT \log K_{MLL'}$$

Where  $K$  is the formation constant of the mixed ligand species.  $T$  is the absolute temperature and  $R$  is the gas constant ( $R=1.987$  cal/mol/deg)

The value of change in enthalpy

$$\Delta H = \frac{2.303 RT_1 T_2 (\log \beta_2 - \log \beta_1)}{T_2 - T_1}$$

Where  $\beta_1$  and  $\beta_2$  are the stability constants at temperature  $T_1$  and  $T_2$  respectively.

The change in entropy can be calculated with the help of Gibb's Helmholtz equation-

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

The calculated values are tabulated in table 2.

**Table – 1: Dissociation Constants of PDA and NICO**

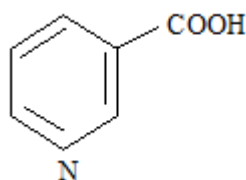
Ligand	PK <sub>1</sub>		PK <sub>2</sub>	
	25±1°C	40±1°C	25±1°C	40±1°C
PDA	2.57	2.63	4.33	4.38
NICO	2.73	2.79	4.72	4.87

All the systems under study were potentiometrically titrated against 0.1M KOH solution at two different temp. viz.  $25 \pm 1^\circ\text{C}$  and  $40 \pm 1^\circ\text{C}$  keeping ionic strength  $m = 0.1$  M KNO<sub>3</sub> The measured pH values were plotted against the moles ( $m$ ) of base (KOH) added per mole metal ion or ligands as depicted in the figs. 1, 2, 3 and 4 being the representative curves for transition metals and ligands in the systems 1:1:1 M<sup>(II)</sup>-L-L' where M<sup>(II)</sup> = Cu<sup>(II)</sup>, Ni<sup>(II)</sup>, Zn<sup>(II)</sup> and Co<sup>(II)</sup>, L' = PDA, L' = NICO.

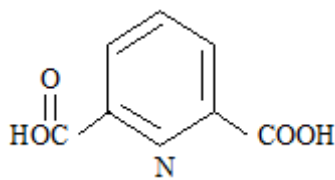
Concentration - Cu<sup>(II)</sup>/Ni<sup>(II)</sup>/Zn<sup>(II)</sup>/Co<sup>(II)</sup> = PDA = NICO =  $5 \times 10^{-3}$ M

**Table – 2: The Stability constants, free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of ternary system**

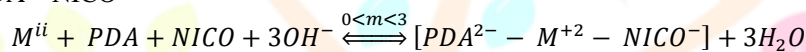
System		Property 25±1°C metal ion			
		Log K <sub>MLL</sub> '	- $\Delta G^\circ$ kcal/mole	- $\Delta H^\circ$ kcal/mole	+ $\Delta S^\circ$ Cal/mole/degree
M <sup>II</sup>	Cu <sup>II</sup>	12.17	16.59	8.54	23.02
PDA	Ni <sup>II</sup>	11.63	15.86	6.26	32.21
NICO	Zn <sup>II</sup>	11.19	15.26	8.25	23.52
	Co <sup>II</sup>	11.71	15.96	6.54	31.61
System		Property 40±1°C metal ion			
		Log K <sub>MLL</sub> '	- $\Delta G^\circ$ kcal/mole	- $\Delta H^\circ$ kcal/mole	+ $\Delta S^\circ$ Cal/mole/degree
M <sup>II</sup>	Cu <sup>II</sup>	11.87	17.00	8.54	27.02
PDA	Ni <sup>II</sup>	12.41	16.34	6.26	32.20
NICO	Zn <sup>II</sup>	10.90	15.61	8.25	23.51
	Co <sup>II</sup>	11.48	16.44	6.54	31.62



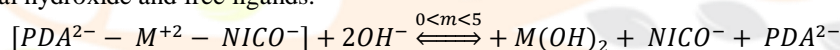
3-Nicotinic acid (NICO)

System 1:1:1 M<sup>(II)</sup> – PDA – NICO

Pyridine di-carboxylic acid (PDA)



The observed inflection on the curve 'f' at m = 5 may probably be attributed to the decomposition of previously formed 1:1:1, ternary complex into metal hydroxide and free ligands.



The simultaneous formation of ternary species may be further supported by the following facts.

1. Non-appearance of any solid phase during the formation of ternary species.
2. Constancy observed in the calculated values of formation constants.

It can be correlated in terms of increasing ionic potential ( $\phi$ ) of the metal ion<sup>33</sup>. The values of free energy change ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of the resulting ternary complexes are recorded in table-2. The calculated  $\Delta G^\circ$  has been found to be negative in all the systems indicating the spontaneity of the complex formation. Calculated positive values of entropy ( $\Delta S^\circ$ ) indicates the formation of ternary complexes in the solution. The negative enthalpy ( $\Delta H^\circ$ ) values indicate the exothermic nature of the reaction.

## CONCLUSION:

On the basis of above study the stability of various ternary complexes have been found in the order Cu<sup>(II)</sup>>Ni<sup>(II)</sup>>Zn<sup>(II)</sup>>Co<sup>(II)</sup>. 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 increasing ionic potential ( $\phi$ ) = change/radius ratio.

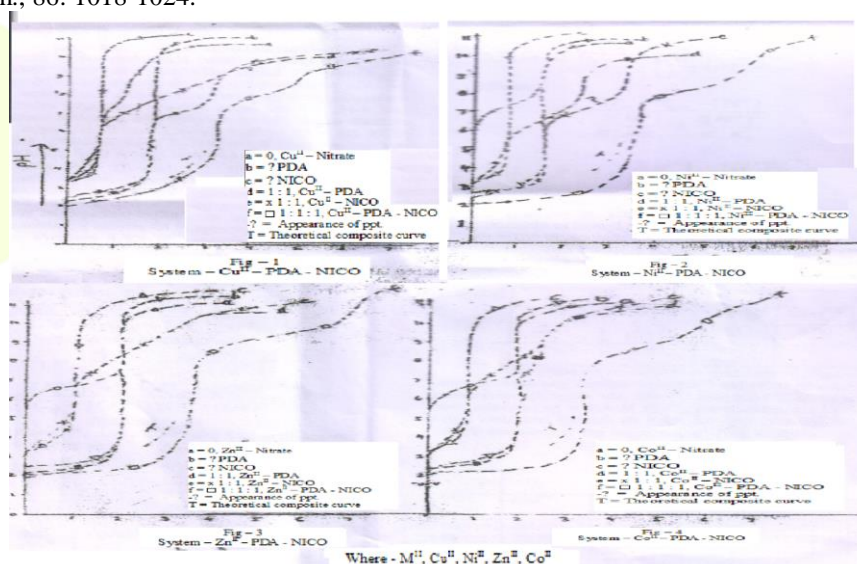
M<sup>(II)</sup> = Cu<sup>(II)</sup>, Ni<sup>(II)</sup>, Zn<sup>(II)</sup> and Co<sup>(II)</sup>

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**Fig. 1, 2, 3 and 4:** Plot of measured pH values for transition metals and ligands in the systems 1:1:1  $M^{(II)}-L-L'$  where  $M^{(II)} = Cu^{(II)}, Ni^{(II)}, Zn^{(II)}$  and  $Co^{(II)}$ ,  $L' = PDA$ ,  $L = NICO$ .