CONDUCTOMETRIC AND THERMODYNAMIC STUDIES OF TERNARY COMPLEXES OF SOME TRANSITION METAL COMPLEXES WITH IMINO DIACETIC ACID AND 2- PICONOLIC 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 potentiomet rically in aqueous solution of Imino diacetic acid and 2-Piconolic acid at 298.15 k and 313.15 k. The ionic strength of 0.1 mol dm^{-3} was kept constant using KNO_3. The stability constant of these 1:1:1 ternary complexes have been evaluated by the computational methods. The relative order of stability has been observed in accordance with the increasing $\phi=$ charge/radius ratio. The changes in the thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) have also been calculated under the same conditions.

Keywords: *Potentiometrically, Thermodynamic Parameters.*

Introduction :

Coordination chemistry of mixed ligand complexes is one of the most dynamic and devastated research fields in inorganic chemistry. In a huge progress in the coordination chemistry of metals has taken on account of the wide application of metal complexes almost every sphere of chemistry in general, analytical, Pharmaceutical, biological, toxicological and industrial [1,2].

The formation of metal chelates with nitrogen containing ligands have been found more biologically active[3-5], such as 2-Piconolic acid and Imino diacetic acid etc are act as potential drugs. They have been widely used as primary ligand in the study of variety of mixed ligand complexes[6-7] it has been found that, their corresponding metal chelates leads are very active against some gram positive and gram negative bacteria and in different fungi.

Ligands play two important roles in complex formation first they act as electron pair donors to single cation. The important function of ligands is to act as bridging groups. The

complex formation depends upon the affinity of the metal ion towards the various ligands present and relative concentration thereof. The ligands have been chosen because of their ability to forming complex with metal ion[8]. The transition metals are attraction for complex studies due to their high charge and tendency to exhibit large and variable coordination number. It is an important characteristic of the transition elements to form numerous co-ordination compounds, in sharp contrast to the s- and p-block elements. They have small, highly charged ions and vacant-d or f-orbitals of appropriate energy to accept lone pairs of e-denoted by other groups or ligands. In case of ternary complexes two different types of ligands are co-ordinate to the central metal ion respectively[9, 10]. The study of the formation of stability and reactivities of mixed ligand complexes have been adopted by many research workers[11, 12]. Recently there has been considerable interest in the study of binary ternary and quarternary complexes by pH metric method[13-16]. In the present study mixed ligand complexes of some transition metal Cu^{II}, Ni^{II}, Zn^{II}, and Co^{II} have been investigated potentiometrically with Imino diacetic acid (IMDA) and 2-Piconolic acid (PICO) in aqueous solution at 298.15k and 313.15k. The change in thermodynamic parameters ΔG^0, ΔS^0, ΔH^0 have also been calculated under the same condition. Sharma and Tondon[17] Kiranmaik, Prashanthiy, Subhashini NJP and Shivraj[18], and Valechas and Mangonkark, have studied on the ternary systems. There are various papers appeared in last few decades regarding ternary complexes of transition and non transition metals[19-28].

Material and Methods:

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 were prepared and standardized by the oxalic acid[29]. IMDA was used in its monoprotonated form and prepared in calculated volume of KOH. The solution of PICO, KNO_3 and potassium hydrogen phathalate 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, used for entire pH, range (0 to 14) having an accuracy of ±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 ± 1^0C and 40 ± 1^0C to ensure the reproducibility of result, keeping the ionic strength at 0.1 mole dm^{-3} (KNO_3) and total volume (50 ml) constant in the beginning of each titration. 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 $M^{(II)}$ –L-L' where $M^{(II)}$ = $Cu^{(II)}$, $Ni^{(II)}$, $Zn^{(II)}$ and $Co^{(II)}$, L-=IMDA, L' = PICO.

The dissociation constants (Table-1) of IMDA and PICO were calculated by the method of **Chaberck** and **Martell**[30]. The values were calculated from titration curves by the direct algebraic method for mono and dibasic ligands.

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

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

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

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 of ligand.

The stability constants (log $K_{MLL'}$) for ternary mixed ligand complexes were calculated by method of **Ramamoorthy** and **Santappa**[31] for simultaneous complexation of ligand to the metal ion. The stability constants for the ternary system were calculated by the following expression.

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

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 (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) from the van't Hoff's isotherm. The data are tabulated in table 2.

Table – 1

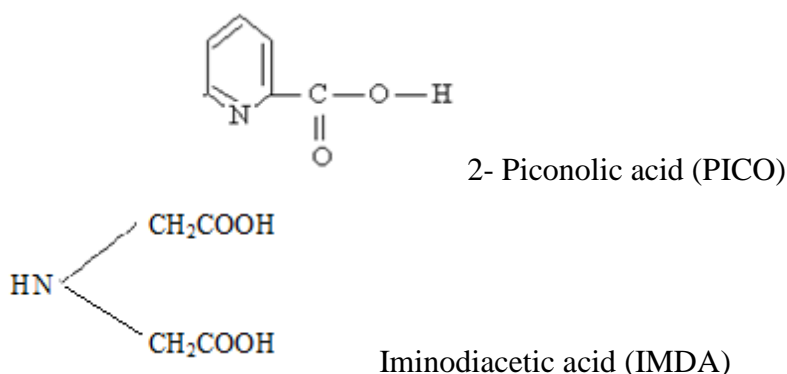| Ligand	PK$_1$		PK$_2$	
	25±1^{0}C	**40±1^{0}C**	**25±1^{0}C**	**40±1^{0}C**
IMDA	2.77	3.10	8.70	8.50
PICO	5.26	5.34	-	-

Table – 2

The systems of section A and section B were potentiometrically titrated against 0.1M KOH solution at two different temp. viz. 25±1^{0}C and 40±1^{0}C keeping ionic strength m = 0.1 M KNO$_3$ concentration of the metal ions and ligands (5 x 10^{-3}M) and total volume (50 ml) constant at the beginning of each titration.

System	Property 25±1^{0}C metal ion				25±1^{0}C metal ion			
	log K$_{MLL'}$	**-ΔG^0 K.C/M**	**-ΔH^0 K.C/M**	**+ΔS^0**	**Cu$^{(II)}$**	**Ni$^{(II)}$**	**Zn$^{(II)}$**	**Co$^{(II)}$**
M$^{(II)}$- Cu^{II}	20.11	27.42	6.54	70.05	20.70	18.16	18.04	17.63
IMDA Ni^{II}	18.69	25.49	5.97	65.48	20.30	18.66	18.30	17.62
PICO Zn^{II}	18.07	24.64	4.84	66.46	20.80	18.11	18.10	17.67
Co^{II}	17.60	24.00	8.53	54.63	20.12	18.74	18.08	17.65
System	Property 40±1^{0}C metal ion				40±1^{0}C metal ion			
	log K$_{MLL'}$	**-ΔG^0 K.C/M**	**-ΔH^0 K.C/M**	**+ΔS^0**	**Cu$^{(II)}$**	**Ni$^{(II)}$**	**Zn$^{(II)}$**	**Co$^{(II)}$**
M$^{(II)}$- Cu^{II}	19.88	28.47	-	70.05	19.95	18.64	17.93	18.07
IMDA Ni^{II}	18.48	26.47	-	65.47	19.90	18.62	17.95	18.05
PICO Zn^{II}	17.90	25.46	-	66.46	19.88	18.60	17.94	18.03
Co^{II}	17.90	25.63	-	54.63	19.86	18.49	17.89	17.98

Results and Discussion:

2- Piconolic acid (PICO)

Iminodiacetic acid (IMDA)

Section A-

Curve f (fig. 1 to 4) indicating the pH metric titration of 1:1:1 $M^{(II)}$ – IMDA – PICO ternary system[1:1:1 $M^{(II)}$ – IMDA – PICO; $M^{(II)}$ = $Cu^{(II)}$, $Ni^{(II)}$, $Zn^{(II)}$ and $Co^{(II)}$]. The initial lowering of pH in this curve with comparison of curve d and e-(1:1, $M^{(II)}$ – IMDA), [1:1, M^{II} - PICO] followed by an inflection at m ≈ 3 may be explained to the simultaneous addition of both the ligands to the metal ions forming 1:1:1 ternary complexes in solution.

$$M^{II} + IMDA + PICO + 3OH^- \overset{0<m<3}{\rightleftharpoons} [IMDA^{2-} - M^{+2} - PICO^-] + 3H_2O$$

One more inflection on this 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.

$$[IMDA^{2-} - M^{+2} - PICO^-] + 2OH^- \overset{0<m<5}{\rightleftharpoons} M(OH)_2 + PICO^- + IMDA^{2-}$$

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 (ϕ) of the metal ion[32]. The values of free energy change (ΔG^0), enthalphy (ΔH^0) and entropy (ΔS^0) of the resulting ternary complexes are recorded in table-2. The calculated ΔG^0 has been found to be negative in all the systems indicating the spontaneity of the complex formation. Computed 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.
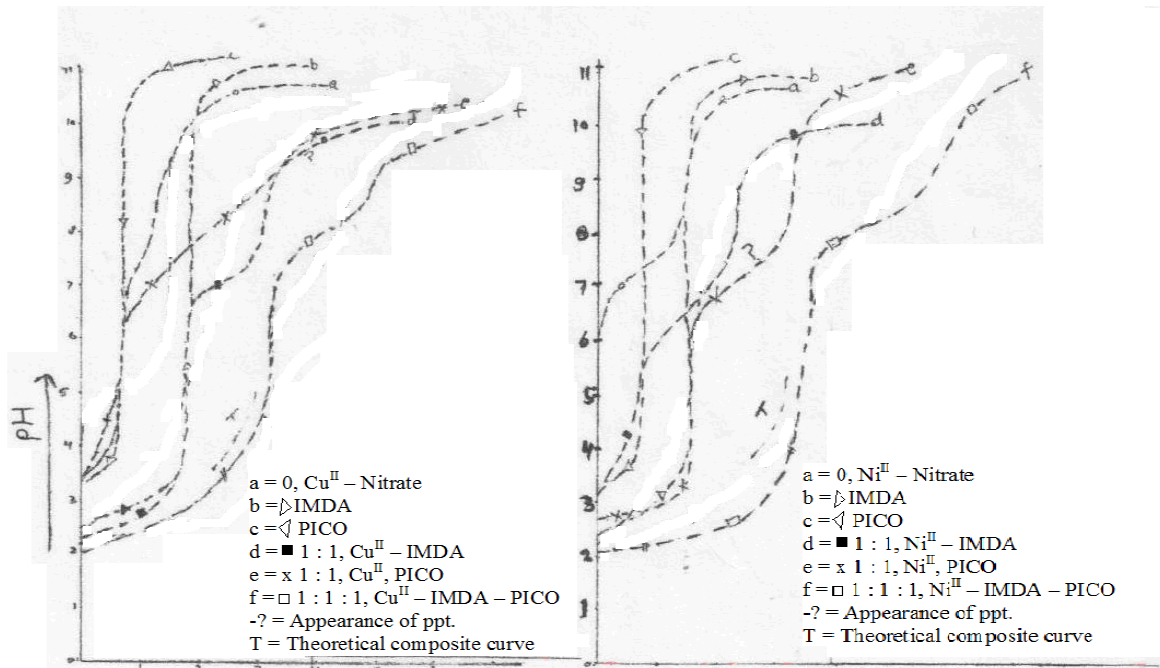
Conclusion :

On the basis of above study the stability of various ternary complexes have been found in the order $Cu^{(II)} > Co^{(II)} > Zn^{(II)} > Ni^{(II)}$. 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 increasing ionic potential (ϕ) = change/radius ratio.
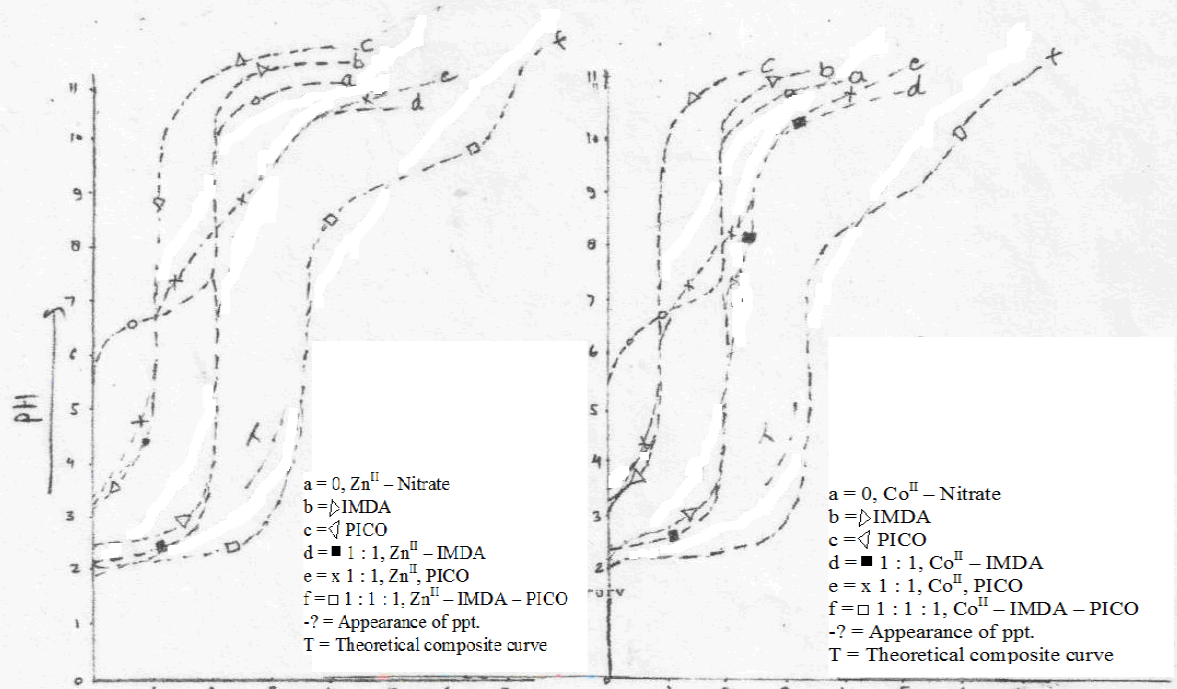
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a = 0, Cu^{II} – Nitrate
b =▷ IMDA
c =◁ PICO
d = ■ 1 : 1, Cu^{II} – IMDA
e = x 1 : 1, Cu^{II}, PICO
f = □ 1 : 1 : 1, Cu^{II} – IMDA – PICO
-? = Appearance of ppt.
T = Theoretical composite curve

Fig - 1
System - Cu^{II}-IMDA-PICO

a = 0, Ni^{II} – Nitrate
b =▷ IMDA
c =◁ PICO
d = ■ 1 : 1, Ni^{II} – IMDA
e = x 1 : 1, Ni^{II}, PICO
f = □ 1 : 1 : 1, Ni^{II} – IMDA – PICO
-? = Appearance of ppt.
T = Theoretical composite curve

Fig - 2
System - Ni^{II}-IMDA-PICO

a = 0, Zn^{II} – Nitrate
b =▷ IMDA
c =◁ PICO
d = ■ 1 : 1, Zn^{II} – IMDA
e = x 1 : 1, Zn^{II}, PICO
f = □ 1 : 1 : 1, Zn^{II} – IMDA – PICO
-? = Appearance of ppt.
T = Theoretical composite curve

Fig – 3
System - Zn^{II}-IMDA-PICO

a = 0, Co^{II} – Nitrate
b =▷ IMDA
c =◁ PICO
d = ■ 1 : 1, Co^{II} – IMDA
e = x 1 : 1, Co^{II}, PICO
f = □ 1 : 1 : 1, Co^{II} – IMDA – PICO
-? = Appearance of ppt.
T = Theoretical composite curve

Fig – 4
System - Co^{II}-IMDA-PICO

Where - M^{II}, Cu^{II}, Ni^{II}, Zn^{II}, Co^{II}