



pH-Metric Study of Picolinic Acid with Ni(II), AND Zn(II) Metal Ions

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Abstract : pH-Metric measurements of picolinic acid were studied with Ni(II) and Zn(II) metal ions at 0.2 M ionic strength in water by Irving–Rossotti titration technique for determination of stability constants. 1:1 complexes were formed in present investigation in between picolinic acid (PA) and Ni(II) and Zn(II) metal ions. Values of proton-ligand stability constant (pK) and metal-ligand stability constants log k were evaluated and compared from resultant data.

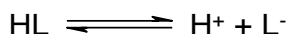
Keywords : Picolinic acid (PA), stability constant, pH-metric measurements.

Introduction

Determination of anatomical, physiological and pharmacological activities of any molecule is essential for knowing its significances and application in medicinal, pharmaceutical agricultural and industrial sciences. One of the important property in these studies is to establish drug activity drug effect, transmission of drug and absorption of drug all these four factors are directly depend stability of the molecule. The stability of molecules during this study can be easily determined from the values of stability constants. The formation of complex can also be determined from these values, hence pH-metric investigation have various significances in life, medicinal and pharmaceutical, agricultural and industrial sciences. Picolinic acid has been reported to possess various effects [1-5]. Potency of drugs can be increased activity in metal complexes and study of metal and nitrogen and sulphur atoms containing ligands have been reported [6-7]. Stability constant of mixed ions was also studied [8]. Proton-ligand and metal-ligand stability constants of Cu(II)-salicylic acid [9], Mn(II), Cu(II), Fe(III), Ni(II) with maleic [11], transition metal ions with 3-amino-5-methyl isoxazole [12] and lanthanide metal ions-pyrazoles [13] were determined. Binary, ternary and quaternary complexes were studied by pH-metric method [14]. Hence, stability constant of complexes formed by interactions of picolinic acid were studied with Ni(II) and Zn(II) metal ions at 0.2 M ionic strength pH-metrically in water.

Materials and Method

Picolinic acid (PA) was gifted from pharmacy department of our college. Nitrates of Ni(II) and Zn(II) were taken. Stock solution of picolinic acid was prepared in water and treated as ligand solution. Titrations of (i) free acid (0.01 M), (ii) free acid (0.01 M) and ligand (20×10^{-4} M) and (iii) free acid (0.01 M), ligand (20×10^{-4}) and metal ion (4×10^{-4} M) against standard 0.1N NaOH solution were carried out. Ionic strength of all the solutions was maintained constant by adding appropriate amount of 2 M solution KNO_3 . All the titrations were carried out in water and readings were recorded for each 0.2 ml addition. Graph of volume of alkali added against pH were plotted. Ligands used in this work is monobasic acid having only one dissociable H^+ ion from phenolic-OH group and it can therefore, be represented as HL. Dissociating equilibrium can be shown as,



By the law of mass action, we have,

$$K = \frac{[HL]}{([H^+][L^-])} \text{----- (1)}$$

Where, quantities in bracket denote activities of species at equilibrium.

Results and Discussion

Calculation of Proton-Ligand Stability Constant i.e. (\bar{n}_A)

Plots between volume of NaOH and pH of the solution were used to determine the proton ligand stability constant. Horizontal difference ($V_2 - V_1$) was measured accurately between titration curves of free acid and acid+ligand. It was used to calculate formation number \bar{n}_A at various pH values and fixed ionic strength $\mu = 0.2$ M using equation 2.

$$\bar{n}_A = \gamma - \left\{ \frac{(V_2 - V_1) \cdot (N + E^0)}{(V^0 + V_1) T_L^0} \right\} \text{----- (2)}$$

Where, V^0 is the initial volume of the solution. E^0 and T_L^0 are initial concentrations of mineral acid and ligand respectively. V_1 and V_2 are volumes of alkali of normality N during acid and ligand titration at given pH. ' γ ' is replaceable proton from ligand. \bar{n}_A Values were determined at $32 (\pm 1)^\circ\text{C}$ in $E^0 = 1 \times 10^{-2}$ M, $T_L^0 = 20 \times 10^{-4}$ M, $V^0 = 50$ ml, $N = 0.2$ N respective ratios of solutions.

Data of \bar{n}_A obtained at various pH along with horizontal difference for some representative systems are represented in **Table 1**. Metal–ligand formation number (\bar{n}) was determined using equation 3.

$$\bar{n} = \frac{(V_3 - V_2) \times (N + E^0)}{(V^0 + V_2) T_M^0} \text{----- (3)}$$

Where, notations have same meaning as given in earlier equation. Horizontal difference ($V_3 - V_2$) between metal complex (A+M+L) and reagent (A+L) curve were used for determination of \bar{n} values. \bar{n}_A and \bar{n} values obtained during study are given in **Table-1**

Table-1

Sr.No.	\bar{n}_A Values		\bar{n} Values	
	PA-Ni(II)	PA-Zn(II)	PA-Ni(II)	PA-Zn(II)
1	0.5847	0.5984	0.8347	1.2143
2	0.5472	0.5672	1.6483	1.3417
3	0.5164	0.5328	1.7942	1.3719
4	0.3893	0.4972	1.8631	1.9421
5	0.3672	0.4517	2.1673	2.2683
6	0.1849	0.2643	2.2648	2.3273

Proton-ligand stability constants (pK) were determined by half integral method as well as point wise calculation methods and it was found to be 4.1 and 4.352 respectively. Metal-ligand stability constant (log K) are given in **Table-2**.

Table-2

System	Log K ₁	Log K ₂	Δ Log K
PA+Ni(II)	4.1331	2.5404	1.5927
PA+Zn(II)	4.3532	2.5291	1.8241

Conclusion

From the titration curves, it is observed that the departure between acid+ ligand (A+L) curve and acid+ligand+metal (A+L+M) curve for all systems started from pH = 4.5. This indicated the commencement of complex formation. Also change in color from colorless to purple in the pH range from 4.5 to 11 during titration showed the complex formation between metal and ligand. The order of pK values of ligand give attributed toward deprotonation of ligand having good activity to form the more stable complex. pK value of PA is good for stable complexation. Observation of **Table-2** showed that less difference between log K₁ and log K₂ values indicates the complex formation between metal ion and ligand occurring simultaneously. **Table-2** shows that 1:1 complexation in between to above metal ions and PA. The values of log K₁ and log K₂ decided the stability of complexes. For PA values of log K₁ and log K₂ is higher with Zn(II) complex than Ni(II). Zn(II) forms more stable complex with PA than Ni(II) metal ions.

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