
Research Article

Theme- *New horizons in chemical sciences.*

Guest Editor- *R.P. Pawar*

Studies of Stability Constants of 4-((3-(4-Chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)methyleneamino)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol with Co(II), Ni(II), Mn(II) and Zn(II) ions.

Ashvini Sonone¹, Mujahed Shaikh¹, Devendra Wagare², Ayesha Durrani*¹

¹Department of Chemistry, Dr. Rafiq Zakaria College for Women, Aurangabad-431001, Maharashtra, India.

²Department of Chemistry, Vivekanand College, Aurangabad-431001, Maharashtra, India.

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***Corresponding author E-mail address:** *drayeshanuzhat101@gmail.com*

ABSTRACT

pH-metry is one of the most successful techniques used for measurement of simultaneous equilibrium of transition metals. Binary complexes of transition metal ions Co(II), Mn(II), Ni(II) and Zn(II) with 4-((3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)methyleneamino)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol as a ligand studied by Calvin-Bjerrum titration technique modified by Irving and Rossotti. Stability constant were studied at $27 \pm 1^\circ\text{C}$. It observed that the transition metal ion forms the 1:1 complex with ligand.

KEYWORDS

pH-metry, Calvin-Bjerrum, Irving-Rossotti, stability constant.

1. INTRODUCTION

Heterocyclic compound shows diverse physical, biological and chemical properties. Since last few decades, Nitrogen containing heterocyclic compounds are attracted by researchers due to its pharmacological activities, also as propellants, explosives, and especially in chemotherapy, gravimetric estimation of silver, copper and lead[1-2]. Triazoles considered isosters of imidazole, where carbon atoms of imidazole are isosterically replaced by nitrogen. Due to various biological activities triazoles are attained good position in heterocyclic chemistry[3-4]. A metal complex of triazole derivatives plays a vital role in the production of pharmaceutical compounds that inhibits the growth of tumors and cancer cells in human. They are also useful to treat bacterial as well as viral infections [5-6]. Substituted 1,2,4-triazole moiety has been studied broadly as bridging ligands with transition metal(II) ions coordinating through their N₁ and N₂ atoms[7]. Potentiometric titration methods commonly adopted for investigating metal-ligand stability constant[8]. In present investigation the study of complex formation of divalent metal ions i.e. Mn(II), Co(II), Ni(II) and Zn(II) with 4-((3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)methyleneamino)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol as a ligand in 50% DMF-Ethanol mixture has been carried out pH-metrically at $27 \pm 1^\circ\text{C}$. Calvin-Bjerrum titration technique adopted for the determination of binary complexes.

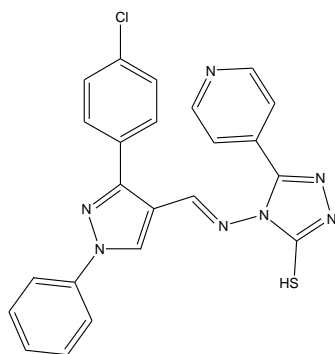


Fig. 1. Structure of binary complex.

Molecular Formula: $\text{C}_{23}\text{H}_{16}\text{ClN}_7\text{S}$; Molecular weight: 457.94 ; Melting Point: 185-187°C

2. MATERIALS AND METHODS

The double distilled water used for preparation of solutions. The water distilled in glass distillation assembly. pH of water obtained within 6.20-6.60.

Transition metals used in the form of their nitrates and chlorides to avoid the possibility of complex formation of metal ions with anion. The measurement carried out using ELICO 120 pH-meter with combined glass electrode. The pH-meter was calibrating using buffer solution of pH 4.01 and 9.18.

The method of Calvin-Bjerrum titration has used in present investigation for the determination of stability constant. The experimental procedure involved pH-metric titration of solutions of 0.2N

NaOH. The ionic strength of all solutions kept constant by addition of 1M NaClO₄ solution. Ligand and metal concentrations are 0.01N and HClO₄ 0.2N.

1. *Acid - HClO₄ (Perchloric acid) (A)*
2. *Acid + Ligand – (A+L)*
3. *Acid + Ligand + Metal ion - (A+R+M)*

The solution of complex titration prepared by three systems:

Acid titration(A) were carried out by using 0.2N HClO₄ solution and 1M NaClO₄ solution were titrated against 0.2N NaOH solution by using pH-meter and readings recorded until constant pH obtained.

Acid-Ligand titration(A+L) carried out by using the mixture of 0.2N HClO₄ and 1M NaClO₄ solution with 0.01N ligand solution were titrated against 0.2N NaOH solution by using pH-meter and readings recorded until constant pH obtained.

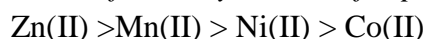
Acid-Ligand-Metal titration(A+L+M) carried out by using the mixture of 0.2N HClO₄ and 1M NaClO₄ solution, 10 ml 0.01N ligand solution and 10 ml of 0.01N transition metal solution were titrated against 0.2N NaOH solution by using pH-meter and readings recorded until constant pH obtained.

3. RESULTS AND DISCUSSION

The above all three pH titration values observed and graph plotted against the volume of alkali added. The acid, acid-Ligand, acid-ligand-metal titration curve for Ni(II), Co(II), Zn(II) and Mn(II) are shown in figure 2. The formation function \bar{n}_A evaluated by deviation between free acid titration curve and secondary ligand titration curve. The proton-ligand formation curve obtained by plotting \bar{n}_A Vs pH.

From titration curves, metal-ligand stability constant values were determined and represented in table 1.

Order of stability constant for present study is as follows,



There are three well-known series to shows the trends in stability constants.

Irving and William Order: Mn(II) < Co(II) < Ni(II) < Cu(II) < Zn(II)

Mellor and Mallay Order: Cu(II) > Ni(II) > Co(II) > Zn(II) > Mn(II)

Pfeiffer Order: Cu(II) > Ni(II) > Fe(II) > Zn(II) > Mn(II)

Table 1. Formation Constant of transition metal ions with Ligands 50% DMF-Ethanol mixture (Temp: 27±1°C).

Log K	Mn(II)	Co(II)	Ni(II)	Zn(II)
	2.91	2.66	2.71	3.27

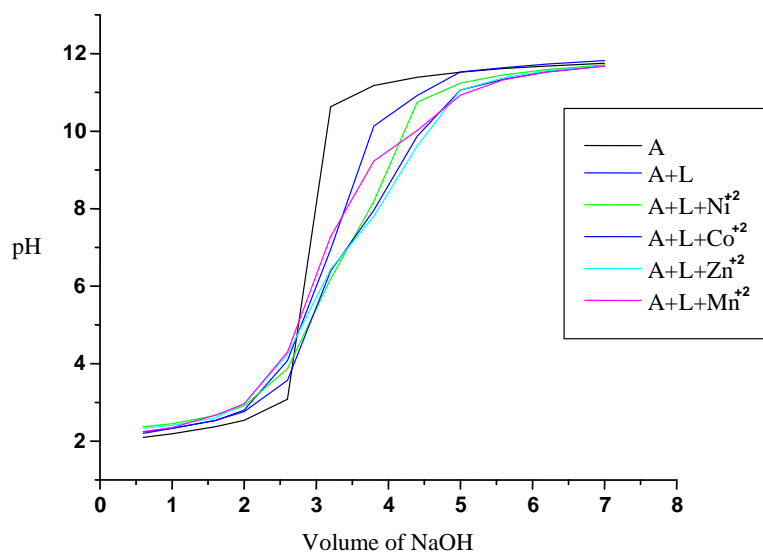


Fig. 2. pH-metric Titration Curve.

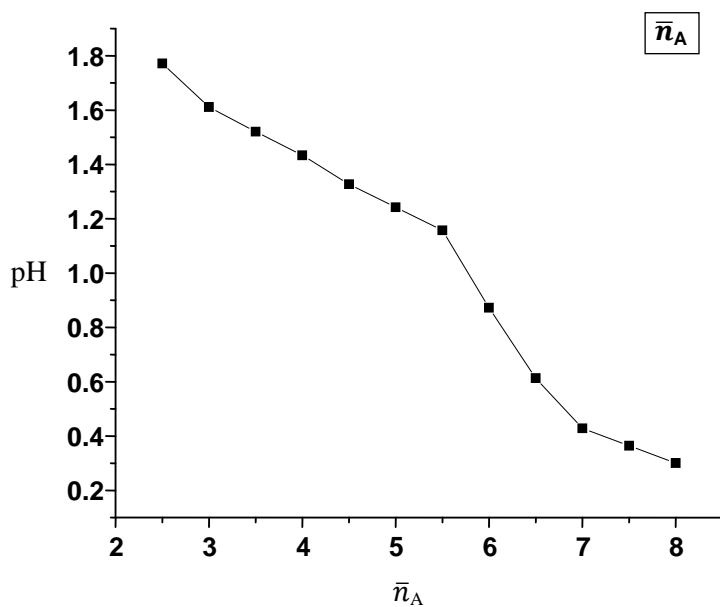


Fig. 2. Formation curve of \bar{n}_A against pH.

4. CONCLUSION

4-((3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)methyleneamino)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol were synthesized by conventional method and used as ligand with transition metal ions such as Mn(II), Co(II), Ni(II) and Zn(II) for complex formation. The change in color during the titration from yellow to milky white with Ni(II) and Zn(II), yellow to green with

Co(II), and yellow to brown with Mn(II) which indicating the formation of complex. Transition metal complex follows the order of stability constant is Zn(II) > Mn(II) > Ni(II) > Co(II).

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