Short Communication

Synthesis and stability constant of schiff's bases of triazole

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Abstract

Objective: Keen of interest to study the stability constant, so that, we developed the environmentally benign protocol for the synthesis of Schiff bases and determine the stability constant of these Schiff bases by the pH-metric method. **Materials and Methods:** Schiff bases were prepared by refluxing the mixture of pyrazole aldehyde and triazole in dry methanol 80-90°C and 3-4 drops of acetic acid added. **Results:** synthesized imine linkage generalizes the scope of reaction. The yield of Schiff bases is very high in dry methanol. **Conclusion:** The proton-ligand stability constant has calculated by using Calvin-Bjerrum titration technique. The observation from titration curve is shown that the deviation of (A+L) at pH range 2.5 to 3.0. (A+L+M) curves were deviated at pH range for Ni(II) is 3.6-4.0, Co(II) is 3.0-3.5, Zn(II) is 3.2-3.6 & Mn(II) is 3.6-3.8. The change in color observed that, yellow to white with Ni(II) and Zn(II), and yellow to brown in Co(II) and Mn(II), this indicates the formation of complex between Ligand and Metal.

***Keywords*:** Dry Methanol, reflux, triazole, stability constant, pH meter

Introduction

Schiff base named after Hugo Schiff. Schiff bases were form by condensation between aldehydes and amines. Schiff bases are containing C=N moiety which possess broad spectrum of biological activity and when they incorporated with metals in the form of metal-complexes then the degree of biological activity enhances. Schiff bases and amides derived from various heterocyclic compounds shows broad range of biological activities such as anticancer, antiviral, antimicrobial, anticonvulsant, antidepressant, angiotension-II receptor antagonist, anti-inflammatory and anti-glycation activity. So far, modifications of the Schiff bases have improved potency and toxicity decreased.

Schiff base and their metal complexes have been extensively studied due to their wide range of applications including catalysts (Cozzi et al., 2004; Gupta et al., 2008), anti-corrosion agent (Antonijevic et al., 2008; Ahamad et al., 2010) crystal engineering (Krishnamohan et al., 2002), medicine (Siji et al., 2011; Eswaran et al., 2009). Bidentate Schiff bases are the very well known for co-ordination with various metal ions and have been attracted a great deal of interest in recent days because of their rich co-ordination chemistry. Schiff bases of 2-amino- 4,6 dihydroxypyrimidine and P-chlorobenzaldehyde reported to have variety of applications including biological, and pharmacological activity (Eswaran et al., 2009; Bringmann et al., 2004; Souza et al., 2007; Isloor et al., 2009; Krishnara et al., 2008; Balsells et al., 1998; Türkkan et al., 2011), analytical and clinical fields (Nagajothi et al., 2012; Prashanthi et al., 2010; Gupta et al., 2012; Abraham et al., 2011).

The study of stability constant shows the complex formation between Metal-Ligand, while the study of Schwarzenback and Ackermann found that, as ring size increases the stability of chelates decreases (Durrani et al., 2011; Schwarzenbach et al., 1948).

Materials and Methods

Synthesis of Schiff bases

a) General procedure for the synthesis of Schiff bases of amide linkage [3a-3e]

Schiff bases were synthesis by refluxing pyrazole aldehyde 1.0 mmol and triazole 1.0 mmole in dry methanol by

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introducing 2-3 drops of acetic acid at 75-85°C temperature for 4-5 hours. Reaction monitored by TLC as soon as single spot obtained reaction mixture poured on crush ice and solid obtained were filtered and recrystalised (Table 1).

b) pH-metric determination of stability constant

All the chemicals were of AR grade used for the pH-metric titration. The solution of metal ions of Ni(II), Co(II), Mn(II) & Zn(II) and perchloric acid, sodium perchlorate, and NaOH were prepare in double distilled water. pH – measurements were carried out by ELICO LI 120 pH-meter standardized by using buffer solutions 4.01 and 9.18 pH. The titrations carried out at 27 ± 1. Procedure for binary system adopted is standard are shown as Acid Titration (A) were carried out by taking 5ml (0.2M) $HClO_4$ and 5ml (1.0M) $NaClO_4$ solution in 50ml standard flask and diluted upto the mark with the help of double distilled water. This was titrated against 0.2N NaOH.

Results and discussion

Our growing interest to find out stability constant of Schiff bases and enhance the yield of schiff bases, hence Initially we have design and developed the method for the synthesis of Schiff bases of triazole by refluxing the triazole with pyrazole aldehyde in dry methanol at 75-85°C temperature for 4-5 hours. In addition, the resultant product, we have found with very high yield. Hence, we have synthesis imine linkage, to generalize the scope of reaction. We have synthesis different derivatives and surprise the method is produced very high yield (Table 1).

^{1}H NMR of compound 3a shows characteristic singlet for SH attached to triazole ring at δ14.2 and for 1H, δ8.77 1H pyrazole ring proton, δ9.9- δ9.3 2H pyridine which is connected with triazole, δ8.5 2H pyridine which is connected with triazole. δ8.00- δ7.9 2H benzene ring having-Br group at Para position to pyrazole ring, δ7.3- δ7.5 2H benzene ring is attached at Nitrogen of pyrazole ring, δ7.46 1H benzene ring is attached at Nitrogen of pyrazole ring and the most important that shows the formation of Schiff base δ5.87 1H because of C=N in conjugated with pyrazole ring. The IR spectral data of the compound 3a shows prominent peaks at 1597 cm^{-1} for Schiff formation C, N, 3121 cm^{-1} for Pyridine C-H, 2361 cm^{-1} for S-H which is attached to pyridine ring. The above spectral information were confirmed the structure of the product 3a.

Table 1. Evaluation of compounds [3a-3e]

Compounds	R	Yield %	M.P. (°C)
3a	Br	93	163-165
3b	H	90	213-215
3c	Cl	92	185-187
3d	NO_2	94	205-207
3e	F	94	220-222

Characterization of synthesized compounds

4-((3-(4-bromophenyl)-1-phenyl-1H-pyrazol-4-yl) methyleneamino)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol (3a)

IR: (cm^{-1}): 3121 (C-H Pyridine), 1597 (C, N), 2361 (S,H).

Table 2. Determination of proton-Ligand stability constant (3b)

pH	V_1	V_2	(V_2-V_1)	$\bar{n}_A$
3	2.5328	1.896	-0.6368	2.212195
3.5	2.7218	2.3568	-0.365	1.692313
4	2.8079	2.7475	-0.0604	1.114377
4.5	2.8237	2.9845	0.1608	0.695591
5	2.8395	3.124338	0.284838	0.460937
5.5	2.8553	3.227852	0.372552	0.295147
6	2.8711	3.291152	0.420052	0.205517
6.5	2.8869	3.354452	0.467552	0.11594
7	2.9027	3.41162	0.50892	0.038008
7.5	2.9185	3.45312	0.53462	-0.01027
8	2.9343	3.49462	0.56032	-0.05852
8.5	2.9501	3.53612	0.58602	-0.10674
9	2.9659	3.57762	0.61172	-0.15493
9.5	2.9817	3.66141	0.67971	-0.28291
10	2.9975	3.79491	0.79741	-0.50462
10.5	3.15246	4.314288	1.161828	-1.18584
11	3.496	5	1.504	-1.81143
11.5	4.92	6.6	1.68	-2.05899
12	14.6	14.4	-0.2	1.309598

NMR: δ8.77 (1H, Pyrazol ring), δ14.2 (1H, Triazole –SH), δ8.00- δ7.46 (5H benzene-P-Br), δ9.9- δ8.5 (4H, pyridine), δ5.87 (1H Schiff base).

4-((3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl) methyleneamino)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol (3d)

IR: (cm^{-1}): 3120 (C-H Pyridine), 1590 (C, N), 2360 (S, H).

^{1}H NMR: δ8.70 (1H, Pyrazol ring), δ14.6 (1H, Triazole –SH), δ8.00 (5H benzene-P-NO_2), δ8.7 (4H, pyridine), δ5.82 (1H Schiff base).

4-((3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4-yl) methyleneamino)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol (3c)

IR: (cm^{-1}): 3122 (Pyridine C-H), 2368 (S-H), 1655 (C, N).

In solution study, the synthesized organic ligand, 4-((3-(4-bromophenyl)-1-phenyl-1H-pyrazol-4-yl) methyleneamino)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol is insoluble in water hence we used 50% DMF-Ethanol mixture which shows readily solubility for the ligand. Thereafter the solution study carried out.

The titrations (Hussain et al., 2012; Durrani et al., 2015; Thakur et al., 2012; Durrani et al., 2014) of Acid, Acid + ligand and Acid + ligand + metal ion was performed as described in literature

(a). Acid titration - (A)

(b). Acid + Ligand titration – (A+L)

(c). Acid + Ligand + Metal Ion titration – (A+L+M)

The Calvin-Bjerrum (Rajbhoj et al., 2000; Calvin et al., 1945; Gouda et al., 2015) pH-metric titration technique was used for determination of proton-ligand stability constant (pK) and metal-ligand stability constant (logK)

Proton-Ligand stability constant [pK]

The proton-ligand stability constant, $\bar{n}_A$ is the average number of protons associated with one-ligand molecules. The replacement of hydrogen ion with respect to pH calculated by Irving-Rossetti's expression

$$\bar{n}_A = \gamma - \frac{(V_3 - V_2)(N + \varepsilon^\circ)}{(V_0 + V_1)T^\circ_L} \quad \ldots\ldots\ldots (1)$$

Where, γ is number of replaceable protons per ligand molecule, N is the normality of NaOH used in titration, V_1 and V_2 are volumes of alkali required in acid and ligand titration at given pH, $\mathcal{E}^\circ$ and T°_L are initial concentrations of free acid and ligand respectively. The formation curve pK constructed by plotting $\bar{n}_A$ against pH.

Metal-Ligand stability constant [logK]

To determine metal-ligand stability constant, the value of $\bar{n}$ was calculated which shown by the equation 2. $\bar{n}$ is the average number of ligand associated with per metal ion at different pH from ligand and metal ion titration curve determined by the equation i.e.

$$\bar{n} = \frac{(V_3 - V_2)}{(V_0 + V_2)} \frac{(N + \varepsilon^\circ)}{\bar{n}_A T^0_M} \quad \ldots\ldots\ldots\ldots 2$$

Where V_3 are the volume of NaOH added in metal ion titration to attain given pH reading. T°_M is initial concentration of metal ion in reaction mask.

The pL values were calculated from $\bar{n}$ by following expression

$$\mathrm{pL} = \log\left[\frac{1 + \frac{H^+}{K}}{T^0_L - T^0_M \bar{n}} \times \frac{V_0 + V_3}{V_0}\right] \quad \ldots\ldots\ldots\ldots 3$$

The graph plotted between volume of alkali (NaOH) added and pH used for determination of proton-ligand stability constant of [3b]. The Acid titration curve and (Acid+Ligand) titration curves used for evaluation of protonation constant ($\bar{n}_A$). The obtained data for $\bar{n}_A$ shown in table 2 along with (V_2-V_1). The proton-Ligand formation number $\bar{n}_A$ were calculated from Acid(A) and Acid+Ligand (A+L) titration curve, from calculation it is found that the $\bar{n}_A$ values were decreases by increasing pH of solution due to replacement of H^+ ions. The protonation curve constructed in between $\bar{n}_A$ and pH. (A+L+M) and (A+L) curves were used for evaluation of metal-Ligand stability constant ($\bar{n}_A$). The metal ligand stability constant ($\bar{n}_A$) shows that $\bar{n}_A$ values are increases with increasing pH (table 3). The values obtained for $\bar{n}_A$ and $\bar{n}$ in between 0.2-0.8 indicating 1:1 complex formation. A graph will plotted in between $\bar{n}_A$ and pH.

Table 3. Proton-Ligand and Metal-Ligand stability constant (3b)

Metals	pK	logK
Mn	5.04	3.14
Co	5.04	2.96
Ni	5.04	3.1
Zn	5.04	2.95

Conclusion

The observation from titration curve is shown that the deviation of (A+L) at pH range 2.5 to 3.0. (A+L+M) curves were deviated at pH range for Ni(II) is 3.6-4.0, Co(II) is 3.0-3.5, Zn(II) is 3.2-3.6 & Mn(II) is 3.6-3.8. The change in color observed that, yellow to white with Ni(II) and Zn(II), and yellow to brown in Co(II) and Mn(II), this indicates the formation of complex between Ligand and Metal.

Conflicts of interest: Not declared.

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