Potentiometric Determination of Stabiliy Constants of Complexes of Divalent Metal Ions With Butyl 4-(2-Hydroxybenzylideneamino) Benzoate

Neha Nanda
Assistant Professor, Dept of Chemistry
Goswami Ganesh Dutta Sanatan Dharam College, Sector 32 Chandigarh-160031, India.

Abstract- *Studies of complexation of Schiff based ligand, BUTYL 4-(2-HYDROXYBENZYLIDENEAMINO) BENZOATE with NI(II), Cd(II), Pb(II) metal ions have been carried out potentiometrically by Calvin Bjerrum pH titration technique. The proton-ligand stability constant and the stepwise stability constants of its metal ligand complexes were determined at three different temperatures (30°, 40°, 50°C), where ionic strength was maintained at 0.1 M using KNO₃. The corresponding thermodynamic parameters ΔG, ΔH and ΔS for the complexation were also calculated from overall stability constant data.*

Keywords- Potentiometric studies, Calvin Bjerrum pH titration technique, BUTYL 4-(2-HYDROXYBENZYLIDENEAMINO)BENZOATE

I. INTRODUCTION

Schiff bases are an important class of ligands and play an important role in the development of coordination chemistry as they readily form stable complexes with most transition metals[1-5].Schiff base, named after Hugo Schiff is a compound with a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, not hydrogen[6]. Schiff bases in a broad sense have the general formula $R^1R^2C=NR^3$, where R is an organic side chain. Schiff bases derived from aromatic aldehydes and racemic amino acids esters. Amino acid ester based Schiff bases are used in analytical chemistry for the selective extraction and determination of some metal ions[7-8]. Additionally, these compounds have become of enormous importance in recent years with respect to biological activities. They can be used in dyestuff production, liquid crystal industries and also in pharmacology. They have been produced from intermediate products in enzymatic reactions and used as antitumors[9-11]. Amino acids are well known for their tendency to form complexes with metals and have great significance in biological, pharmaceutical field and are directly involved in all the metabolic, enzymatic activities in every living being[12]. The main advantages of these ligands are the liability of the N-protective group, their increased solubility in organic and aqueous-organic solvents, and high R-C-H bond acidity of the amino acid moiety[13].Schiff base complexes are very important in medicinal and pharmaceutical fields because of their wide spectrum of biological activities. Aromatic Schiff bases or their metal complexes catalyze reactions on oxygenation, hydrolysis, electro reduction and decomposition.[14]Development of the field of bioinorganic chemistry has also led to an increased interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species especially for metalloenzymes[15].

In present work we have worked upon the potentiometric studies of BUTYL 4-(2-HYDROXYBENZYLIDENEAMINO) BENZOATE with Ni(II), Cd(II), Pb(II) metal ions, which have been carried out by Calvin Bjerrum pH titration technique, where ionic strength was maintained at 0.1 M using KNO₃.We report herein the proton-ligand stability constants, stepwise stability constants and corresponding thermodynamic parameters associated with the complexation calculated from overall stability constant data.

II. EXPERIMENTAL

2.1. MATERIALS AND SOLUTIONS

All the chemicals used were of A.R. grade and were used without any further purification. Double distilled water was used as prepared in laboratory and was kept in well stoppered bottle. Chemicals used like potassium hydroxide pellets, nitric acid, potassium nitrate salt and metal nitrous salts was bought from SDFCL, India. Solutions were prepared in 50% v/v water/dioxane solution and double distilled water and were standardized by titrating with a standard solution of oxalic acid and of KOH respectively. Metal salt solutions were estimated for the amount of metal present by titrating against standard solution of EDTA. From the stock solution of 0.01M metal solutions were prepared.1, 4-dioxane (bought

from Loba Chemie company, India) was stored out of contact from air.

Preparation of ligand: Equimolar mixture of the (2-hydroxybenzaldehyde) (2.1ml) (bought from Spectrochem company, India) and Butyl4-aminobenzoate (bought from Sigma-Aldrich, China) (4g) was dissolved in the acetonitrile (bought from Loba Chemie) (15 ml) and stirred for 24 hours at room temperature. The resulting orange coloured precipitates were collected, dried and washed with methanol to give pure products. Molecular weight of the ligand is 297 g.

Butyl 4-aminobenzoate   2-Hydroxybenzaldehyde

Butyl 4-(2-hydroxybenzylideneamino)benzoate.
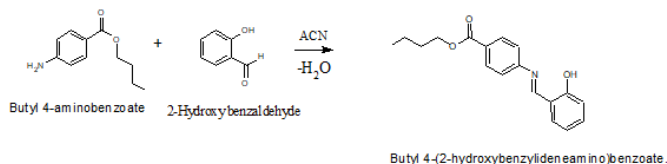
Reaction scheme for ligand

Preparation of ligand solution:0.025M was prepared by dissolving by requisite amount of ligand i.e. Butyl 4-(2-hyroxybenzylideneamino) benzoate in pure 1,4-dioxane.

Other solution used:A)0.1M EDTA solution was prepared from its salt (bought from Qualigens fines chemicals, India) for the standardization of metal salt solution,B) 0.1M $Pb(NO_3)_2$ solutions was used for the standardization of EDTA solution and C) Buffer of pH 4.0 and 9.2 were used for the calibration of pH meter.

2.2 APPARATUS AND INSTRUMENTS

A digital pH meter Model 101 E Deluxe pH meter (Standard Instruments Corporation) with a glass electrode assembly was used for the pH measurements. The water thermostat provided with a pump arrangement for circulating the water and maintaining the temperature of the titration vessel in which various titrations were performed at various temperatures.

2.3 METHOD:POTENTIOMETRIC METHOD

Potentiometric methodinvolves the interaction of the metal ion (M) with the ligand which acts as weak acid (LH) leads to the formation of a metal complex [ML] by the replacement of the proton.

$$M + LH \rightarrow ML + H^+$$
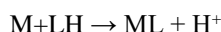
Due to complexation of bivalent metal ions with the ligand, pH of the solution is directly affected resulting in the change in the pH of the solution, and thereafter stability constants of the metal ions are calculated. Calvin and Wilson[14] have shown that stability constants of metal ligand complex can be calculated by determining the degree of formation of complex n and the free ligand exponent (pL). This can be accomplished by the pH measurements made during the titration of solution of ligand in the presence or in the absence of the metal ions with the standard alkali solution. In the present investigation Bjerrum method as modified by Calvin and also by Irving and Rossotti[15] has been used. The determination of formation constants or stability constants from the given experimental data consists of following steps:
1) The determination of formation curve of the system under consideration. This expressed as a plot of n versus pL = log (1/L) where [L] represents the free ligand concentration. 2) The calculation of values of K_1 by the solution of the formation functions of the system.(3) The conversation of the stoichiometric formation constants so obtained to thermodynamic values.4) Calculations of thermodynamic parameters like ΔG, ΔH and ΔS etc. from the values of stability constants by using Gibbs–Helmholtz equation.

Titration details

For evaluating the stability constants, following set of reaction mixtures were prepared, (a)2.5ml of acid(0.01M) + 5 ml of KNO_3 (1M)+ 17.5 ml of water+ 25 ml of 1,4-Dioxane(b).2.5ml of acid(0.01M)+ 5 ml of ligand(0.025M) + 4.85 ml of KNO_3 (1M)+ 17.65 ml of water+ 20 ml of 1,4-Dioxane (c)2.5ml of acid(0.01M)+ 5 ml of ligand(0.025M) +5 ml of metal(0.01M) 4.80 ml of KNO_3 (1M)+ 15.2 ml of water+ 20 ml of 1,4-Dioxane. The ionic strength of all the solutions have been adjusted at 0.1M.pH titrations were carried out at in 50% v/v dioxane water medium and each set of experiment consist of three titrations. The solutions were titrated against standard solution of KOH in thermostat. The pH meter readings were noted after addition of small increments of standard KOH to the titration cell.

Three titration curves of solutions (Free mineral acid, Free mineral acid+ ligand and Free mineral acid + ligand +metal salt solution.)were obtained by plotting pH vs. volume of alkali added as shown in fig (1) for temperature at $30^{\circ}C$ and these are referred to as: (a)Acid titration curve(b)Ligand titration curve (c)Metal titration curve. In all the titrations involving metal ion, pH readings were noted only for homogenous solutions. Readings were not considered when solid phase separated during the course of titration or if the pH meter readings showed a downward trend indicating metal ion hydrolysis.
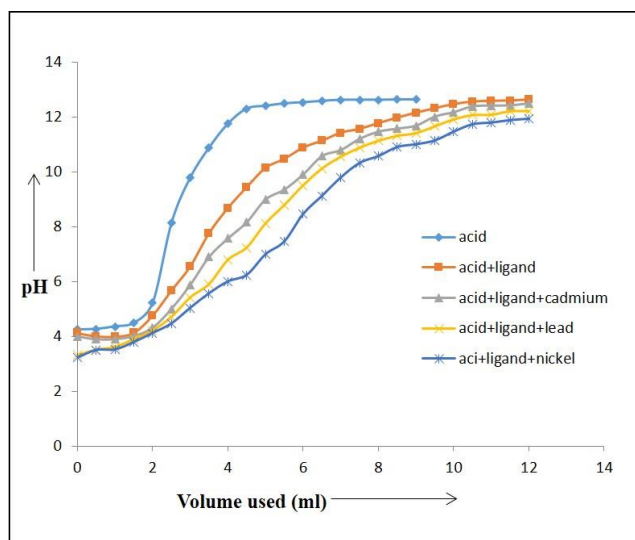
Fig 1: Titration curve of Butyl 4-(2-hydroxybenzylideneamino) benzoate at 30°C and 0.1M ionic strength.

III. RESULTS AND DISCUSSION

Compounds containing an azomethine group (-CH=N-), known as Schiff bases are formed by the condensation of a primary amine with a carbonyl compound The complexing properties of Schiff bases are related to the presence of electron donor amine and hydroxyl sites, which are of importance in binding to metals and stability of resulting complex[16].

Characterization of ligand: Butyl 4-(2-hydroxybenzylideneamino) benzoate was characterized by CHN, IR and melting point data:

1.Melting point: Melting point of the Butyl-4-(2-hydroxybenzylideneamino) benzoate was found sharp at 80°C.
2.CHN Analysis: Structure of Butyl 4-(2-hydroxybenzylideneamino) benzoate is analyzed from following CHN data.:C,72.89(72.72); H,6.45(6.41), N,4.65(4.71).
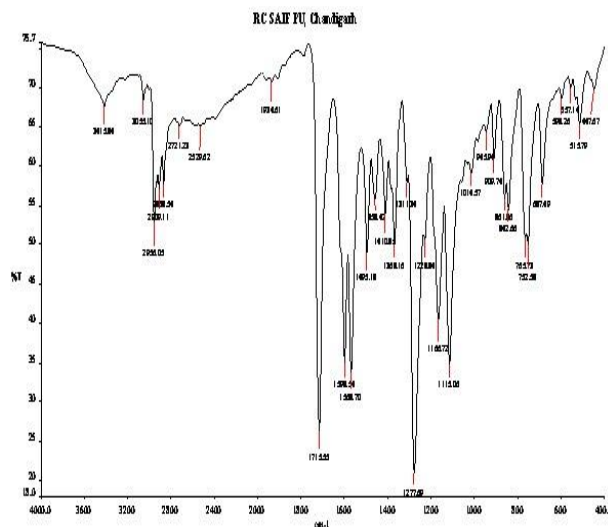

Fig 2: Infra Red Spectra of the ligand

3. I.R. Spectra analysis: In Butyl 4-(2-hydroxybenzylideneamino)benzoate the main stretching frequencies were observed at 3415 cm^{-1}(O-H stretching),1715.55cm^{-1}(C=O stretching), 1368.16cm^{-1}(C=N stretching), 1598.54 cm^{-1}(C=C stretching aromatic), 2956 cm^{-1} (C-H symmetric stretching) from fig (2).

3.1 CALCULATION OF $\overline{n_A}$ and $\overline{n}$

The values of the average number of hydrogen ions per free ligand n_A and the number of ligands bound per metal ion n were calculated from the titration curves for all the metal ions complexes as shown in fig (1) for temperature30°C at a particular pH reading and the volume of V', V", V''' respectively using the following equations:

$$n_A = Y + \frac{(v' - v'')}{(v° + v')} \frac{(N + E°)}{T_L°} \quad \text{...(3.1)}$$

$$n = \frac{(v''' - v'')}{(v° + v'')} \frac{(N + \overline{E})}{n_A T_M°} \quad \text{...... (3.2)}$$

Where:

Y= no. of replaceable Hydrogen ions
V°= Total volume (50 ml)
V'= Volume of alkali used by acid
V"= Volume of alkali used by acid +ligand
V'''= Volume of alkali used by acid +ligand +metal
N   = Strength of alkali used(0.05 M)
E° =   Total strength of acid used (0.0005 M)
T$_L$°= Total concentration of ligand(0.0025 M)
T$_M$°= Total concentration of metal (0.0005M)

3.2 PROTON LIGAND STABILITY CONSTANTS

Irving and Rossotti[17] method has the advantage that simultaneous determination of proton ligand stability constant is possible from the values of n_A .The stages which lead to the formation of acid from its conjugate base are as follows:

$$L^{2+} + H^+ \rightarrow [LH]^{-}$$
$$[LH]^{-} + H^+ \rightarrow LH_2$$
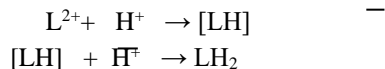
$p_{k1}{}^H$ and $p_{k2}{}^H$ are the equilibrium constants for each step of formation. In order to determine the proton-ligand stability constants, the protonation curves for the ligand at three different temperatures, 30°, 40° and 50° C, were obtained by plotting n_A values versus pH. pH at n_A =0.5, 1.5 corresponds to $\log K_1{}^H$ and $\log K_2{}^H$, the method of linear plot (fig.3) is applied.

In case of Butyl 4-(2-hydroxybenzylideneamino) benzoate, the values of n_A does not exceed one and lies as $1 > n_A > 0$ indicating that only one proton dissociated from the ligand. $\log K_1{}^H$ at three different temperatures i.e 30°, 40° and 50° C are given in table 3.2.The values of $\log K_1{}^H$ were observed to increase with an increase in temperature, showing that the dissociation of the ligand was endothermic and favorable at high temperatures.

3.3 CALCULATION OF pL: Irving and Rossotti[17] used the following equation for the calculation of negative logarithm of mono protonated ligand.

$$pL = log\left[\frac{1 + K_1^H\left(\frac{1}{antilog\ B}\right)(V^\circ + V''')}{(T_L^\circ - nT_M^\circ)\qquad V^\circ}\right]$$

Where B is the pH meter reading. pL values have been calculated and summarized in the different tables as shown in table. 3.1 for Cd(II)-complex at 30°C. These values are found to constantly decrease with increasing pH signifying the metal ligand complexation.

Table 3.1
Cd (II)-Butyl4-(2-hydroxybenzylideneamino)benzoate system μ=0.1 M, t = (30 ±0.1)°C

pH	V'	V''	V'''	n_A^-	n^-	pL
6.3	2.4	2.7	2.9	0.884351	0.433427	7.065943
6.4	2.42	2.72	3.02	0.884395	0.649862	6.988018
6.5	2.44	2.76	3.12	0.876735	0.786051	6.902656
6.7	2.46	2.8	3.15	0.869081	0.770363	6.701304
6.8	2.48	2.83	3.16	0.865282	0.729117	6.597182
6.9	2.5	2.85	3.2	0.865333	0.772967	6.502005
7	2.52	2.9	3.24	0.853846	0.807676	6.40593
7.1	2.54	3	3.26	0.823144	0.856766	6.311231
7.2	2.56	3.06	3.29	0.807839	1.023527	6.229345
7.3	2.58	3.10	3.3	0.800228	1.235657	6.153271
7.4	2.6	3.14	3.34	0.792624	1.345777	6.066536
7.5	2.65	3.2	3.38	0.788984	1.357879	5.968358
7.6	2.75	3.23	3.42	0.775657	1.368788	5.870057
7.7	2.8	3.25	3.45	0.767878	1.378989	5.771612
7.8	2.83	3.3	3.46	0.757888	1.38879	5.672983
7.9	2.89	3.35	3.48	0.756767	1.397686	5.574358
8	2.95	3.4	3.5	0.755678	1.417878	5.477139
8.1	2.97	3.46	3.54	0.747878	1.427878	5.382564
8.2	3	3.48	3.56	0.744577	1.438788	5.288053
8.3	3.04	3.49	3.6	0.736767	1.446565	5.193443
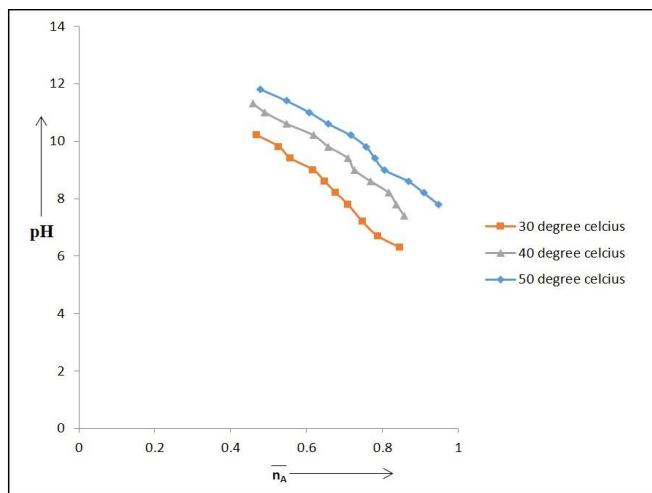
Figno.3: Proton–ligand formation curve of Butyl 4-(2-hydroxybenzylideneamino) benzoate at three different temperatures 30°, 40° and 50° C at 0.1 M ionic strength.
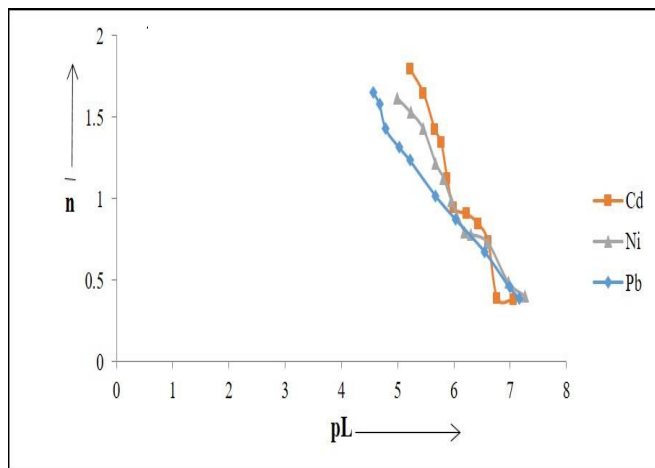
Fig no.4: n versus pL for Butyl 4-(2-hydroxybenzylideneamino)benzoate at 30° C at 0.1 KNO$_3$

3.4 METAL LIGAND STABILITY CONSTANTS

In the present work, metal-ligand binding constants were determined using the Calvin-Bjerrum technique modified by Irving-Rossotti[17] from three titration curves.Then values of metal complexes were determined at various pH. From these data, the corresponding pL values were calculated. Then n values were then plotted against pL to obtain the formation curves of metal complex equilibria. A comparison between ligand and metal titration curves indicates that the metal curves are well separated from the ligand curves as shown in fig. (3), hence this suggests the formation of metal-ligand complexes in solution. The logK values have been calculated by Bjerrum half integral method. Values calculated for logK$_1$ and logK$_2$for various metal ions are summarized in Table 3.2. Observed value for logK$_1$ is found to be always greater that logK$_2$ suggesting that the coordination of the first ligand molecule to the metal ion is more favorable than the bonding of the second one.

Table 3.2
Protonation constants of Butyl 4-(2-hydroxybenzylideneamino) benzoate, metal ligand stability constants of complexes and thermodynamic parameters at three different temperatures.

Cation	Stability constant	Temperature °C			-ΔG KJmol^{-1}			-ΔH KJ mol^{-1}	ΔS K mol^{-1}
		30°C	40°C	50°C	30°C	40°C	50°C	30°C	30°C
H$^+$	LogK$_1^H$	10.3	10.9	11.8	-	-	-	-	-
Cd^{2+}	LogK$_1$	6.4	6.7	6.8	-	-	-	-	-
	LogK$_2$	5.2	5.4	5.1	-	-	-	-	-
	Logß	11.6	12.1	11.9	67.218	72.516	73.595	225.39	-0.521
Pb^{2+}	LogK$_1$	6.1	7.4	6.6	-	-	-	-	-
	LogK$_2$	4.1	6.3	4.7	-	-	-	-	-
	Logß	10.2	13.7	11.3	59.176	82.104	69.885	753.91	-2.292
Ni^{2+}	LogK$_1$	7.6	8.3	6.7	-	-	-	-	-
	LogK$_2$	5.9	7.0	6.3	-	-	-	-	-
	Logß	13.5	15.3	13.0	75.420	91.693	83.595	568.49	-1.627

3.5 EFFECT OF TEMPERATURE

The data in table 3.2 for the ligand Butyl 4-(2-hydroxybenzylideneamino)benzoate shows regular pattern in the values of overall protonation constants, protonation constants increases with increase in temperature showing that the dissociation of the ligand was endothermic and favorable at high temperatures but metal-ligand stability constants decreases at higher temperature as compared to the lower temperature(as in the case of 40°C to 50°C), this is probably because at higher temperature the M-L bond stretches and becomes weak and therefore rate of dissociation gets increases. The table values show that the negative ΔG values increases with increase in temperature for Cd(II) complex, indicates that complexation process with these metal ions are favorable at high temperature.

3.6 ORDER OF STABILITY

The stability of complexes of Butyl 4-(2-hydroxybenzylideneamino)benzoate with Ni(II), Cd(II) and Pb(II) metal ions at 0.1 M KNO$_3$ are calculated from the logß(overall stability constants) values for different metal ions i.e., Ni(II), Cd(II) ,Pb(II) at 30°Care13.0,11.6,10 respectively.Therefore order of stability will follow the pattern as Ni(II)>Cd(II) >Pb(II) which is in accordance with Irving-Williams series.

3.7 THERMODYNAMIC PARAMETERS

The thermodynamic parameters i.e. ∆G, ∆H,∆S of stability constants of Butyl 4-(2 hydroxybenzylideneamino) benzoate complexes are summarized in table 3.2.It was suggested[18-19]that the ions in aqueous solution are surrounded by the water molecules and complex formation between oppositely charged ions (ligand L⁻ and M^{n+}) will lead to the breakdown of metal–water arrangement resulting in positive entropy and enthalpy changes. Examination of these values from the table 3.2 shows that. (a)High negative values of ∆G for various complexation process of Ni(II), Cd(II) and Pb(II) with Butyl 4-(2-hydroxybenzylideneamino)benzoate suggests they are spontaneous in nature.(b)∆H values are negative for the complexation process of the ligand with Ni(II), Cd(II) ,and Pb(II) ions, this makes the process exothermic and enthalpy favoured. (c)The ∆S being negative in case of Ni (II) Cd(II) and Pb(II) predicts that it is unfavourable.

IV. CONCLUSION

In the present case,(a)The stability of complexes of Butyl 4-(2- hydroxybenzylideneamino)benzoate with Ni(II), Cd(II) and Pb(II) metal ions at 0.1 M constant ionic strength follows the general order Ni(II)>Cd(II) > Pb(II) as arranged on the basis of logß value from the table 3.2(b) Negative ∆G values for complexation process of Ni(II), Cd(II) and Pb(II) with Butyl 4-(2-hydroxybenzylideneamino)benzoate at all temperatures suggests a spontaneous nature of process.(c). The ∆H values were also negative indicating exothermic process and enthalpy favoured reactions.(d)∆S value being negative in case of Ni(II), Cd(II) and Pb(II) suggests that it is not favoured by entropy but ∆S values are very low as compared to the other thermodynamic functions therefore we can say that the importance of the enthalpy rather than the entropy factor in the complexation processes.

V. ACKNOWLEDGEMENT

REFERENCES

[1] Sousa C., Freire C., and de Castro B., Molecules., vol. 8, pp. 894, 2003.

[2] Singh V. K., Sinha R., Kant R., and Sinha B. K., Asian J. Chem., vol. 10,pp. 532, 1998.

[3] Yildirm L. T. and AtakolO. Cryst.,Res. Technol., vol.37, pp. 1352, 2002.

[4] Pui A., Croat. Chem.Acta., vol.75, pp. 165, 2002.

[5] GarnovskiA. D., Nivorozhkin A. L., and Minkin V. I., Coord. Chem. Rev,vol.126, pp.1, 2009.

[6] IUPAC, Compendium of Chemical Terminology, The "Gold Book"internet edition: "Schiff base"., 2006

[7] ShahawM. S. E., Analytical Sciences, vol.7, pp. 443, 1991.

[8] Macit M., Bat B., and Ozdemir M., Tr. J. of Chem., vol.19, pp.127, 1995.

[9] Kiss Tamás., Deák György and Gergely Arthur., Inorganica Chimica Acta.,vol. 91, pp. 269,1984.

[10] Yalcan M., Cankurtaran H., and Kunt G,. Kunt, Chim. ActaTurcica,vol.21, pp. 309,1993.

[11] Capitan F., Capitan-Valcnley L. F., and Kiranmai K., Prashanthi Y., Subhashini N. J. P. and Shivaraj.,J. Chem. Pharm. Res., vol.2, pp. 375, 2010.

[12] Kajala Anita and Gupta O. D., RASAYAN J. chem., vol. 2, pp. 833**,** 2009.

[13] Parmar S. Virinder.,SinghAmarjit.Bisht S. Kirpal.,Kumar Naresh., Belokon Y. S., Kochetkov A. K., Ikonnikov N. S., Orlova S. A., Tararov V. I., and Saveleva T. F., J. Org. Chem., vol.61, pp. 1223, 1996

[14] Calvin M., Wilson K. W., J.Am.Chem.Soc.,vol. 751, pp. 415,1953.

[15] Irving H., Rossotti H. S., Acta. Chem. Scand., pp.213, 1954.

[16] Golcu¨ A., Tumer M., Demirelli H.and Wheatley R. A., Inorg. Chim.Acta, vol.358, pp.1758, 2005.

[17] Irving H., Rossotti H. S., Acta.Chem. Scand., pp.213, 1954.

[18] Aggarwal Y. K.,and Rathi B. N., Transistion Met. Chem.,vol.11, pp.472,1986.

[19] Mubarak A. T., J. Sol. Chem., vol.33, pp. 149,2004.