



STUDY OF METAL-LIGAND STABILITY CONSTANTS OF La (III), Sm(III) & Nd(III) METAL ION COMPLEXES WITH SUBSTITUTED SCHIFF'S BASES AT 0.1 M IONIC STRENGTH PH- METRICALLY

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ABSTRACTS

In present work, the interaction of **La(III)**, **Sm(III)** and **Nd(III)** metal ion with 6,6'((ethane1,2diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-methyl-2-nitrophenol) [**L₁**] and 6,6'((ethane1,2diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-chloro -2-nitrophenol) [**L₂**] was investigated at 0.1 M ionic strength (27 ± 0.1 °C) in 70% DMF- water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that La (III), Sm(III) and Nd(III) metal ions forms 1:1 & 1:2 complexes with Schiff base ligand. The substituted Schiff bases show formation of simultaneous complexes. From estimated data (pK & log K), the effect of substituents were studied.

KEYWORDS: Schiff base, Metals ions La (III), Sm(III) and Nd(III), DMF-Water mixture, Stability constant.

INTRODUCTION

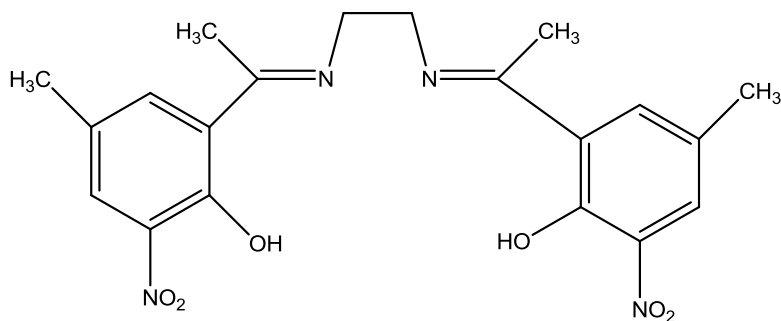
The stability of metal complexes with medicinal drugs plays a most important role in the biological & chemical activity.^[1-2] Generally metal complexes play a very major role in biological process such as metalloproteins, metalloenzymes, storage, transport, detoxification etc. The physico-chemical properties of organic reagents are necessary to understand their nature, reactivity and analytical applicability. Schiff bases are versatile complexing reagents. Studies on the metal complexes of the Schiff bases require the knowledge of their ionization constants. The ionization constants in particular are essential for the metal-ligand stability constants and to have knowledge of selectivity of the relevant analytical reactions. Schiff's Bases and their derivatives possess effective antibacterial^[3], antitumour^[4], antimicrobial^[5] properties. Schiff bases and their complexes shows a high variety of applications in biological clinical and analytical fields.^[6-8] Narwade *et al*^[9] have investigated the equilibrium constants of Cu(II) complexes with some substituted chalcones at 0.1M ionic strength pH metrically. Deshmukh has studied proton -ligands stability constants with dichlorosubstituted pyrazolines, is oxazolines, pyrazoles and isoxazoles.^[10] Recently Khambre and Narwade have studied stability constant of Cu(II),Ni(II),Co(II) complexes of substituted schiff's bases.^[11] Mandakmare *et al* have investigated the interaction between UO₂ (II) and substituted coumarins at 0.1M ionic strength potentiometrically and

spectrophotometrically.^[12] Looking into wide range of activities of Schiff bases and their metal complexes, the present work describe the interaction between La(III), Sm(III) and Nd(III) metal ions with substituted Schiff base complexes in mixed solvent at 0.1M ionic strength that are studied pH-metrically by Calvin- Bjerrum titration technique.

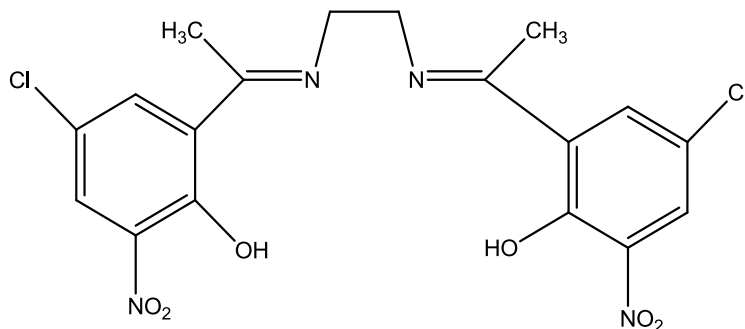
EXPERIMENTAL

MATERIALS AND METHOD

Substituted Schiff's base ligand 6,6'((ethane1,2diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-methyl-2-nitrophenol) [**L₁**] and 6,6'((ethane1,2diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-chloro -2-nitrophenol) [**L₂**] were synthesized in the laboratory by known literature method & their purity was checked by TLC on microscopic slides with silica gel-G layer thickness 0.3mm. The structure was confirmed by IR, NMR spectra and melting point. All the chemicals used were of AR grade. The solution of ligands was prepared in DMF. DMF (A.R.) was purified by the method described by Vogel.^[13] All solutions were prepared in double distilled, CO₂ free water. Metal ion solutions were prepared by dissolving the requisite quantities of metal nitrate in double distilled water and standardized by using conventional procedures. Sodium hydroxide solution was prepared in deionised water and solution were standardized before use by known methods & used as afresh.



L₁ : 6,6'-((ethane-1,2-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-methyl-2-nitrophenol)



L₂ : 6,6'-((ethane-1,2-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-chloro-2-nitrophenol)

Measurements

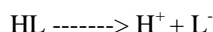
All the pH measurements and titrations were carried out with Systronic microprocessor based pH meter with magnetic stirrer (accuracy ± 0.01 units) using glass electrode & calomel electrode at 27 ± 0.1 °C. pH meter was calibrated by standard buffer solution (pH 4.0, 7.00 & 9.2).

The experimental procedure involved the titrations of

- (i) Free acid HNO_3 (0.01 mol.dm^{-3})
- (ii) Free acid HNO_3 (0.01 mol.dm^{-3}) and ligand ($2 \times 10^{-3} \text{ mol.dm}^{-3}$)
- (iii) Free acid + ligand ($2 \times 10^{-3} \text{ M}$) + metal ion titration ($4 \times 10^{-4} \text{ M}$) with standard NaOH solution (0.13 mol.dm^{-3}) in presence of an inert atmosphere by bubbling a constant flow of nitrogen gas. The ionic strength of all these systems was maintained constant 0.1M by adding appropriate amount of KNO_3 solution.

RESULTS AND DISCUSSION

The substituted Schiff bases L_1 and L_2 having replaceable H^+ ion in phenolic hydroxy group may be ionized as i.e.



The titration data were obtained used to construct the formation curves [acid curve (A), acid + ligand curve (A + L) and acid + ligand + metal ion curve (A + L + M)] by plotting pH Vs volume of NaOH. It is observed from

titration curves that for all systems ligand start deviating from the free acid curves at $\text{pH} = 2.9$ and deviation continuous up to $\text{pH} = 12$. The deviation presents dissociation of proton in Schiff base. The average number of proton dissociated from the ligand (n_A) was determined from free acid and acid - ligand titration curves by employing the equation (1) proposed by Irving and Rossotti (Table 1)

$$n_A = \gamma - \frac{(E^\circ + N) \times (V_2 - V_1)}{(V^\circ + V_1) \times T^\circ_L} \quad \text{..... (1)}$$

Where, γ is the number of replaceable H^+ ions, V° is the total volume of the solution, E° & T°_L are the total concentrations of Nitric acid & ligand respectively, V_1 & V_2 are volume of alkali added to reach the same pH reading during titration of free acid and free acid plus ligand respectively. $V_2 - V_1$ is the horizontal difference in the volume at the given pH and N is the concentration of sodium hydroxide (0.13 mol.dm^{-3}).

The pK_1 and pK_2 values were determined from formation curves by half integral method (n_A Vs pH) by noting the pH at which $n_A = 1.5$ and $n_A = 0.5$ respectively. The accurate values of pK_1 and pK_2 were calculated by point wise calculations which are presented in Table 1.

Table 1: Proton ligand formation number at (27 ± 0.1 °C) and at ionic strength $\mu = 0.1 \text{ mol dm}^{-3}$

Medium: 70% DMF -water

$\mu = 0.1 \text{ M}$

$T^\circ_L = 2 \times 10^{-3} \text{ M}$

$T^\circ_M = 4 \times 10^{-4} \text{ M}$

$N = 0.13 \text{ N}$

$V_0 = 25 \text{ ml}$

$E^\circ = 1 \times 10^{-2}$

Temp. = 27 ± 0.1 °C

System: Ligand 1

pH	V ₁	V ₂	ΔV	nA
5.6	3.41	3.49	0.08	1.845125
5.8	3.45	3.56	0.11	1.797346
6	3.49	3.61	0.12	1.75834
6.2	3.5	3.69	0.19	1.633333
6.4	3.51	3.75	0.24	1.537005
6.6	3.54	3.82	0.28	1.460406
6.8	3.55	3.88	0.33	1.394273
7	3.58	3.93	0.35	1.356452
7.2	3.6	3.96	0.36	1.307692
7.4	3.63	4	0.37	1.289207
7.6	3.66	4.04	0.38	1.270761
7.8	3.69	4.08	0.39	1.252353
8	3.7	4.1	0.4	1.233449
8.2	3.74	4.15	0.41	1.215379
8.4	3.76	4.18	0.42	1.196801
8.6	3.79	4.22	0.43	1.178534
8.8	3.8	4.25	0.45	1.140625
9	3.83	4.29	0.46	1.122442
9.2	3.86	4.33	0.47	1.104297
9.4	3.88	4.36	0.48	1.085873
9.6	3.91	4.43	0.52	1.050723
9.8	3.95	4.48	0.53	0.999092
10	4	4.54	0.54	0.975862
10.2	4.03	4.58	0.55	0.957975
10.4	4.08	4.64	0.56	0.940853
10.6	4.12	4.69	0.57	0.92342
10.8	4.16	4.75	0.59	0.887174
11	4.21	4.83	0.62	0.832592
11.2	4.26	4.91	0.65	0.778195
11.4	4.35	5.05	0.7	0.688245
11.6	4.44	5.24	0.8	0.505435
11.8	4.5	5.43	0.93	0.266102
12	4.6	5.55	0.95	0.234797

System: Ligand 2

pH	V ₁	V ₂	ΔV	nA
5.2	3.35	3.4	0.05	1.902998
5.4	3.39	3.48	0.09	1.815643
5.6	3.41	3.53	0.12	1.767687
5.8	3.45	3.58	0.13	1.748682
6	3.48	3.62	0.14	1.729635
6.2	3.5	3.65	0.15	1.710526
6.4	3.52	3.7	0.18	1.652875
6.6	3.54	3.74	0.2	1.614576
6.8	3.55	3.8	0.25	1.538389
7	3.57	3.83	0.26	1.499475
7.2	3.6	3.87	0.27	1.480769
7.4	3.62	3.9	0.28	1.461915
7.6	3.65	3.95	0.3	1.424084
7.8	3.69	4	0.31	1.400716
8	3.7	4.05	0.35	1.349268
8.2	3.73	4.09	0.36	1.310825
8.4	3.76	4.15	0.39	1.269172
8.6	3.79	4.2	0.41	1.226742
8.8	3.82	4.24	0.42	1.198473
9	3.85	4.28	0.43	1.180243

9.2	3.86	4.31	0.45	1.142412
9.4	3.9	4.37	0.47	1.105536
9.6	3.93	4.42	0.49	1.068441
9.8	3.96	4.47	0.51	1.031423
10	4	4.52	0.52	1.013793
10.2	4.05	4.58	0.53	0.996558
10.4	4.09	4.65	0.56	0.951217
10.6	4.13	4.7	0.57	0.92379
10.8	4.17	4.76	0.59	0.887556
11	4.23	4.85	0.62	0.83339
11.2	4.27	4.95	0.68	0.732241
11.4	4.35	5.05	0.7	0.688245
11.6	4.43	5.14	0.71	0.673123
11.8	4.5	5.23	0.73	0.638983
12	4.57	5.35	0.78	0.566921
12.2	4.7	5.49	0.79	0.537037
12.4	4.8	5.65	0.85	0.431208

Table 2: Determination of proton-ligand stability constant (pK) of Schiff base at 0.1 M ionic Strength

System	Constants (pK)			
	Half integral method		Pointwise calculation	
Schiff Base L1	pK ₁	pK ₂	pK ₁	pK ₂
	Schiff Base L2	6.50	11.52	6.61
	7.18	12.42	7.07	12.32

Determination of Metal-Ligand Stability Constant (Log k) of Schiff base at 0.1 M ionic Strength

Metal-ligand stability constant of metal chelates with Schiff bases of L₁ and L₂ were determined by employing Calvin -Bjerrum pH- metric titration method as adopted equation (2) by Irving and Rossotti . The formation of chelate between metal ions with Schiff bases L₁ and L₂ were indicated by the significant separation starting from pH =2.9 for all complexes.

$$n = \frac{(E^{\circ} + N) \times (V_3 - V_2)}{(V^{\circ} + V_2) \times T^{\circ}m} \quad \text{----- (2)}$$

Where E^o is the concentration of acid, N is the normality of the NaOH, T^om is the concentration of metal, V^o is the total volume and V₃- V₂ is the horizontal difference in the volume at the given pH.

The metal ligand stability constants for La(III), Sm(III) and Nd(III) with Schiff base ligands L₁ and L₂ in 70% DMF-water can be found by the half integral method and pointwise calculation method (Table -3).

Table 3: Determination of LogK1 & LogK2 Value

Medium: 70% DMF-water

T^oM = 4 x 10⁻⁴M

E^o = 1 x 10⁻² M

μ = 0.1M

N = 0.13N

Temp. = 27 ± 0.1^o C

T^oL = 2 x 10⁻³M

V^o = 25 ml

System	Metal ligand stability constants (log K)			
	Half Integral		Pointwise Calculation	
	Log K1	Log K2	Log K1	Log K2
La(III)-L1 Complex	9.38	7.39	9.18	7.29
Sm(III)-L1 Complex	9.12	7.52	8.908	7.379
Nd(III)-L1 Complex	9.48	7.53	9.383	7.390
La(III)-L2 Complex	3.39	3.11	3.610	3.047
Sm(III)-L2 Complex	3.62	3.01	2.816	2.748
Nd(III)-L2 Complex	4.68	3.41	4.307	3.494

Table: 4 Metal-Ligand Stability constants (Log K).

System	Log K1	Log K2	Log K1-Log K2	Log K1/Log K2
La(III)-L1 Complex	9.38	7.39	1.99	1.269
Sm(III)-L1 Complex	9.12	7.52	1.6	1.212
Nd(III)-L1 Complex	9.48	7.53	1.95	1.258

La(III)-L ₂ Complex	3.39	3.11	0.28	1.090
Sm(III)-L ₂ Complex	3.62	3.01	0.61	1.202
Nd(III)-L ₂ Complex	4.68	3.41	1.27	1.372

CONCLUSION

In the present study, it is observed from titration curve that the extent of deviations confirms complete dissociation of -OH group. The deviation between acid+ligand curve and acid+ligand+metal curve indicates the commencement of complex formation. The change in colors during titration with respect to pH also indicates the complex formation between ligand and metal ions.

Proton-Ligand stability constant (pK)

It could be observed from Table No. 2 that there is good agreement of Proton-liand stability constants between half integral method and pointwise calculation method. The pK values for ligand depend on structures and resonance stabilization of ligands. The ligand L₂ shows higher pK values than L₁. This indicates that the chlorine atom present at para position to the phenolic hydroxy group, is exhibiting strong electron donating positive resonance effect than the electron donating hyperconjugation effect of methyl group in ligand L₁, in the DMF-water system. Symmetrical and asymmetrical structures for ligands are also responsible for the pK values for the ligands.

Metal-Ligand stability constant (Log K)

Determination of metal-ligand stability constants requires the accurate value of proton-ligand stability constant. Higher values of log K₁ and log K₂ showed that ligand are stronger chelating agents and vice versa. In the present investigation values of log K₁ and log K₂ have been calculated with half integral and pointwise calculation methods. The values obtained are in good agreement (shows in Table No. 3). The difference between log K₁ and log K₂ values are studied for all the systems and is represented in Table No.4.

The difference between log K₁ and log K₂ values are less. The difference between log K₁ and log K₂ values indicated the simultaneous formation of 1:1 and 1:2 complexes in the solution. They showed the linear relationships between log K and pK values of ligands suggesting identical binding sites in all ligands.

The higher value of ratio (Log K₁/ Log K₂) for La(III)-Ligand- L₁ & Nd(III)-ligand- L₁ & L₂ complex indicates the more stable simultaneous complex formation as compare to Sm(III) -Ligand-L₁ & L₂ and La(III)-Ligand L₂ complexes. Stability constants depend upon the size of cation.

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