

STUDIES OF PROTON AND METAL-LIGAND STABILITY CONSTANTS OF PR (III), ND (III) AND GD (III) COMPLEXES OF SUBSTITUTED SCHIFF'S BASES & DIBROMO CHALCONES

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ABSTRACT

The Interaction of metal ions with Pr(III),Nd(III) and Gd(III) metal ions with

- i) 2-Hydroxy,3-Bromo,5-Chloro,4-Methoxy,N-(Orthonitro Phenyl) Chalcone Imine(L₁).
- ii) 2-Hydroxy,5-Chloro,5-Methoxy,N-(Orthonitro Phenyl) Chalcone Imine (L₂).
- iii) 2-Hydroxy,5-Chloro Chalcone Dibromide (L₃).
- iv) 2-Hydroxy,5-Chloro,4-Methoxy Chalcone Dibromide (L₄).
- v) 2-Hydroxy,3-Bromo,5-Chloro,4-Methoxy Chalcone Dibromide (L₅).

have been studied at 0.1M Ionic strength.It is observed that, Pr(III),Nd(III) and Gd(III) metal ions form 1:1 and 1:2 complexes with L₁ to L₅.

The substituted Schiff's Bases & Dibromo Chalcones show formation of simultaneous complexes.The order of proton-ligand stability constant is as $pKL_3 > pKL_2 > pKL_5 > pKL_1 > pKL_4$. The data obtained for pK and logK are used i)To see the effect of substituents,ii) To check the validity of $\log k = a.pK + b$.Here proton-ligand & metal-ligand stability constants have been studied pH-metrically by Calvin-Bjerrum titration technique.

Keywords: Metal Ions(Pr(III),Nd(III),Gd(III)),Ligand(Substituted Pyrazoles),Solvent(1,4-Dioxane) Etc

INTRODUCTION

Schiff's Bases & Dibromo Chalcones and their derivatives are biologically important compound having antibacterial¹⁻²,antitumour³,antimicrobial⁴ properties.Shelke *et al*⁵ have investigated the interaction between UO₂(II) and Cu(II) with dicarboxylic acids in dioxane-water mixture. Narwade *et al*⁶ have studied the equilibrium constants of Cu(II) complexes with some substituted chalcones at 0.1M ionic strength pH metrically. Sawalakhe and Narwade⁶ have studied stability constants of Cu(II) complexes with some substituted chalcones at 0.1M ionic strength. Rajput⁷ has studied proton-ligand stability constants with some chlorosubstituted pyrazolines,isoxazolines,pyrazoles and isoxazoles.Deshmukh⁸ has studied proton-ligands

stability constants with some dichlorosubstituted pyrazolines, isoxazolines, pyrazoles and isoxazoles. Banerjee *et al*⁹ have synthesized number of mixed ligands of alkaline earth metal complexes with a view to understand the bio-inorganic chemistry of metal ions.

Raghuwanshi *et al*¹⁰ have studied stability constants of Cu(II) complexes with some substituted isoxazolines in 70% dioxane-water mixture spectrophotometrically. Mandakmare *et al*¹¹ have studied the interaction between UO₂(II) and substituted coumarins at 0.1M ionic strength potentiometrically and spectrophotometrically. Recently Palaskar¹² has studied the effect of ionic strength and dielectric constant of Cu(II) -3-nitrophthalic acid potentiometrically at 0.02, 0.04, 0.06, 0.08 and 1.0M ionic strength in aqueous medium at 30°C. The present work deals with the study of complex formation between Pr(III), Nd(III) and Gd(III) ions & substituted Schiff's Bases & Dibromo Chalcone & determination of proton-ligands and metal-ligand stability constants of some substituted Schiff's Bases & Dibromo Chalcone pH-metrically by Calvin- Bjerrum titration technique.

II. EXPERIMENTAL

Substituted Schiff's Bases & Dibromo Chalcone L₁ to L₅ were synthesized in the laboratory & their purity was checked by TLC on microscopic slides with silica gel-Glayer thickness 0.3. The structure of L₁ to L₅ were confirmed by IR & NMR spectra.

The solution of ligands were prepared in 1,4-dioxane. The solution of NaOH, HNO₃, KNO₃ & metal ions (Pr(NO₃)₂, Nd(NO₃)₂ & Gd(NO₃)₂) were obtained from BDH grade chemicals.

The pH measurements were carried out with ELICO-LI-10 pH meter (accuracy ± 0.05 units) using glass electrode & calomel electrode at 28 ± 0.1°C. The B values (pH meter reading in 70% dioxane-water mixture) were converted to pH values by applying the correction given by Van Vilters & Hass. pH meter was calibrated by standard buffer solution (pH 4.01, 7.00 & 9.11).

Experimental procedure involves following three sets of titrations :

- i) Free acid titration (HNO₃, 1 x 10⁻²M)
- ii) Free acid + ligand titration (20 x 10⁻⁴M)
- iii) Free acid + ligand (20 x 10⁻⁴M) + metal ion titration (4 x 10⁻⁴M)

were carried out with standard NaOH solution (0.2N) in presence of an inert atmosphere by bubbling a constant flow of nitrogen gas.

III. RESULTS AND DISCUSSION

The ligands are monobasic containing only one OH group; hence its dissociation is represented as below.



The deviations between acid curves (acid + ligand curves) started at about pH 2.40-3.00 for L₁, for all the systems this deviation gradually increases up to pH 12.00, which shows the dissociation of -OH group of ligands.

3.1 Determination of Proton-Ligand Formation Numbers (n_A)

The values of (n_A) are estimated by using Irving and Rossotti experiments. Formation curves are prepared by plotting values of n_A vs pH.

3.2 Calculations

The values of pK are calculated from formation curves (i.e. half integral method). The pH at nA=0.5 corresponds the proton-ligands stability constant (pK). The order of proton-ligand stability constant is $pK_{L_3} > pK_{L_2} > pK_{L_5} > pK_{L_1} > pK_{L_4}$. The correct value is also calculated by pointwise calculation method. The pK values for L₁ to L₅ are given in Table-1.

The sudden increase in pK value of ligand is due to the presence of group attached to phenyl ring as electron withdrawing group. In case of ligand, the inductive effect of benzoyl group may be compensated due to the presence of electron releasing group that results in an increase in the pK value of ligand.

TABLE – 1

DETERMINATION OF PROTON LIGAND STABILITY CONSTANTS (pK)

Medium : 70% Dioxane-water

$\mu = 0.1M$

$T^0L = 20 \times 10^{-4}M$

$T^0M = 4 \times 10^{-4}M$

$N = 0.2N$

$V^0 = 50 \text{ ml}$

$E^0 = 1 \times 10^{-2} M = 0.01M$

Temp. = $28 \pm 0.01^\circ C$

System	Constants (pK)	
	Half integral method	Pointwise calculation
L ₁	3.70	3.7932 ± 0.03
L ₂	3.80	3.8260 ± 0.05
L ₃	6.00	6.1294 ± 0.04
L ₄	3.60	3.6536 ± 0.04
L ₅	3.80	3.5535 ± 0.06

IV. DETERMINATION OF METAL LIGAND STABILITY CONSTANTS

The deviation between (acid + ligand) and (acid + ligand + metal) curves started from pH 1.60 & increased continuously up to pH 12. It shows the commencement of complex formation. Intense colouration was observed which also indicated the formation of complex.

4.1 Calculation of n values and determination of logK₁ and Log K₂ values

The values of n is estimated by applying Irving-Rossotti expression. The maximum value of n was obtained at about pH 2.00 for Gd(III)L₁. This showed the formation of 1:1 & 1:2 complexes respectively are calculated and presented in Table-2.

Table – 2

Medium : 70% Dioxane-water

$\mu = 0.1M$

$T^0L = 20 \times 10^{-4}M$

$T^0M = 4 \times 10^{-4}M$

$N = 0.2N$

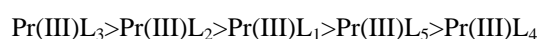
$V^0 = 50 \text{ ml}$

$E^0 = 1 \times 10^{-2} M = 0.01M$

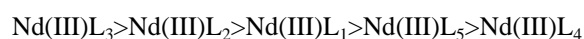
Temp. = $28 \pm 0.01^\circ C$

From Table-2 the order of LogK₁ is presented as below:

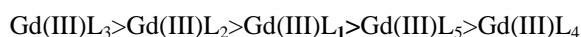
1) LogK₁ for Pr(III) Complexes:



2) LogK₁ for Nd(III) Complexes :



3) $\text{Log}K_1$ for Gd(III) Complexes:



It could be seen from Table-3 that the difference between $\text{Log}K_1$ & $\text{Log}K_2$ is smaller (<1) which shows the formation of simultaneous complex. If the difference is very greater that indicates the formation of stepwise complex formation.

System	Metal ligand stability constants (log K)			
	Half Integral		Pointwise Calculation	
	Log K_1	Log K_2	Log K_1	Log K_2
Pr(III) - L_1 Complex	4.68	3.79	4.70	3.83
Nd(III) - L_1 Complex	4.58	4.17	4.71	3.90
Gd(III) - L_1 Complex	3.99	3.09	4.32	3.17
Pr(III) - L_2 Complex	4.85	4.45	5.06	4.42
Nd(III) - L_2 Complex	4.65	3.85	4.74	3.92
Gd(III) - L_2 Complex	4.75	4.05	4.84	4.07
Pr(III) - L_3 Complex	7.01	6.59	7.09	6.54
Nd(III) - L_3 Complex	7.09	6.78	7.27	6.65
Gd(III) - L_3 Complex	6.79	6.39	7.10	6.51
Pr(III) - L_4 Complex	3.36	2.95	3.50	2.97
Nd(III) - L_4 Complex	3.19	2.74	3.37	2.59
Gd(III) - L_4 Complex	3.47	2.96	3.32	3.01
Pr(III) - L_5 Complex	3.64	2.94	4.10	2.86
Nd(III) - L_5 Complex	3.87	3.63	4.02	3.51
Gd(III) - L_5 Complex	3.94	3.43	4.29	3.46

Table-3

System	Log K_1	Log K_2	Log K_1 /Log K_2	
	Half Integral	Pointwise calculation	Half Integral	Pointwise Calculation
Pr(III)- L_1 Complex	0.89	0.87	1.23	1.22
Nd(III)- L_1 Complex	0.41	0.81	1.09	1.20
Gd(III)- L_1 Complex	0.90	1.15	1.29	1.36
Pr(III)- L_2 Complex	0.40	0.64	1.09	1.14
Nd(III)- L_2 Complex	0.80	0.82	1.20	1.21
Gd(III)- L_2 Complex	0.70	0.77	1.17	1.19
Pr(III) - L_3 Complex	0.42	0.55	1.06	1.08
Nd(III)- L_3 Complex	0.40	0.59	1.06	1.09
Gd(III)- L_3 Complex	0.41	0.53	1.06	1.09
Pr(III)- L_4 Complex	0.41	0.53	1.13	1.17
Nd(III)- L_4 Complex	0.45	0.78	1.16	1.30
Gd(III)- L_4 Complex	0.51	0.31	1.23	1.43
Pr(III)- L_5 Complex	0.24	1.24	1.23	1.43
Nd(III)- L_5 Complex	0.24	0.51	1.06	1.24
Gd(III)- L_5 Complex	0.51	0.83	1.14	1.24

V. CONCLUSION

The maximum value of n - was obtained at about pH 2.00 for $Gd(III)L_1$. This showed the formation of 1:1 & 1:2 complexes respectively. The difference between $\log K_1$ & $\log K_2$ is smaller (<1) which shows the formation of simultaneous complex. If the difference is very greater that indicates the formation of stepwise complex formation.

REFERENCE

- [1] M.A.Ramekar and M.M. Chincholkar, J. Indian Chem. Soc. 71, 199 (1994).]
- [2] H.S.Patel and N.P.Patel Orient J. Chem., 13, 69 (1997).]
- [3] H.I.E1-Subbagh, A.H. Abadi, i.E. Al-Khawad, K.A. A1- Rashood, Arch, Pharm, 332, 19 (1999).]
- [4] A.W.Raut and A.G. Doshi, Orient J. Chem, 11, 205 (1995).]
- [5] D.N.Shelke and D.V. Jahagirdar, J, Indian Chem., Soc. 53, 613, (1976).]
- [6] M.L.Narwade and P.D. Sawalakhe J. Indian Chem., Soc. 70, 201, (1993).]
- [7] P.R.Rajput, Ph.D. Thesis, Amravati University (1993).]
- [8] M.S.Deshmukh Ph.D Thesis, Amravati University (1996).]
- [9] A.K.Banerjee and T.V.R, K. rao J. Indian Chem., Soc. 63, 480, (1986).]
- [10] P.B.Raghuwanshi, A.G.Doshi and M.I.Narwade, Asian J. Chem., 8, 211, (1996).]
- [11] A.U.Mandakmare and M.L. Narwade, Acta Ciencia Indica, 16C, 30, (1994)].
- [12] N.G.Palaskar, Samyak j. chem., 2, 26, (1998).]