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(L_1).
ii) 2-Hydroxy,5-Chloro,5-Methoxy,N-(Orthonitro Phenyl) Chalcone Imine (L_2).
iii) 2-Hydroxy,5-Chloro Chalcone Dibromide (L_3).
iv) 2-Hydroxy,5-Chloro,4-Methoxy Chalcone Dibromide (L_4).
v) 2-Hydroxy,3-Bromo,5-Chloro,4-Methoxy Chalcone Dibromide (L_5).

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 L_1 to L_5 .

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 logk = 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 antibacterial[1-2],antitumour[3],antimicrobial[4] properties.Shelke *et al*[5] have investigated the interaction between UO_2(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 Narwade[6] have studied stability constants of Cu(II) complexes with some substituted chalcones at 0.1M ionic strength. Rajput[7] has studied proton-ligand stability constants with some chlorosubstituted pyrazolines,isoxazolines,pyrazoles and isoxazoles.Deshmukh[8] has studied proton-ligands stability constants with some dichlrosubstituted 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 UO_2(II) and substituted coumarins at 0.1M ionic strength potentiometrically and spectrophotometrically. Recently Palaskar[12] 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^oC. 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 L_1 to L_5 were synthesized in the laboratory & their purity was checked by TLC on microscopic slides with silica gel-Glayer thickness 0.3.The structure of L_1 to L_5 were confirmed by IR & NMR spectra.

The solution of ligands were prepared in 1,4-dioxane. The solution of NaOH,HNO_3,KNO_3 & metal ions ($Pr(NO_3)_2$,$Nd(NO_3)_2$ & $Gd(NO_3)_2$) 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 & calmel electrode at 28 ± 0.1^OC. The B values (pH meter reading in 70% dioxane-water mixture) were converted to pH values by applying the correction given by Van Viterts & 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 (HNO_3,1 x 10^{-2}M)

ii)Free acid + ligand titration (20 x 10^{-4} M)

iii)Free acid + ligand (20 x 10^{-4}M) + metal ion titration (4 x 10^{-4}M)

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 it's dissociation is represented as below.

$$HL \Leftrightarrow H^+ + L^-$$

The deviations between acid curves (acid + ligand curves) started at about pH 2.40-3.00 forL1,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 (Na)

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

3.2 Calculations

The values of pK are calculated from fornation 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 $pKL_3>pKL_2>pKL_5>pKL_1>pKL_4$. The correct value is also calculated by pointwise calculation method. The pK values for L_1 to L_5 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 STABILITYCONSTANTS(pK)

Medium : 70% Dioxane-water **μ** =0.1M **T^0L** = 20×10^{-4}M

T^oM = 4×10^{-4}M **N** = 0.2N **V^O** = 50 ml

E^o = 1×10^{-2} M = 0.01M **Temp.** = 28 ± 0.01°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 $\log K_1$ and $\log K_2$ values

The values of n is estimated by applying Irving-Rossotti expression. The maximum value of n was obtained at about pH2.00 for Gd(III)L_1.This showed the formation of 1:1 & 1:2 complexes respectively are calculated and presented in Table-2.

Table – 2

Medium : 70% Dioxane-water μ = 0.1M $T^0L = 20 \times 10^{-4}$M

$T^oM = 4 \times 10^{-4}$M N = 0.2N V^O = 50 ml

$E^o = 1 \times 10^{-2}$ M = 0.01M Temp. = 28 ± 0.01°C

From Table-2 the order of $\log K_1$ is presented as below:

1)$\log K_1$ for Pr(III) Complexes:

Pr(III)L_3>Pr(III)L_2>Pr(III)L_1>Pr(III)L_5>Pr(III)L_4

2) $\log K_1$ for Nd(III) Complexes :

Nd(III)L_3>Nd(III)L_2>Nd(III)L_1>Nd(III)L_5>Nd(III)L_4

3) LogK$_1$ for Gd(III) Complexes:

Gd(III)L$_3$>Gd(III)L$_2$>Gd(III)L$_1$>Gd(III)L$_5$>Gd(III)L$_4$

It could be seen from Table-3 that the difference between LogK$_1$ & 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.

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	LogK$_1$	LogK$_2$	LogK$_1$/LogK$_2$	
	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 LogK_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.

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