

Metal-Ligand Stability Constants of Eu(III), Sm(III), Tb(III), Nd(III) and Pr(III) Metal Ion Complex with Some Substituted Isoxazolines

Y.K. MESHRAM* and M.L. NARWADE†

Department of Chemistry
G.S. College, Khamgaon-444 312, India

The interactions of Eu(III), Sm(III), Tb(III), Nd(III) and Pr(III) metal ions with 3-(2-hydroxy-3-bromo-5-methyl-phenyl) 5-(3,4-dioxy methylene) isoxazoline (Ligand No. 1), 3-(2-hydroxy-5-methyl phenyl)-5-(4 methoxyphenyl) isoxazoline (Ligand No 2) and 3-(2-hydroxy-3-bromo-5-methyl phenyl)-5-(4-methoxyphenyl) isoxazoline (Ligand No. 3) have been studied at 0.1M ionic strength. It is observed that lanthanide ions form 1 : 1 and 1 : 2 complexes with all the isoxazoline ligands. The data obtained of pK and log K are used (i) to see the effect of substituents, and (ii) to check the validity of $\log K = a \text{ pK} + b$.

INTRODUCTION

The studies in metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols, etc. would be interesting which throw light on the mode of storage and transport of metal ions in the biological kingdom.

Banarjee *et al.*¹ have synthesised a number of mixed ligand alkaline earth metal-complexes with a view to understand the bio-inorganic chemistry of metal ions. Narwade *et al.*² have investigated metal-ligand stability constants of some lanthanides with some substituted sulphonic acids. Chincholkar *et al.*³ have reported Fe(III) complexes with some substituted chalcones and isoxazolines. Ali Ashgar⁴ has studied the formation constants of transition metal ions with some substituted pyrazolines and isoxazolines. Raghuwanshi *et al.*⁵ have studied conditional stability constants of Cu(II) complexes with some substituted isoxazolines in 70% dioxane-water mixture spectrophotometrically. The interaction between UO₂(II) and substituted coumarines has been studied by Mandakmare *et al.*⁶ The formation constants of Cu(II) chelates with 2-hydroxy aromatic ketones have been studied by Rabindranath.⁷

Here an attempt has been made to study the interactions between lanthanide ions and substituted isoxazolines at 0.1 M ionic strength pH-metrically.

EXPERIMENTAL

Substituted isoxazolines (ligands) were synthesised in the laboratory and their purity was checked by IR, NMR and m.p. The solutions of ligands were prepared in purified methyl alcohol ($1.002 \times 10^{-2} \mu$); HClO₄ and NaOH were used of AR grade. Lanthanide metal ions were obtained from BDH and the solution of

Department of Chemistry, Govt. Vidarbha Mahavidyalaya, Amravati-(M.S.), India

lanthanide metal ions was prepared in double distilled water and its concentration was checked by EDTA.

pH-meter Elico-LI-12T was used for the measurement of pH of solution. It was calibrated by standard buffer solution of pH 4.01, 7.00 and 9.20.

Calvin-Bjerrum Titration: The present work deals with the study of pH metric titration between lanthanide ions (Pr^{3+} , Nd^{3+} , Eu^{3+} and Tb^{3+}) and substituted isoxazolines at 0.1 M ionic strength at $27 \pm 0.1^\circ\text{C}$.

Titration was carried out in an inert atmosphere by bubbling a constant flow of nitrogen gas.

Experimental procedure involves following three sets of experiments:

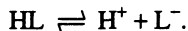
(I) Free acid HClO_4 (1.00×10^{-2} M)

(II) Free acid HClO_4 (1.00×10^{-2} M) + isoxazoline ligand (20×10^{-4} M)

(III) Free acid HClO_4 (1.00×10^{-2} M) isoxazoline ligand (20×10^{-4} M + metal ions (4×10^{-4} M). The three sets were titrated separately against standard solution of 0.2001 M NaOH and 0.1 M ionic strength was maintained constant by adding an appropriate amount of 1 M HClO_4 solution. All the titrations were carried out in 70% methyl alcohol-water mixture. pH-meter readings were converted into actual pH values by making Van-Uitert and Haas correction⁸

RESULTS AND DISCUSSION

Proton-ligand stability constants: Isoxazolines may be considered as monobasic acids having only one dissociable H^+ ion from $-\text{OH}$ group. It can, therefore, be represented as HL



The proton-ligand formation numbers (\bar{n}_A) were calculated by Irving and Rossotti's expression⁹. pK values (proton-ligand stability constants) were calculated from the formation curves between pH vs. \bar{n}_A by noting the pH at which $\bar{n}_A = 0.5$ (half integral method). The accurate values of pK were determined by pointwise calculations which are represented in Table-1.

It could be seen from Table-1 that there is reduction in pK values of Ligand No. 1 and Ligand No. 3, This may be due to the fact of presence of bromo ($-\text{Br}$) electron withdrawing group.

Metal-ligand stability constants: The stepwise formation constants of Pr^{3+} , Nd^{3+} , Eu^{3+} , Sm^{3+} and Tb^{3+} metal ions with Ligand No. 1-3 in 70% methanol-water mixture were determined. The values of $\log K_1$ and $\log K_2$ were directly computed from the formation curves (\bar{n} vs. pL) using half integral method. The most accurate values were calculated by pointwise calculations which are presented in Table-2.

The deviation between acid curve and (acid + ligand) curve showed the dissociation of $-\text{OH}$ group from ligand. The departure between (acid + ligand) curve and (acid + ligand + metal) curve started from pH 3.0 that showed the commencement of formation of complex. The change of colour from yellow to brown in the range of pH from 3 to 7 also showed the formation of complex. It could be seen from Table-2 that there is difference in $\log K_1$ and $\log K_2$ values

that showed the stepwise formation of complexes except Sm(III) and Tb(III) for Ligand No. 2 as shown in Table-3. It showed that Sm(III)-Ligand No. 2 and Tb(III)-ligand No. 2 complexes are occurring simultaneously.

TABLE-1
PROTON LIGAND STABILITY CONSTANTS OF SUBSTITUTED ISOXAZOLINE IN
70% METHANOL-WATER MIXTURE.

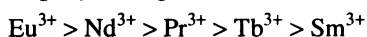
S. No.	System	Constant half integral method	pK pointwise calculation
1	3-(2-hydroxy-3-bromo-5-methyl-phenyl)-5-(3,4-dioxy-methylene) isoxazoline (Ligand No 1)	11.55	11.58 ± 0.06
2	3-(2-hydroxy-5-methyl-phenyl)-5-(4-methoxy-phenyl)-isoxazoline (Ligand No 2)	11.65	11.69 ± 0.07
3	3-(2-hydroxy-3-bromo-5-methyl-phenyl)-5-(4-methoxy-phenyl) isoxazoline (Ligand-3)	11.30	11.33 ± 0.05

TABLE-2
METAL LIGAND STABILITY CONSTANTS OF LANTHANIDES WITH SOME
SUBSTITUTED ISOXAZOLINES AT 0.1 M IONIC STRENGTH

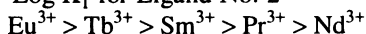
System	Constant	
	Log K ₁ <i>i.e.</i> , pL ₁	log K ₂ , <i>i.e.</i> , pL ₂
Pr(III)-Ligand-1	10.29	7.95
Nd(III)-Ligand-1	10.34	6.95
Sm(III)-Ligand-1	9.84	6.45
Eu(III)-Ligand-1	10.44	6.45
Tb(III)-Ligand-1	10.09	7.45
Pr(III)-Ligand-2	11.39	9.75
Nd(III)-Ligand-2	10.89	8.50
Sm(III)-Ligand-2	11.64	10.75
Eu(III)-Ligand-2	11.79	10.25
Tb(III)-Ligand-2	11.69	11.25
Pr(III)-Ligand-3	10.04	6.40
Nd(III)-Ligand-3	11.04	6.15
Sm(III)-Ligand-3	12.54	11.40
Eu(III)-Ligand-3	11.04	9.15
Tb(III)-Ligand-3	11.54	8.15

The relation of $\log K = a pK + b$ was also studied. The order of stability of complex is as follows.

(I) Log K₁ for Ligand No. 1



(II) Log K₁ for Ligand No. 2



(III) Log K_1 for Ligand No. 3



Same order was observed by Kadu¹⁰ for substituted pyrazolines.

TABLE-3
METAL LIGAND STABILITY CONSTANTS AT 0.1 M IONIC STRENGTH

System	log $K_1 - \log K_2$	log $K_1/\log K_2$
Pr(III)-Ligand No. 1	2.14	1.26
Pr(III)-Ligand No. 2	1.64	1.16
Pr(III)-Ligand No. 3	3.64	1.56
Nd(III)-Ligand No. 1	3.39	1.48
Nd(III)-Ligand No. 2	2.39	1.28
Nd(III)-Ligand No. 3	4.89	1.79
Sm(III)-Ligand No. 1	3.39	1.58
Sm(III)-Ligand No. 2	0.89	1.08
Sm(III)-Ligand No. 3	1.14	1.10
Eu(III)-Ligand No. 1	3.89	1.60
Eu(III)-Ligand No. 2	1.54	1.15
Eu(III)-Ligand No. 3	1.89	1.35
Tb(III)-Ligand No. 1	2.64	1.35
Tb(III)-Ligand No. 2	0.44	1.03
Tb(III)-Ligand No. 3	3.39	1.41

ACKNOWLEDGEMENT

Author's are thankful to Principal, Govt. V.M.V. Amravati and Principal G.S. College Khamsaon for providing facilities.

REFERENCES

1. A.K. Banarjee and T.V.R.K. Rao, *J. Indian Chem. Soc.*, **63**, 480 (1986).
2. M.L. Narwade, M.M. Chincholkar and S.W. Sathe, *J. Indian Chem. Soc.*, **62**, 194 (1985)
3. B.G. Khobragde and M.L. Narwade, *J. Indian Chem. Soc.*, **71**, 870 (1984).
4. Ali Ashgar, M.L. Narwade and V.S. Jamode, *Acta Ciencia Indica*, **18C**, 261 (1992).
5. P.B. Raghuvanshi, A.D. Doshi and M.L. Narwade, *Asian J. Chem.*, **8**, 211 (1996).
6. A.U. Mandakmare and M.L. Narwade, *Acta Ciencia Indica*, **16C**, 30 (1994).
7. Rabindranath and R.P. Bhatnagar, *J. Indian Chem. Soc.*, **62**, 463 (1986).
8. L.G. Van Uiert and C.G. Haas, *J. Am. Chem. Soc.*, **95**, 457 (1953).
9. H. Irving and H.S. Rossotti, *J. Indian Chem. Soc.*, **54**, 3397 (1953).
10. Manjusha Kadu, Ph.D. Thesis, Amravati University (1999).