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

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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-hydoxy-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 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 Ashgar[4] 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 UO_2(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 (1.002×10^{-2} μ); $HClO_4$ and NaOH were used of AR grade. Lanthanide metal ions were obtained from BDH and the solution of

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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 ± 0.1°C.

Titrations were 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 correction[8]

RESULTS AND DISCUSSION

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

$$HL \rightleftharpoons H^+ + L^-.$$

The proton-ligand formation numbers ($\bar{n}_A$) were calculated by Irving and Rossotti's expression[9]. 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 (—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 —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.e.*, pL_1	log K_2, *i.e.*, 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 K_1 for Ligand No. 1

$Eu^{3+} > Nd^{3+} > Pr^{3+} > Tb^{3+} > Sm^{3+}$

(II) Log K_1 for Ligand No. 2

$Eu^{3+} > Tb^{3+} > Sm^{3+} > Pr^{3+} > Nd^{3+}$

(III) Log K_1 for Ligand No. 3

$Sm^{3+} > Tb^{3+} > Nd^{3+} > Eu^{3+} > Pr^{3+}$

Same order was observed by Kadu[10] 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

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