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pH-Metric Study on Determination of Metal-Ligand Stability constants of some substituted Isoxazolines

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ABSTRACT
The interaction of Cu(II), Co(II), fe(III), Al(III) and Nd(III) with 3-(2"-hydroxy-3"-nitro-5" methylphenyl)-5-phenyl isoxazoline (Ligand-1), 3-(2"-hydroxy-3"-nitro-5"-methylphenyl)-5-(4'-methoxyphenyl)-isoxazoline(Ligand-II), 3-(2"-hydroxy-3"-nitro-5" methylphenyl)-5-(3'-nitrophenyl)-isoxazoline(Ligand-III) and 3-(2"-hydroxy-3"-nitro-5" methylphenyl)-5-(3', 4'-methylene dioxyphenyl)-isoxazoline (Ligand-IV) have been studied by spectrophotometric technique at 0.1 M ionic strenghth and (30±0.1° c) in 70 % dioxane-water mixture. The data obtained were used to estimate the values of metal-ligand stability constant of substitututed isoxazolines. Spectrophotometric investigation of Co(II), Cu(II), Fe(III), Al(III) and Nd(III) complexes with Ligand(I), Ligand (II), Ligand (III) and Ligand(IV) showed l:l and l:2 complex formation simultaneously. The information of complexes has been studied by Calvin-Bjerrum titration technique. The results obtained of stability constants are in good agreement.
Keywords: Stability Constants, Complex Formation, Ph-Metric Study, Cu(II), Co(II), Fe(III), Al(III), Nd(III) Metal-Ligand Stability Constants, Substituted Isoxazolines.

I. INTRODUCTION

2-Hydroxy substituted isoxazolines are good chelating agents due to the presence of electron donor nitrogen and oxygen atom and liberation og H^+ ion from –OH group[1,2].

In view of biological importance and analytical applications[3,4] of substituted isoxazolines, it was interesting to know the physics-chemical properties such as stabilities of complexes with Cu(II), Co(II), Fe(III), Al(III) and Nd(III) metal ions pH-metrically. Study of complexes under identical set of experimental conditions is still lacking.

All chemical such as $NaNO_3$, HNO_3 and NaOH used were of AR grade. The ligand (I-IV) were prepared by literature method[1-4] . These ligands were crystallized and their purity was checked by analytical and spectral study. 1:4 Dioxane was purified by the standard methods. The metal ions used were in the form of their nitrates, A-VSI-01 AT digital pH-meter was used for measurement of pH. Standard NaOH and 1M $NaNO_3$ solution were prepared in double distilled water.

The pH-metric titrations of (i)1×10^{-2} M HNO_3 (ii)1×10^{-2} M ligand and (iii)1×10^{-2} M HNO_3+2×10^{-3} M ligand+4×10^{-4} M metal ion solutions against carbonate free 0.1008 M NaOH were carried out by Calvin[6] – Bjerrum pH-metric titration technique in 70 % dioxane water mixture at 0.1 M ionic strength maintained by addition of appropriate quantity of 1 M $NaNO_3$ The total volume of each system was made upto 50 ml. so that the solution were 70 %(V/V) with respect to 1:4 dioxane. All titrations were carried out in the environment of oxygen free nitrogen gas. The readings were recorded for each addition of 0.2 ml. The pH-metric titration data of acid,(acid+ligand) and (acid+ligand+metal) systems were used to construct acid, ligand and metal curves between volume of NaOH added vs. pH of respective system.

***Determination of Proton ligand stability constant(pK)**
The ligand(I-IV) in the present investigation are monobasic acids having only one dissociable proton from hydroxyl group of the ligand. In general, ligands can be represented as HL and dissociated as

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

It is found that , the deviation of (acid+ligand) curves from acid curve started at about pH 4. This indicates that dissociation of hydroxyl group occurs which is present

in the ligand part of the complex structure. The proton ligand formation number (n A) were calculated by the Irving and Rossotti expression[7].

The values of pK(dissociation constant) were estimated by noting the pH at nA=0.5 which were calculated by half integral method and presented in Table-1. Most accurate values were calculated from pointwise calculations.

Table 1. DETERMINATION OF PROTON-LIGAND STABILITY CONSTANT (pK) OF SOME SUBSTITUTED ISOXAZOLINES AT 0.1 M IONIC STRNGTH AT (30±0.1)° c. TEMPARATURE.

Sr. No.	System	Constant pK	
		By half integral method	By pointwise calculation
1.	Ligand-1, 3-(2"-hydroxy-3"-nitro-5" methylphenyl))-5-phenyl isoxazoline	9.57	9.62±0.05
2.	Ligand-2, 3-(2"-hydroxy-3"-nitro-5"-methylphenyl)-5-(4'-methoxyphenyl)-isoxazoline	8.25	8.35±0.03
3.	Ligand-3, 3-(2"-hydroxy-3"-nitro-5" methylphenyl)-5-(3'-nitrophenyl)-isoxazoline	8.79	8.87±0.06
4.	Ligand-4,3 -(2"-hydroxy-3"-nitro-5" methylphenyl)-5-(3', 4'-methylene dioxyphenyl)-isoxazoline	8.97	9.05±0.07

It can seen from table-1 that value of ligand-1 is greater than ligand-2, ligand-3 and ligand-4. This may be due to the fact that presence of electron withdrawing nitro group near to the –OH group of respective ligand. The electron withdrawing group reduces the pK value of the ligand.

***Determination of metal-ligand Stability constants(log K)**

The deviation of (acid+ligand) curves from (acid+ligand+metal) curves were observed at about 2.7 pH in media of 70 % dioxane-water mixture. This indicates the commencement of complex formation from this pH. During titration process there is colour change of solution from pale yellow to orange. This indicates the formation of complex between ligand and metal ion. The value of metal-ligand formation number (n) were evaluated by the Irving-Rosotti's expression. The values are presented in Table 2.

Table 2. DETERMINATION OF METAL-LIGAND STABILITY CONSTANTS (Log K) OF METAL COMPLEXES WITH LIGAND(I), LIGAND(II), LIGAND(III), AND LIGAND(IV) AT 0.1 M IONIC STRENGTH AND AT (30±0.1)° C TEMPERATURE.

Sr. No.	System	Constant	Constant
		Log K1	Log K2
1.	Cu(II) Ligand (I)	6.35	5.95
	Co(II) Ligand(I)	9.78	9.37
	Fe(III) Ligand(I)	10.11	9.74
	Al(III) Ligand(I)	9.15	8.63
	Nd(III) Ligand(I)	8.65	7.90
2.	Cu(II) Ligand (II)	8.65	8.17
	Co(II) Ligand(II)	8.57	8.09
	Fe(III) Ligand(II)	8.03	7.37
	Al(III) Ligand(II)	8.51	8.07
	Nd(III) Ligand(II)	7.55	6.95
3.	Cu(II) Ligand (III)	7.55	6.67
	Co(II) Ligand(III)	8.67	7.71
	Fe(III) Ligand(III)	8.53	8.17
	Al(III) Ligand(III)	8.37	7.41
	Nd(III) Ligand(III)	7.69	6.57
4.	Cu(II) Ligand (IV)	7.55	6.85
	Co(II) Ligand(IV)	8.57	7.77
	Fe(III) Ligand(IV)	8.35	7.45

	Al(III) Ligand(IV)	8.75	7.87
	Nd(III) Ligand(IV)	7.73	5.65

It could be seen from table 2 that there is slight difference between the values of log K_1 and log K_2. This indicates the stepwise complex formation between ligand and metal ion. The order of stability constant of complexes is represented as,

i) For ligand(I)

Fe(III)>Co(II)>Al(III)>Nd(III)>Cu(II)

ii) For ligand(II)

Cu(II)>Co(II)>Al(III)>Nd(III)>Fe(III)

iii) For ligand(III)

Co(II)>Fe(III)>Al(III)>Cu(II)>Nd(III)

iv) For ligand (IV)

Al(III)>Co(II)>Fe(III)>Nd(III)>Cu(II)

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