Asian Journal of Chemistry Vol. 18, No. 1 (2006), 750–752

NOTE

pH-Metric Study on Determination of Metal-Ligand Stability Constants of Some Substituted Isoxazolines

N.N. PAWAR* and A.G. DOSHI†

Department of Chemistry, Shri Shivaji College, Akola-444 001, India

The interaction of Cu(II), Co(II), Fe(III), Al(III) and Nd(III) with 3-(2-hydroxy-5-chlorophenyl)-5-(4-methoxy phenyl) isoxazoline (1), 3-(2-hydroxy-3-nitro-5-chlorophenyl)-5-(4-methoxy phenyl) isoxazoline (2) and 3-(2-hydroxy-3-bromo-5-chlorophenyl)-5-(4-methoxy phenyl) isoxazoline (3) have been studied by Calvin-Bjerrum titration technique in media of 70% dioxane-water mixture at 0.1 M ionic strength and at (30 ± 0.1°C) temperature. It is observed that the formation of 1 : 1 and 1 : 2 complexes is occurring simultaneously.

Key Words: pH-metric study, Cu(II), Co(II), Fe(III), Al(III), Nd(III), Metal-ligand stability constant, Substituted isoxazolines.

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

In view of analytical applications and biological importance[3, 4] of substituted isoxazolines, it was interesting to know the physico-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 chemicals such NaOH, HNO_3, $NaNO_3$ were of AR grade. The ligands (1–3) were prepared by literature method[1–4]. These ligands were recrystallized and their purity was checked by analytical and spectral study. 1 : 4 Dioxane was purified by the standard method[5]. 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 1 M $NaNO_3$ solutions were prepared in double distilled water.

The pH-metric titrations of (i) 1×10^{-2} M HNO_3, (ii) 1×10^{-2} ligand, and (iii) 1×10^{-2} M $HNO_3 + 2 \times 10^{-3}$ 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 up to 50 mL, so that the solutions 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

†Department of Chemistry, Vidya Bharati College, Amravati-444 602, India.

+ 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 ligands (**1–3**) used 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 numbers ($\bar{n}A$) were calculated by the Irving and Rossotti's expression[7].

The values of pK (dissociation constant) were estimated by noting the pH at $\bar{n}A = 0.5$ 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 STRENGTH AND AT (30 ± 0.1)°C TEMPERATURE

Sr. No.	System	Constant pK	
		By half integral method	By pointwise calculation
1.	Ligand **1** 3 (2-Hydroxy-5-chlorophenyl)-5-(4-methoxyphenyl) isoxazoline	9.50	9.55 ± 0.04
2.	Ligand **2** 3-(2-Hydroxy-3-nitro-5-chlorophenyl)-5-(4-methoxyphenyl) isoxazoline	8.20	8.32 ± 0.02
3.	Ligand **3** 3-(2-Hydroxy-3-bromo-5-chlorophenyl)-5-(4-methoxyphenyl) isoxazoline	8.70	8.75 ± 0.06

It can be seen from Table-1 that pK value of ligand **1** is greater than ligand **2** and ligand **3**. This may be due to the fact that —NO_2 group in ligand **2** and —Br group in ligand **3** is present as electron withdrawing 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 deviations of (acid + ligand) curves from (acid + ligand + metal) curves were observed at about 2.5 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 values of metal-ligand formation number ($\bar{n}$) were evaluated by the Irving-Rossotti's expressions. The values are presented in Table-2.

TABLE-2
DETERMINATION OF METAL-LIGAND STABILITY CONSTANTS (log K) OF METAL COMPLEXES WITH LIGAND 1, LIGAND 2 AND LIGAND 3 AT 0.1 M IONIC STRENGTH AND AT (30 ± 0.1)°C TEMPERATURE

Sr. No.	System	Constant	
		$\log K_1$	$\log K_2$
1.	Cu(II) Ligand 1	6.32	5.92
	Co(II) Ligand 1	9.88	9.33
	Fe(III) Ligand 1	10.13	9.81
	Al(III) Ligand 1	9.13	8.60
	Nd(III) Ligand 1	8.61	7.86
2	Cu(II) Ligand 2	8.63	8.20
	Co(II) Ligand 2	8.59	8.06
	Fe(III) Ligand 2	8.07	7.33
	Al(III) Ligand 2	8.48	8.02
	Nd(III) Ligand 2	7.52	6.98
3	Cu(II) Ligand 3	7.52	6.65
	Co(II) Ligand 3	8.69	7.75
	Fe(III) Ligand 3	8.51	7.13
	Al(III) Ligand 3	8.38	7.39
	Nd(III) Ligand 3	7.69	6.60

It could be seen from Table-2 that there is a 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 1 Fe(III) > Co(II) > Al(III) > Nd(III) > Cu(II).

(ii) For ligand 2 Cu(II) > Co(II) > Al(III) > Nd(III) > Fe(III).

(iii) For ligand 3 Co(II) > Fe(III) > Al(III) > Cu(II) > Nd(III).

AKNOWLEDGEMENTS

The authors are thankful to Principal, Vidya Bharati College, Amravati and Principal, Shri Shivaji College, Akola for providing necessary facilities.

REFERENCES

1. P.B. Raghuwanshi, A.G. Doshi and M.L. Narwade, *J. Indian Chem. Soc.*, **73**, 21 (1996).
2. P.R. Athappan, P. Shanthi and C. Natrajan, *Indian J. Chem.*, **34**, 648 (1995).
3. G.F. Duffin and J.D. Kendall, *J. Chem. Soc.*, 405 (1954).
4. Z.H. Khalil and A.S. Yanni, *J. Indian Chem. Soc.*, **58**, 168 (1981).
5. A.I. Vogel, A Text Book of Practical Organic Chemistry, Longmans, London (1966).
6. M. Calving and N.C. Melchior, *J. Chem. Soc.*, **70**, 3270 (1948).
7. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 3397 (1953).

(*Received*: 2 April 2005; *Accepted*: 27 October 2005) AJC-4480