



ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(3):77-82

Studies in Formation Constant of Al(III), Cr(III) and Fe(III) Complexes with Some Substituted Isoxazoline, Pyrazole and Pyrazoline pH-metrically, Spectrophotometrically and Polarizability Constant Refractometrically

U. P. Meshram*¹, B. G. Khobragade², M. L. Narwade³ and A. R. Yaul¹

¹Department of Chemistry, Model Arts, Commerce & Science College, Karanja (Ghadge), Dist. Wardha (M.S.)

²P.G. Department of Chemistry, Government Vidarbha Institute of Science & Humanities, Amravati, India

³Department of Chemistry, Vidyabharti Mahavidyalaya, Amravati (M.S.), India

ABSTRACT

Spectrophotometric investigation of Cr(III), Fe(III) and Al(III) complexes with 3-(2-hydroxyl-4-methyl phenyl)-5-phenyl isoxazoline (L_1), 1-phenyl-3-(2-hydroxy-3-bromo-4-methyl phenyl)-5-phenyl pyrazole (L_2), 1-phenyl-3-(2-hydroxy-3-nitro-4-methyl phenyl)-5-phenyl pyrazoline (L_3), 1-phenyl-3-(2-hydroxy-3-nitro-4-methyl phenyl)-5-phenyl pyrazoline (L_4), 3-(2-hydroxyl-3-nitro-4-methyl phenyl)-5-phenyl isoxazole (L_5) showed 1:1 and 1:2 complex formation between the pH range of 3.0 to 6.0 studied by Job's variation method at 0.1M ionic strength and 30°C \pm 1°C spectrophotometrically. The conditional stability constants are determined for 1:1 complexes at about pH 3.0 and molar refraction and polarizability constant for L_2 , L_4 & L_5 at different percentage of dioxane are calculated.

Key words : Isoxazolines, Pyrazole, Pyrazoline, Dioxane solvent, Spectrophotometer, Refractometer.

INTRODUCTION

In view of analytical applications and antibiotic drugs as isoxazoline, pyrazole, pyrazoline which act as a ligand and are selected in the present investigation.

The metal chelates of hydrazo-dimedone dyes are studied by Atef et al [1]. Conditional stability constants of transition metal ions with some amino acid peptides have been studied by Sondawale and Narwade [2]. Sunita and Gupta [3] have worked on spectrophotometric

determination of cyanide in biological complex using a new reagent. Narwade et al [4] have studied Fe(III) complexes with some substituted chalcones spectrophotometrically. Raghuwanshi et al [5] have shown 1:1 and 1:2 complex formation of Cu(II), Ni(II) and Co(II) with some substituted chalcones and isoxazoline potentiometrically. Meshram et al [6-8] have investigated metal ligand with some substituted isoxazolines by spectrophotometric and pH-metric techniques. Acoustical properties of peptides have been studied in 20% methanol-water mixture by Sondawale et al [9]. Raut et al [10] studied the conditional stability constant and confirmation of complex formation of Cu(II), Ni(II) and Co(II) complexes with captopril spectrophotometrically. Spectrophotometric determination of Ni(II) with 2-hydroxy-3-methoxybenzaldehyde thiosemicarbazone was investigated by Praveenkumar et al [11]. Metal-ligand stability constant of Cu(II) complex has been studied by Pethe et al [12].

The study of conditional stability constants of transition metal ion complexes with antibiotic drugs. Isoxazoline, pyrazole and pyrazoline with Fe(III), Al(III) and Cr(III) is still lacking, therefore, the present work has been undertaken to study the complex formation and their confirmation. The present work has been carried out by using Job's method.

The properties of liquid such as viscosity, refractive index and ultrasonic speed of binary mixtures are studied by many workers [13-19]. Oswal et al [20] have studied dielectric constants and refractive indices of binary mixtures. Mahajan [21] have studied molar refraction and polarizability constant of 2-amino-5-chlorobenzene sulphonic acid in different percentage of dioxane-water mixture. Study of refractive indices in mixed solvents is done by Burghate et al [22]. The measurement of viscosity and refractive index with some substituted pyrazoles and diketones at 0.1 M strength has been done by Pethe et al [12]. Refractometric study on molecular interaction between some bromoalkane and non-polar hydrocarbon is studied by Yadav [23].

EXPERIMENTAL SECTION

Isoxazoline, pyrazole and pyrazoline are antibiotic drugs having many applications for living things. It has been synthesized in laboratory by standard method. The Nitrate salts of aluminium and iron and chromium and potassium nitrate (BDH) were used and their solutions were prepared in double distilled water (0.01 M). The solutions of potassium nitrate were prepared (0.1 M) and used for maintaining ionic strength constant. Systronic Spectrophotometer No. 108 was used for measuring absorption of solution.

The solution of ligand L₁, L₂, L₄ in different percentages of dioxane-water mixture were prepared by weight. All weighing were made on Mechaniki Zaktady Precyzyjng Gdansk Balance, made in Poland (± 0.001 gm). The accuracy of density measurements was within 0.1% kgm⁻³. The refractive indices of solvent mixture and solutions were measured by Abbe's refractometer. The accuracy of Abbe's refractometer was within ± 0.001 unit. The temperature of the prism box was maintained constant by circulating water from thermostat maintained at 30 (± 0.1 °C). Initially, the refractometer was calibrated with glass piece ($n = 1.5220$) provided with the instrument.

The molar refraction of solvent, dioxane-water mixtures are determined from –

$$R_{D-w} = X_1R_1 + X_2R_2$$

where, R₁ and R₂ are molar refraction of dioxane and water respectively.

The molar refraction represents actual or true volume of the substance molecules in 1 mole. The molar refraction of solutions of ligand in dioxane-water mixture is determined from –

$$R_{\text{Mixture}} = [(n^2 - 1)/(n^2 + 2)] \{[X_1M_1 + X_2M_2 + X_3M_3]/d\}$$

where, n is the refractive index of solution, X_1 is mole fraction of dioxane, X_2 is mole fraction of water, X_3 is mole fraction of solute, M_1 , M_2 and M_3 are molecular weights of dioxane, water and solute respectively. 'd' is the density of solution.

The molar refraction of ligand is calculated as –

$$R_{\text{Lig.}} = R_{\text{Mixture}} - R_{\text{D-W}}$$

RESULTS AND DISCUSSION

pH-Metric :

pH-Metric work can be done with a limited aim to compare the formation constant value obtaining spectrophotometrically. The agreement between the formation constant value from above technique is found to be satisfactory (Table 1).

Table – 1: Metal-Ligand Stability Constants by Different Methods

System	Constants	Method	
		Half Integral	Pointwise
Cr(II) - Ligand (L ₁)	log K ₁	3.8965	3.7706
	log K ₂	2.7197	3.1207
Al(III) - Ligand (L ₁)	log K ₁	4.297	5.1449
	log K ₂	4.0195	4.3738
Fe(III) - Ligand (L ₁)	log K ₁	3.996	3.785
	log K ₂	2.318	2.438
Cr(II) - Ligand (L ₂)	log K ₁	6.2787	5.9032
	log K ₂	4.3010	4.5774
Fe(III) - Ligand (L ₂)	log K ₁	7.496	7.0565
	log K ₂	6.000	4.888
Al(III) - Ligand (L ₃)	log K ₁	6.5468	6.4901
	log K ₂	4.1172	4.3284

The difference between log K₁ and log K₂ is smaller in some of the systems. It seems, therefore, that both the 1:1 and 1:2 complexes are formed simultaneously and not in a stepwise process.

For each system the pH values at which metal complex formation started and hydrolysis commenced have been tabulated and data are presented in Table 2.

Table – 2

Metal Ion	pH at the commencement of the Hydrolysis	pH at the commencement of complete formation
Fe(III)	6.5	5.90
Cr(III)	5.5	5.10
Al(III)	5.8	5.00

Spectrophotometric Measurement :**Job's Method :**

Jobs variation method was used to know the nature of complexes. The compositions of metal ion solution (1×10^{-2} M) and ligand (20×10^{-2} M) were prepared in series. Ionic strength was maintained constant (0.1 M) by adding an appropriate amount of 1 M KNO_3 solution in 10 ml volume. λ_{max} was determined using one of the composition at which there is maximum absorption.

The absorption for all the compositions were recorded at a constant wavelength (λ_{max}). The data of absorption and percentage composition of metal ion and ligand solution at constant pH can be used and curves were constructed.

It was observed that 1:1 complex formation curve occur in pH range of 3 to 4 and 1:2 complex formation in the pH range of 4 & 5. Each solution is diluted up to 15 ml and recorded absorptions at same (λ_{max}). Conditional stability constants of metal-ligand complexes were calculated for all the systems using following equation.

$$K = \frac{X}{(a_1-x)(b_1-x)} = \frac{X}{(a_2-x)(b_2-x)}$$

K = Conditional stability const. of complex

x = Concentration of complex

a_1 & a_2 = Concentration of metal ions

b_1 & b_2 = Concentration of ligand

Conditional stability constant of metal-ligand complexes were calculated and presented in table 3.

Table - 3 : Determination of conditional stability of metal-ligand complex

System	Concentration of complex (x) mole lit^{-1}	Conditional stability constant (K)	log K
1) Al(III) - L_2	2.8939×10^{-3}	1.2256×10^{-3}	0.0883
2) Fe(III) - L_1	2.9775×10^{-3}	2.514780×10^{-3}	0.4004
3) Cr(III) - L_3	2.91666×10^{-3}	1.263528×10^{-3}	0.10158
4) Cr(III) - L_1	2.91509×10^{-3}	1.462208×10^{-3}	0.16500

The conditional stability constants are found to be smaller than real stability constants.

The conditional stability constants are found to be slightly smaller than real stability constants, this is because of the concentration of free acid at particular pH was not taken into account and may be due to variation in temperature.

Al(III), Cr(III) and Fe(III) act hard acids and forms 1:1 complexes in the pH range 2.5 to 3.5. Stability constant depends upon the size of cations. It could be seen from table-1 that reduction in the value of stability constant of Al(III) complexes is due to its smaller cationic size as compared to cationic size of Cr(III) and Fe(III). The order of stability constant is presented as

$\text{Al(III)} < \text{Cr(III)} < \text{Fe(III)}$

Table - 4: Molar refraction and polarizability constant for L₁, L₂ and L₄ at different percentage of Dioxane

% of Dioxane	Ligand - L ₂		Ligand - L ₄		Ligand - L ₅	
	[R] cm ³ mole ⁻¹	$\alpha \times 10^{-23}$ mole ⁻¹	[R] cm ³ mole ⁻¹	$\alpha \times 10^{-23}$ mole ⁻¹	[R] cm ³ mole ⁻¹	$\alpha \times 10^{-23}$ mole ⁻¹
65%	2.514762	0.0997277	2.4829381	0.0984639	2.957062	0.1172680
70%	2.504169	0.0993076	2.4882516	0.0986764	2.504169	0.0993076
75%	2.957062	0.1172680	2.498867	0.0999074	2.498867	0.0990974
80%	2.514762	0.0997277	2.5094680	0.0995151	2.509468	0.0995178
85%	2.514762	0.0997277	2.514762	0.0997272	2.498867	0.0990974
90%	2.640711	0.1047225	2.488251	0.0989676	2.450978	0.0971982
92.5%	2.450978	0.0971982	2.477620	0.0982548	2.461646	0.0976220

The polarizability constant (α) of ligand is calculated from the following relation,

$$R_{\text{Lig.}} = (4/3) \pi N_0 \alpha$$

where, N_0 is Avogadro's number.

The value of molar refraction and polarizability constants of ligand L₂, L₄ and L₅ in different percentage of dioxane-water mixture are represented in Table 4. It shows that with increase in percentage of dioxane, the molar polarizability constant of ligand increases but there is no regular order of molar refractivity with increase in percentage of dioxane-water mixture. This may be due to the fact of effect of bulky solvent dioxane.

This may be attributed to the fact that the dipole in the ligand lies perpendicular to the longer axis of the molecules and with increase in the percentage of dioxane causing decrease in dielectric constant of medium, considerable dipole association (inter molecular attraction) takes place which would be accompanied by increase in polarizability constant because of mutual compensation of the dipoles.

Acknowledgement :

The authors are very thankful to the Director and Head of Chemistry Department, Govt. Vidarbha Institute of Science & Humanities, Amravati.

REFERENCES

- [1] A Atef & T Ramdas. *Asian J. Chem.*, **1987**, 4, 457.
- [2] PJ Sondawale & ML Narwade. *Oriental J. Chem.*, **1997**, 13(1), 41.
- [3] S Sunita & VK Gupta. *J. Ind. Chem. Soc.*, **1987**, 64, 431.
- [4] ML Narwade; SW Sathe & MM Chincholkar. *J. Ind. Chem. Soc.*, **1985**, 62, 194.
- [5] PB Raghuvanshi; AG Doshi & ML Narwade. *Acta Ciencia Indica*, **1993**, 19C, 18.
- [6] YK Meshram; AU Mandakmare & ML Narwade. *Oriental J. Chem.*, **1999**, 15(3), 531.
- [7] YK Meshram & ML Narwade. *Asian J. Chem.*, **2000**, 12(2), 493.
- [8] YK Meshram & ML Narwade. *Acta Ciencia Indica*, **2001**, XXIIC (1), 3.
- [9] SD Chachere; PJ Sondawale & ML Narwade. *Ultra Scientist of Physical Sciences*, **2001**, 13(2), 210.
- [10] AR Raut; AD Khamre; SA Ikhe; SN Quazi & ML Narwade. *Ultra Science*, **2004**, 16(2), 203-206.
- [11] A Praveenkumar; Ravindra Reddy & Krishna Reddy. *Indian J. Chem.*, **2007**, 46A, 1630-1634.
- [12] GB Pethe; AA Ramteke; TR Lawankar; DT Mahajan & ML Narwade. *J. Chem. Pharma. Res.*, **2010**, 2(4), 68-74.

-
- [13] SK Raikar; TM Aminabhavi; SB Harogoppad & RH Balundgi. *Ind. J. Tech.*, **1993**, 31, 581.
[14] SS Joshi; TM Aminabhavi & SS Shukla. *Can. J. Chem.*, **1990**, 68, 319.
[15] VA Aminabhavi; TM Aminabhavi & RH Balundgi. *Ind. Eng. Chem. Res.*, **1990**, 29, 2106.
[16] SS Joshi & TM Aminabhavi. *Fluid Phase Equil.*, **1990**, 60, 319.
[17] SS Joshi; TM Aminabhavi; RH Balundgi & SS Shukla. *J. Chem. Eng. Data*, **1990**, 35, 185.
[18] MI Aralaguppi; TM Aminabhavi; RH Balundgi & SS Joshi. *J. Phys. Chem.*, **1991**, 95, 5299.
[19] AS Burghate; PB Agrawal; SW Quazi & ML Narwade. *Asian J. Chem.*, **2001**, 13(4), 1652.
[20] SL Oswal & MV Rathnam. *Ind. J. Chem.*, **1987**, 26, 29.
[21] DT Mahajan. Ph.D. Thesis in Chemistry Submitted to Amravati University, Amravati, **1997**.
[22] AS Burghate; PB Agrawal; SW Quazi & ML Narwade. *Asian J. Chem.*, **2001**, 13(4), 1652.
[23] SS Yadav; Anirudh Yadav; Neetu Kushwaha & Neetu Yadav. *Indian J. Chem.*, **2009**, 48A, 650-657.