



Studies in metal-ligand stability constants of the pyrazoles complexes with some lanthanide metal ions pH-metrically and spectrophotometrically

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ABSTRACT

Chloro substituted pyrazoles such as 3-(2'-Hydroxy-5'chlorophenyl)-4-(4'-chlorobenzoyl)-5-(4'-N,N-dimethyl aminophenyl)-1-phenyl pyrazole (L_1), 3-(2'-Hydroxy-5'chlorophenyl)-4-(4'-chlorobenzoyl)-5-(3',5'-dimethoxy-4'-hydroxy phenyl)-1-phenyl pyrazole (L_2) and 3-(2'-Hydroxy-3'nitro-5'-methylphenyl)-4-(4'-chlorobenzoyl)-5-(4'-N,N-dimethyl aminophenyl)-1-phenyl pyrazole (L_3) are synthesized in laboratory. The interaction of the above substituted pyrazoles have been studied with Nd (III), Pr(III) and Sm(III) and Metal -ligand stability constants have been evaluated in 70 % dioxane-water mixture at 0.1 ionic strength.

Keywords: Antibiotic drugs, Lanthanide metal ions, Dioxane.

INTRODUCTION

In view of medicinal and analytical application of substituted pyrazoles which act as antibiotic drugs and good chelating agents are undertaken to study their physical characters first by Knorr and Bank [1]. This has led to the considerable commercial interest in pyrazole and pyrazoline as optical brightening agents for textile paper and fabrics [2]. In medicines, pyrazoles and pyrazolines are used for their antiaggregation [3], antidepressant [4], antiarthritic [5], antidiabetics [6] and antibacterial [7] activities. Beam [8] synthesized some new pyrazoles derivatives and reported their antifungicidal activities. Pratibha Agrawal [9] has determined metal-ligand stability constants of some carbamide complexes in solution at 0.1M ionic strength. Gulwade et al [10] have studied ultrasonic behavior of some azoles at different temperatures. Solanki and Narwade [11] have synthesized some substituted pyrazoles and studied their physical characters in 70% dioxane-water mixture. Fukude et al [12] have studied formation constants and showed that constants decreased with increasing size of the metal cations.

Meshram et al [13] have studied the acoustical parameters of some substituted Isoxazolines and effect on seed germination in 70% dioxane-water mixture. Rafique [14] has studied the metal-ligand stability constants of some substituted azoles and observed the phenomenon. Vandana Khobragade et al [15] have studied ultrasonic behavior of some hydroxylacid in dioxane-water and DMF-water mixtures at 303.15 °K. No work has been done on Metal-ligand stability constants of some substituted pyrazoles with Lanthanides Metal ions pH-metrically at 0.1M ionic strength. Therefore, the study of metal -ligand stability constants of some substituted pyrazoles with some Lanthanides Metal ions has been undertaken for making systematic study at 0.1 M ionic strength pH-metrically.

EXPERIMENTAL SECTION

Material and Methods : In the present investigation following antibiotic drugs (pyrazoles) and metal ions are used.

• **Ligands (antibiotic drugs)**

1. 3-(2'-Hydroxy-5'chlorophenyl)-4-(4'-chlorobenzoyl)-5-(4'-N,N-dimethylaminophenyl)-1-phenyl pyrazole (L_1)

2. 3-(2'-Hydroxy-5'chlorophenyl)-4-(4'-chlorobenzoyl)-5-(3',5'-dimethoxy-4'-hydroxyphenyl)-1-phenyl pyrazole (L_2)

3. 3-(2'-Hydroxy-3'-nitro-5'-methylphenyl)-4-(4'-chlorobenzoyl)-5-(4'-N,N-dimethylaminophenyl)-1-phenyl pyrazole (L₃).

• **Metal ions** Nd(III), Pr (III) and Sm (III).

• 1 M KNO₃ solution, 0.1 M HNO₃ solution, 0.2M NaOH and 0.01M Lanthanide metal ions solution are prepared in double distilled water .

• 0.01 M Pyrazole solution in 70% dioxane –water mixture.

• **Calvin –Bjerrum titration methods**

Titration are carried out pH-metrically (pHmeter with model E614 accuracy ± 0.05 unit) at $27 \pm 0.1^\circ\text{C}$ in 70% dioxane-water mixture and at an inert atmosphere by bubbling nitrogen gas .

Ionic strength is maintained constant by adding an appropriate amount of 1M KNO₃ solution.

General procedure : Types of Titrations

1. Acid titration : 5ml HNO₃(0.1M)+ 5ml KNO₃(1M) +35ml dioxane +5ml water
(A) (V₀=50ml)

2. Ligand titration : 5ml HNO₃(0.1M)+5ml KNO₃(1M) +10ml ligand (in dioxane)+ 25 ml dioxane +5ml water
(A+L) (V₀=50ml)

3. Metal Titration : 5ml HNO₃(0.1M)+ 5ml KNO₃(1M) +10ml ligand (in dioxane) + 20ml dioxane+2ml metal ion solⁿ+ 3ml water.
(A+L+M) (V₀ =50ml)

All three solutions are titrated against 0.2 M NaOH solution , and titration data are used to construct the curves between volume of NaOH and pH values.

Detection Method :

Titration curves are used to estimate the values of \bar{n}_A (proton -ligand formation numbers) which are presented in Table(1) to(3) . **Formation curve** are constructed between \bar{n}_A values and pH. The pH values at 0.5 \bar{n}_A values corresponds the pK values (proton-ligand dissociation constants) of respective ligand. Proton ligand dissociation constants (pK values) are evaluated and presented in Table(4), which are calculated by Half Integral and Pointwise calculations method.

RESULTS AND DISCUSSION

The (acid +ligand) curves deviated from acid curves at pH 4.0 and continued up to pH 12.0. It clearly indicated the dissociation of ⁻OH.



Metal ligand stability constants :

Metal ion hydrolysis : The pH at which metal ion starts hydrolyzing should be known to as certain the complex formation with the ligand . The formation of hydroxide M(OH) is given by equation



It may cause deviation of metal titration curve even in absence of the reagent . The departure of metal complex titration curve is observed always at lowest pH values than the pH of hydrolysis . This indicated the complex formation before hydrolysis of metal ion.

Formation curves : The departure of metal titration curve from ligand curve (acid + ligand) is found from pH 2.95 and increased upto pH 11.0. This showed the commencement of complex formation. The change in colour also indicated the formation of complex.

The values of \bar{n} (Metal-ligand formation number) are evaluated by applying Irving-Rossotti's expression presented in Table (5, 6, 7) for respective systems. Metal-ligand stability constants of complex are determined by applying Irving-Rossotti's expression as shown in the Table (8).

TABLE 1: Determination of \bar{n}_A values System L₁

pH	V ₁	V ₂	$\Delta V=V_2-V_1$	\bar{n}_A
6.4	2.12	2.14	0.02	0.8597
6.6	2.16	2.24	0.08	0.7384
6.8	2.18	2.30	0.12	0.7585
7.0	2.22	2.36	0.14	0.7085
7.2	2.24	2.40	0.16	0.5930
7.4	2.25	2.45	0.20	0.5579
7.6	2.26	2.48	0.22	0.5177
7.8	2.26	2.50	0.24	0.4977
8.0	2.28	2.54	0.26	0.4579

TABLE 2: Determination of \bar{n}_A values System L₂

pH	V ₁	V ₂	$\Delta V=V_2-V_1$	\bar{n}_A
6.4	2.6	2.62	0.02	0.8187
6.6	2.64	2.68	0.04	0.7969
6.8	2.70	2.78	0.08	0.6752
7.0	2.72	2.82	0.10	0.5942
7.2	2.74	2.90	0.16	0.5216
7.4	2.76	2.90	0.16	0.4937
7.6	2.77	2.98	0.21	0.4731
7.8	2.78	2.00	0.22	0.4326
8.0	2.80	2.04	0.24	0.4126

TABLE 3: Determination of \bar{n}_A values System L₃

pH	V ₁	V ₂	$\Delta V=V_2-V_1$	\bar{n}_A
6.4	2.60	2.62	0.02	0.7969
6.6	2.64	2.68	0.04	0.6525
6.8	2.70	2.78	0.08	0.5335
7.0	2.72	2.82	0.10	0.4803
7.2	2.74	2.90	0.16	0.4465
7.4	2.76	2.96	0.20	0.4135
7.6	2.77	2.98	0.21	0.4055
7.8	2.78	2.00	0.22	0.3985
8.0	2.80	2.04	0.24	0.3505
8.2	2.81	2.06	0.25	0.3155

TABLE 4 : Proton –Ligand stability Constants (pk values)

Systems	pk values Half integral method	pk values pointwise calculation
Ligand L ₁	7.65	7.70 ± 0.05
Ligand L ₂	7.15	7.05 ± 0.06
Ligand L ₃	6.45	6.25 ± 0.03

TABLE 5 : Determination of Metal –ligand formation number (\bar{n}) System- Nd(III)-L₁ Complex

pH	V ₂	V ₃	$\Delta V'$	$\bar{n}_A \eta$
2.6	1.83	1.86	0.03	0.3018
2.8	1.86	1.90	0.04	0.4040
3.0	1.89	1.94	0.05	0.5058
3.2	1.92	1.98	0.06	0.6067
3.4	1.97	2.04	0.07	0.7071
3.6	2.01	2.10	0.09	0.9084
3.8	2.04	2.40	0.10	1.008
4.0	2.04	2.16	0.12	1.2106
4.2	2.07	2.22	0.15	1.5123
4.4	2.07	2.24	0.17	1.7140
4.6	2.10	2.28	0.18	1.8138

TABLE 6 : Determination of Metal –ligand formation number (n) System- Pr(III)-L₁ Complex

pH	V ₂	V ₃	$\Delta V'$	n
3.00	1.92	1.94	0.02	0.202
3.20	1.96	2.00	0.04	0.4041
3.40	1.99	2.04	0.05	0.5049
3.60	2.02	2.10	0.08	0.8023
3.80	2.03	2.12	0.09	0.9081
4.0	2.06	2.16	0.10	1.0080
4.20	2.08	2.19	0.11	1.1082
4.40	2.11	2.23	0.12	1.2083
4.60	2.13	2.26	0.13	1.3079
4.80	2.14	2.28	0.14	1.4075
5.0	2.18	2.34	0.16	1.5071
5.2	2.22	2.40	0.18	1.6350

TABLE 7 : Determination of Metal –ligand formation number (n) System- Sm(III)-L₁ Complex

pH	V ₂	V ₃	$\Delta V'$	n
3.78	0.92	0.94	0.02	0.2033
3.82	0.93	0.97	0.04	0.4054
3.90	0.94	0.99	0.05	0.5085
4.00	0.94	1.01	0.07	0.7106
4.10	0.985	1.03	0.08	0.8119
4.30	0.96	1.05	0.09	0.9081
4.30	0.96	1.06	0.10	1.0131
4.40	0.97	1.10	0.13	1.3072
4.50	0.98	1.12	0.14	1.4172
4.60	0.99	1.14	0.15	1.5199
4.70	1.00	1.16	0.16	1.6191

TABLE 8 : Metal –ligand Stability Constants of Binary Complexes

System of complex	Stability constants	
	log k ₁ 1:1 complex	log k ₂ 1:2 complex
Nd(III)-L ₁	6.35	6.00
Nd(III)-L ₂	6.05	5.55
Nd(III)-L ₃	6.15	5.25
Pr(III)-L ₁	5.95	5.15
Pr(III)-L ₂	5.50	4.45
Pr(III)-L ₃	5.40	4.30
Sm(III)-L ₁	5.10	4.00
Sm(III)-L ₂	5.25	4.15
Sm(III)-L ₃	5.35	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 KNO₃ 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 -9 : Determination of conditional stability of metal-ligand complex

System	Concentration of complex (x) mole lit ⁻¹	Conditional stability constant (K)	log K
1) Nd(III) – L ₁	3.6929×10^{-3}	2.1256×10^{-3}	0.0963
2) Pr(III) – L ₂	3.6775×10^{-3}	2.414750×10^{-3}	0.6204
3) Sm(III) - L ₃	3.62661×10^{-3}	3.035528×10^{-3}	0.20178
4) Sm(III) – L ₃	3.41507×10^{-3}	3.232214×10^{-3}	0.38510

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.

Nd(III), Pr(III) and Sm(III) act hard acids and form 1:1 complexes in the pH range 2.5 to 3.5. Stability constant depends upon the size of cations.

Nd(III) < Pr(III) < Sm(III)

CONCLUSION

It could be seen from Table (8), that there is no an appreciable difference between log k_1 and log k_2 values . This indicated the formation of 1:1 and 1:2 complex simultaneously. It means antibiotic ligands used are found to be weak complexing agents. The change in the colour w.r.t. pH value of solution and deviation of ligand curve from metal ion curve also show the commencement of complex formation.

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