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Determination of stability constants of Pr(III) and Nd(III) chelates with some substituted pyrazoles

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ABSTRACT

The reaction of Pr(III) and Nd (III) metal ions with L_1 : 3 (2'- chlorophenyl) - 4- benzoyl - 5 (2-hydroxy phenyl) pyrazole, L_2: 3 (2'-chlorophencyl) - 4- pyridoyl -5 (2-hydroxy phenyl) pyrazole , L_3: 3 (2'-aminophenyl)- 4-pyridoyl - 5 (2- hydroxyl phenyl) pyrazole and L_4: 3 (4'-chlorophenyl) - 4- Benzoyl - 5 (2-hydroxy-phyenyl) pyrazole, have been studied pH-metrically at 0.1M ionic strength at 28 ± 0.1^{0}C in 70% ethanol -water mixture. The data obtained were used to estimate the values of proton-ligand (pK) and metal-ligand (logK) stability constants. It is observed that Pr(III) and Nd(III) metal ions formed 1:1 and 1:2 complexes with all the ligands.

Key words: Substituted pyrazole, stability constants, chelates.

INTRODUCTION

Pyrazoles are fall in the class of aromatic heterocyclic compounds, and unique structural feature involving pyrazoles nitrogen and make them interesting ligands. Pyrazoles are the good complexing agent[1-3]. The metal ligand stability constants of transition metal ions complexes with some substituted pyrazoles and pyrazolines have been reported[4]. The influence of ionic strength on the stability constants of transition and lanthanide metal ions complexes with substituted pyrazoles reported by Agrawal *et al.,*[5]. Sawalkahe *et al.,*[6] have studied the interaction on metal ions with 1,3 diketones, pyrazoles and pyrazoline specrtophotometrcally. Stability constants of transition metal ion complexes with substituted pyrazoles was studied and observed that, ligand L_1 is better chelating agent than the ligand L_2[7]. The interactions of some lanthanide metal ions with substituted isoxazolines at 0.1M ionic strength have been reported pH metrically[8-11]. Recently ultrasound promoted synthesis of substituted pyrazoles and isoxazoles have reported[12].

The study of proton-ligand stability constants and metal-ligand stability constants of Pr(III) and Nd(III) complexes with some substituted pyrazoles is still remaining. It was therefore interesting to study the chelating properties of some substituted pyrazoles (mentioned above) under suitable condition pH metrically.

EXPERIMENTAL

Substituted pyrazoles were synthesized in the laboratory by standard method[13]. The substituted pyrazoles are insoluble in water; hence 70% ethanol-water (v/v) was used as solvent. Lanthanide metal nitrates were dissolved in double distilled water and their concentration estimated by standard method[14]. Sodium hydroxide, KNO_3, and nitric acid, used were

of AR grade. Ethanol was purified by standard method (15). pH measurement were carried out with ELICO pH meter (accuracy ± 0.05 units) using combined electrode at 28 ± 0.1^{0}C.

Calvin bjerrum titration technique

The titrations were carried out in an inert atmosphere of nitrogen. The ionic strength of solution was maintained constant by adding an appropriate amount of 1M KNO_3 solution. The values were recorded by pH meter. These values converted to [H^+] values by applying the correction proposed by Van Uitert & Hass[16].

The overall 0.1 ionic strength of solution was calculated by expression

$$\mu = \tfrac{1}{2}\sum_{i=1} C_i Z_i^2 \qquad ...(1)$$

The contribution of the other ions in addition to K^+ and NO^-_3 also taken into consideration.

RESULTS AND DISCUSSION

The titration data were used to construct the curve between volume of NaOH *vs* pH. They are called as acid titration curve, ligand titration curve and metal titration curve. The pKvalues of ligand and logK values of Pr(III) and Nd(III) complexes at various ionic strength were calculated by Irving and Rossotti's method[17].

Proton – ligand stability constants

Substituted pyrazoles may be considered as monobasic acids having one replaceable H^+ ion from phenolic -OH^- group and can therefore be represented as HL

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

The titrations data were used to construct the curve between volume of NaOH *Vs* pH. It is observed from the titration curve that the ligand curves start deviating from free acids curve at about pH – 3.50 for L_1, at about pH 2.80, at about pH 3.45 for L_3 and at about pH 2.88 for L_4. The deviation increased continuously up to pH 12.50. It indicated that OH^- group start to dissociated at about 3.50 and complete its dissociation at about pH 12.50. It can be summarized in table -01.

The average number of proton associated with the ligand ($\bar{n}$A) was determined from ligand titration curves employing the equation of Irving and Rossotti (17). The pK values were estimated from formation curves (*Vs* pH) by noting the pH, at which = 0.5. The accurate values of pK were estimated by pointwise calculations which are presented in table -02. The pK values of ligands increases in the following order.

Ligand 03 > Ligand02 > Ligand01 > Ligand 04

It could be seen from the values, the more reduction in pK values of ligand L_4 may be due to presence of chlorophenyl and benzoyl groups which act as stronger electron withdrawing groups.

Metal – ligand stability constants

Metal ligand stability constants of Pr(III) and Nd(III) complexes with some substituted pyrazoles were determined by employing Calvin-$\bar{n}$Bjerrum pH-metric titration technique as adopted by Irving and Rossotti. The formation of chelates

Table 1: pH of Deviation of various ligand

S. No.	Ligand	pH of deviation
1	L_1	3.50
2	L_2	2.80
3	L_3	3.45
4	L_4	2.88

Table 2 : Determination of proton ligand stability constants (pK) of ligands at 0.1M ionic strength

Ligand	Proton ligand stability constants (pK)	
	Half integral method	Pointwise method
L_1	8.40	8.45 ± 0.03
L_2	10.50	10.20 ± 0.05
L_3	10.54	10.68 ± 0.03
L_4	7.00	7.18 ± 0. 04

Table 3: Metal ligand stability constants of Pr (III) Nd(III) complexes with ligands at 0.1M ionic strength

System	M-L Stability Constants		$logK_1 - logK_2$	$logK_1 / logK_2$
	$logK_1$	$logK_2$		
Pr(III)-L_1	5.94	0.253	5.68	2.34
-L_2	9.85	2.96	6.89	3.33
-L_3	7.74	2.45	5.29	3.16
-L_4	6.70	2.75	3.95	2.43
Nd(III)-L_1	5.97	0.346	5.62	1.72
-L_2	9.96	6.16	3.80	1.62
-L_3	8.24	4.85	3.39	1.70
-L_4	6.74	2.65	4.04	2.54

between Pr(III) and Nd(III) with substituted pyrazoles was indicated by

1. The significant departure starting from pH 2.95 for Pr(III) and pH 2.90 for Nd(III) complex system.
2. The change in colour from, colourless to yellow and then dark yellow as pH increased from 3.50 to 12.50.

The logK values were directly read from the formation curves ($\bar{n}$ *Vs* PL) using half integral method. The most accurate logK values were calculated by pointwise calculation method are presented in table -03 for all the systems. The $logK_1$ and $logK_2$ values follow the order as

Pr (III) < Nd (III)

It could be seen that logK values follow increasing trend. This is due to the electron releasing group (Cl^-, Br^- and I^-). The values of logK, ($logK_1 - logK_2$), and ($logK_1 / logK_2$) are in good agreement with excepted values. It is observed that the similar difference may be due to trans structure.

The results show that, the ratio $logK_1 / logK_2$ is positive in all cases. This implies that there is little or no steric hindrance to the additions of secondary ligand molecule.

$$\text{Validity of } \log K = a\,pK + b$$

The linear relationship logK = a pK + b has been found[18], to hold good for transition metal complex of series of closely related ligands. The stability of the metal complexes of substituted pyrazoles follows the order Pr(III) < Nd(III) .

The plot of $logK_1$ *Vs* pK and $logK_2$ *Vs* pK show satisfactory linear relationship giving slope values of 1.00 and 1.05 respectively. The partial molar free energies of metal ligand and proton ligand complexes exactly compensate with each other.

When logK *Vs* pK plot is linear with a slope of unity. From table-03 Pr(III) and Nd(III) metal ions formed 1:1 and 1:2 complexes with all the ligands.

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