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STUDIES ON INTERACTION BETWEEN La (IIl), AND Nd(III) METAL IONS AND 1-(4-HYDROXY-6-METHYL PYRIMIDINO)-3-SUBSTITUTED THICARBAMIDE AT 0.1 M IONIC STRENGTH pH METRICALLY

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ABSTRACT

The interactions of La(III) and Nd(III) metal ions with 1-(4-hydroxy-6-methyl pyrimidino)-3-phenylthiocarbamide [(L_1), HMPPT)] and 1-(4-hydroxy-6-methyl pyrimidino)-3-methylthiocarbamide [(L_2), HMPMT)] have been studied at 0.1 M ionic strength in 70 % Dioxane-water mixture by Bjerrum method as adopted by Calvin and Wilson, It is observed that La(III) and Nd(III) metal ions form 1:1 and 1:2 complexes with ligands (L_1 and L_2). The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK.) and metal-ligand stability constants (log k).The effect of substituents were stud-ied from estimated data (pK & log k).

Keywords: Phenylthiocarbamide, methylthiocarbamide, Bjerrum method, proton-ligand stability constant.

INTRODUCTION

The manifold research work has been done on the study of complexes[1-2]. The many workers[3-18] have reported their results on metal-ligand stability constants. With the view to understand the bio-inorganic chemistry of metal ions, Banarjee et al[19] have synthesized a number of mixed-ligand alkaline earth metal complexes. The studies in metal-ligand complexes in solution of number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw a light on the mode of storage and transport of metal ions in biological kingdom. Bejerrum's[20] dissertation has taken the initiative to develop the field. Metal complexation not only brings the reacting molecules together to give activated complex[21] but also polarized electrons from the ligands towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy change value. Bulkier group increases the basicity of ligands as well as stability. The stability of the complexes is determined by the nature of central metal atom and ligand. The stability of complexes is influenced by the most important characteristics like degree of oxidation, radius and electronic structure. Irving and Williams had studied the order of stability of metal complexes of transition metal ions by comparing the ionic radius and second ionization potentials of metal ions, as it is valid for most nitrogen and oxygen donor ligands. Narwade et al[23] have investigated metal-ligand stability constants of some lanthanides with some substituted sulphonic acids. Bodkhe et al[24] have reported the metal-ligand stability constants of some b-dikctones. Tekade ct al[25] have investigated stability constants of some substituted pyrazolines. isoxalline and diketone. Prasad et al[26] have studied mixed ligand complexes of alkaline earth metals, Mg(II). Ca(II)m Sr(II) & Ba(II) complexes with 5-nitrosalicyladehyde and b-diketones, Recently, Thakur et al[27] studied the interaction between some lanthanide and radioactive metal ion with substituted Schiff's bases at with 0.1molar ionic strength pH metrically and spectrophotometrically.

In present work an attempt has been made to study the interactions between La(III) and Nd(III) and substituted-s-triazines (L_1 and L_2) at 0. 1 M ionic strength pH metrically in 70% dioxane-water mixture.

EXPERIMENTAL

The chemicals used in present work were of AR grade. Substituted-s-triazines (ligand L_1 and L_2) were synthesized by literature method in laboratory and -their purity was checked by IR, NMR and M.P. techniques before used. The solutions of ligands were prepared in purified 70% dioxane-water mixture and standardised by pH metric technique.

Systronic microprocessor based instrument with accuracy in 0.01 unit with glass and saturated calomel electrode was used for the titrations. It was calibrated by buffer solution of pH 7.00 and 9.20 at 28 ± 0.1 °C before processing the titrations.

Titrations were carried out in an inert atmosphere by bubbling a constant flow of nitrogen gas.

The experimental procedure involved the titrations of

1. Free acid $HClO_4$ (0.01 M)
2. free acid $HClO_4$ (0.01 M) and ligand (20×10^{-4})
3. Free acid $HClO_4$ (0.01 M) and ligand (20×10^{-4}) and metal ion (4×10^{-4}M) against standard NaOH solution

The ionic strength of all the solution were maintained constant (O.1 M) by adding appropriate amount of $NaClO_4$ solution. All the titrations were carried out in 70 % dioxane-water mixture and the reading were recorded for each O.1 ml addition. The graph of volume of alkali (NaOH) against pH were plotted.

RESULTS AND DISCUSSION

Proton-ligand stability constants

The substituted-s-triazines in present investigation are monobasic acids having only one dissociable H^+-ion from OH group. It can therefore, he represented as HL

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

The titration curves of the acid and ligand deviate at about 3.0 pH. The deviation between acid curve from ligand for all the systems showed the dissociation of H- ions from -OH groups of ligands.

The proton-ligand formation number ($\bar{n}_A$) were calculated by Irving and Rossotti expression.

$$\bar{n}_A = \gamma - \frac{(V_2 - V_1) \times (E^0 + N)}{(V^0 + V_1)\, T_L{}^0}$$

Where,

V_0 = Initial volume of solution (50 ml)
E^0 = Initial concentration of free acid ($HClO_4$)
$T_L{}^0$ = Concentration of ligand in 50 ml solution
□= Number of dissociable protons from ligand
$(V_2 - V_1)$ = Volume of alkali (NaOH) consumed by acid and ligand on the same pH

The pK values were calculated from the formation curves between pH Vs ($\bar{n}_A$ noting the pH at which $\bar{n}_A$ = 0.5 (half integral method) and point wise calculations which are represented in Table-1.It is observed that, the order of pK values of ligands is found to be as, pK ligand 2 > pK ligand 1.The reduction in pK values of ligand 1 is attributed to presence of electron withdrawing -OH group.

Metal-Ligand Stability Constants

The stepwise formation constants of La(III), and Nd(III) metal ions with ligands (L_1 and L_2) in 70% dioxane-water mixture were determined. The values of log K_1 and log K_2 were directly computed from the formation curves ($\bar{n}_A$ Vs pL) using half integral method. The most accurate values were calculated by point wise calculations which are presented in Table-2.

CONCLUSION

From the titration curves, it is observed that the departure between (acid + ligand) curve and (acid + ligand + metal) curve for all systems started from pH = 3.0. This indicated the commencement of complex formation. Also change in colour from yellow to red in the pH range from 3 to 11 during titration showed the complex formation between metal and ligand.

Observation of Table 2 and 3, shows that the less difference between log K_1 and log K_2 values indicates the complex formation between metal ion and ligand occuring simultaneously. The values of log K_1 and log K_2 (table 2) for La(III)-ligand 1 are higher than Nd(III)-ligand 1 and Nd(III) - ligand 2 are higher than La(III)-ligand 2 complexes. It indicates that La(III) forms more stable complex with ligand 1 than Nd(III) while, Nd(III) forms more stable complex with ligand 2 than La(III) metal ions.

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Table-1

S. No.	System	pK	
		Half internal method	Point wise method
1.	1-(4-Hydroxy)-s-triarino-3-p-Cl-phenyl thiocarbamide	5.4	5.6
2.	1-(4-Hydroxy)-s-triarino-3-tert-butyl thiocarbamide	6.7	7.3

Table-2: Metal-ligand stability constants (log K)

System	Metal-ligand stability constants	
	$\log K_1$	$\log K_2$
La(III) - ligand - 1	3.3969	2.5198
Nd(III) - ligand - 1	1.2969	1.0198
La(III) - ligand - 2	1.8969	1.6198
Nd(III) - ligand - 2	3.8968	2.8198

Table-3: Metal-ligand stability constants (log K)

System	Metal-ligand stability constants	
	$\log K_1 - \log K_2$	$\log K_1 / \log K_2$
La(III) - ligand - 1	0.8771	1.3481
Nd(III) - ligand - 1	0.2771	1.2717
La(III) - ligand - 2	0.2771	1.1711
Nd(III) - ligand - 2	1.0771	1.3820

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