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Studies on Interaction between Sm (III) and Nd (III) Metal Ions and Novel Chalcones at 0.1M Ionic Strength pH Metrically

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Abstract:
The interaction of Sm (III) and ND (III) metal ions with 3-Bromo-2-hydroxy-5-Methyl chalcone (L1) and 3-Bromo-(2-hydroxy-5-methyl benzoyl) -4-phenyl-1, 3-butadine chalcones (L2) have been studied in 0.1M ionic strength at 70% Dioxane-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Sm(III) and Nd(III) metal ions from 1:1 and 1:2 complexes with ligands (L1 & L2). The data obtained were used to estimate and compare the values of proton-ligand stability constant (pk) and metal-legand stability constants (logK). The effect of substituents was studied from estimated data (pK & logK).

1. Introduction

The manifold research work has been done on the study of complexes 1-2. The many workers 3-7 have reported their results on metal – ligand stability constants. With the view to understand the bio-inorganic chemistry of metal ions.

The studies in metal – ligand complexes in solution of a 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.

Bejerrums's [B] dissertation has taken the initiative to develop the field. Metal complexation not only bring the reacting molecules together to give activated complex [g] but also polarised electrons from the ligands is indicated towards the metal. The relation between stability and bsicity 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 the central metal atom and ligand. The stability of the complexes is influenced by the most important characteristics like degree of oxidation, radius and electonic structure. Irviin and Williams [10] have studied the order of stability of metal complexes of transition metal ions by compairing the ionic radius and the second ionization potential of metal ions, as it is valid for most nitrogen and oxygen donor ligands. Tekade et al. [11] have investigated stability constants of some substituted pyrazoline, isoxaline and diketone. Prasad et at [12] have studied mixed igand complexes of alkaline earth metals, Mg[II], Ca[II], Sr[II] & Ba[II] complexes with 5 – nitrosalicylaldehyde and β – dicketones.

In the present work an attempt has been made to study the interaction between Sm(II) and Nd(II) and novel chalcones (L1 & L2) at 0.1M ionic strength pH-metrically in 70% dioxane – water mixture.

2. Experimental

The chemicals used in present work, were novel chalcone (Ligand 1&2) were synthesized by literature method in laboratory.

The chemicals used in the present work, were of AR grade. Chalcones [ligands L1 & L2] used were synthsized by literature method in laboratory. The solutions of ligands were prepared in purified 70% dioxane-water mixture and standard ised by pH metric technique.

Systronic microprocessor based instrument with accuracy of+-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 0C, 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 $HCl0_4$ (0.01 M)
2. Free acid $HCl0_4$ (0.01 M) and ligand (20 x 10^{-4}M)
3. Free acid $HCL0_4$ (0.01M) and ligand (20 x 10^{-4}M) and metal ion (4 x 10^{-4}M) against standard NaOH solution.

The ionic strengths of all the solution were maintained constant (0.1 M) by adding appropriate amount of Nacl04solution. All the titrations were carried out in 70% dioxane – water mixture and the reading were recorded for each 0.1 ml addition. The graph of volume of alkali (NaOH) against pH was plotted.

3. Results and Discussions

3.1. Proton – Ligand Stability Constants

The chalcones used in present investigations are monobasic acid having only one dissociable H+ ion from OH group. It can therefore, be represented as HL

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

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 group of ligands. The proton - ligand formation number (n-A) were calculated by Irvin and Rossotti expressions:

$$\bar{n}A = \gamma - \frac{(E0 + N)(V2 - V1)}{(V0 + V1)T0L}$$

Where,

V_0 – Initial volume of solution (50ml)

E^0 – Initial concentrations of free acid (Hcl04)

T^0L – Concentration of ligand in 50 ml solutionn

N – Normality NaoH solution

γ – Number of dissociable protons from ligand

$(V_2 - V_1)$ – Volume of alkali (NaoH) consumed by acid and ligand on same pH

The pk values were calculated from the formation curves between pH Vs nA noting the pH at which nA=0.5 (half integral method) and point wise calculations which are represented in table 1.

Sr No	System	pK	
		Half Integral method	Pointwise method
1	L1:[Beomo-2-hydroxy-5-methyl chalcone]	6.5	6.8536
2	L2:[3-Bromo-(2-hydroxy-5-methyl benzoyl)-4-phenyl-1, 3-butadine chalcones	5.5423	5.233

Table 1: Proton – ligand stability constants pK

It is observed that the order of pK values of ligandsis found to be as pK ligand 1>pK ligand 2.

The reduction in pK values of ligand 2 may be due to strond inductive effect and resonance effect of benzyl group.

3.2. Metal – Ligand Stability Constants

The stepwise formation constants of Nd (III) and Sm(III) metal ions with ligands (L1 & L2) in 70% dioxane – water mixture were determined. The values of log K1 and log K2 were directly computed from the formation curves (-nVspL) using half integral method. The most accurate values were calculated by pointwise calculations which are represented in table 2.

System	Metal - ligand stability constants	
	log K1	log K2
Sm(III)-ligand -1	10.3846	10.0583
Nd(III)-ligand -1	10.2192	9.9243
Sm(III)-ligand -2	9.4703	9.3256
Nd(III)-ligand -2	9.5849	9.2931

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

4. Conclusion

From the titration curves, it is observed that the departure between (acid + ligand) curve ad (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 brown in the pH range from 3 to 10 during titration showed the complex formation between metal and ligand.

System	Metal-ligand stability constants	
	logK1-logK2	logK1/logK2
Sm(III)-ligand-1	0.3263	1.0324
Nd(III)-ligand-1	0.2949	1.0297
Sm(III)-ligand-2	0.1447	1.0155
Nd(III)-ligand-2	0.2918	1.0313

Table 3: Metal – ligand stability constants (logK)

From the table 2 and 3, It shows that the difference between log k1 and log k2 values in these ligands is less, indicated Nd(III) and Sm(III)complexes are occurring simultaneously.

The value of log k1 and log K2(table 2) for Sm(III) ligand-1 complex are higher than Nd(III)-1 complex, indicates that Sm(III)forms stable complex with ligand 1than Nd (III) metal ions.

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