ph-metric studies of formation constants of the complexes of substituted thiazolyl Schiff's bases with some lanthanide metal ions in 70% ethanol-water mixture

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ABSTRACT

The Present work is undertaken to make a systematic solution study of the complex formation of La(III), Pr(III) and Sm (III) with 2-[3-(4-methoxy phenyl)-1-(4-phenyl-thiazol-2-ylimino)-allyl]-phenol. And 2-[3-phenyl-1-(4-phenyl-thiazol-2-ylimino)-allyl]-phenol. have been determined by the p^H-metric method in media of 70% ethanol -water mixture at 0.1 M ionic strength and at $(30 \pm 0.1)^oC$ temperature.

Keywords: *Thiazolyl Substituted Schiff's Bases, Ph-Metric Study, La(Iii), Pr(Iii), Sm(Iii), Metal-Ligand Stability Constants.*

1. INTRODUCTION

Most of the binary complexes of transition and inner transition metals have been studied Potentiometrically[1-2] . Literature survery[3-4] reveals that the thiazole nucleus is the centre of attraction in developing various chemical entities of biological interest. Metal complexes of thiazoles have been extensively studied because they possess good synthetic flexibility, selectivity and sensitivity towards the central metal atom. Some thiazole derivatives reported as antiphycotics, antimalerial antibacterial[5] and antinflamatory[6].Metal ligand stability constant determination has wide significance in different fields of physical chemistry, medicinal chemistry and thermochemistry**.**

The study of coordination compounds specifically the metal complexes containing thiazole based ligand is of much interest due to their importance in various chemical and biological systems. A perusal of literature has revealed that schiff's bases belongs to a widely used group of organic intermediates, important for production of specialty chemicals such as pharmaceuticals, rubber additives and as amino protective groups in organic synthesis.

The studies on complex formation by tripositive rare-earth metal ions with biologically important ligands are in progress because of their role in biological process[7].

KB Vyas et al[8] have studied the stability constants of Ferrous (II) complexes of substituted derivative of Coumarin. Doshi and Pawar[9] has studied the interaction of Cu(II), Co(II), Fe(III), Al(III) and Nd(III) with isoxazolines. They showed the formation of 1:1 and 1:2 complexes in the pH range at about 2-9 in 70% dioxane-water mixture.

The stability constants of synthesized compounds have been studied pH-metrically by Irving and Rossotti method[10.]The present paper reports pH-metric studies on the interaction of rare earth metal ions La(III), Pr(III) and Sm (III) with 2-[3-(4-methoxy phenyl)-1-(4-phenyl-thiazol-2-ylimino)-allyl]-phenol L^4 , 2-[3-phenyl-1-(4-phenyl-thiazol-2-ylimino)-allyl]-phenol L^5 and 2-[3-(4-chlorophenyl)-1-(phenol-thiazol-2-ylimino)-allyl]-phenol L^6 in 1:1 ratio at 30±0.1°C. For this study 70% Ethanol-water mixture were used as solvent. The ionic strength was maintained constant at 0.1M. The proton-ligand and metal-ligand stability constants were calculated by point wise calculation method and half integral method.
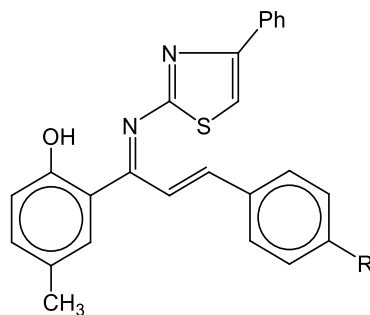
Where R = H, OCH3 and Cl

2. EXPERIMENTAL

Materials and solutions

The microwave irradiation was used for the synthesis of the ligands. Purity was verified by analytical and spectral study i.e. melting point determination, IR and NMR spectra. The stock solution of the ligands (0.01N) were prepared by dissolving the required amount of the ligands in a minimum volume of 70% ethanol-water mixture. 0.01 M metal solutions were prepared by dissolving the requisite quantities in distilled water. The concentrations of metal ions were estimated by titrating against disodium salt of E.D.T.A. solution by procedure of Schwarzenbach[11] The standard NaOH solution was prepared by Vogel'smethod[12].

Apparatus and procedure

The pH of the solutions was measured with a EQUIP-TRONICS microcontroller pH meter (Model EQ-621) equipped with a combined electrode and magnetic stirrer. The instrument was calibrated before each titration with an aqueous standard buffer solution of pH 4, 7 and 9 prepared from Qualigens buffer tablets. All the weighings were done on electronic balance [ConTech CB-Series with accuracy ±0.001]. The following titrations were carried out pH metrically.

- Acid titration
- Acid + ligand titration
- Acid + ligand + metal. titration

Ionic strength 0.1M was maintained by using HNO_3 and KNO_3 solutions. The titrations were carried out by using Calvin Bjerrum pH metric titration technique.[13] The same techniques were applied for 70% ethanol-water mixture and 70% acetone-water mixture. The total volume of each system was made up to 25ml. The proton-ligand stability constants were calculated from the pH values obtained from the titrations using the Irving–Rossotti method was mentioned in Table1.

Table1: Proton ligand stability constants (pK) of ligand L^1 to L^3at 0.1 M ionic strength and at $(30\pm0.1)°C$ Temperature.

Medium	Ligand	pK (half integral method)	pK (point wise calculation method)
Ethanol-water	L^4	4.80	5.10
Ethanol-water	L^5	4.80	5.10
Ethanol-water	L^6	5.8	5.8
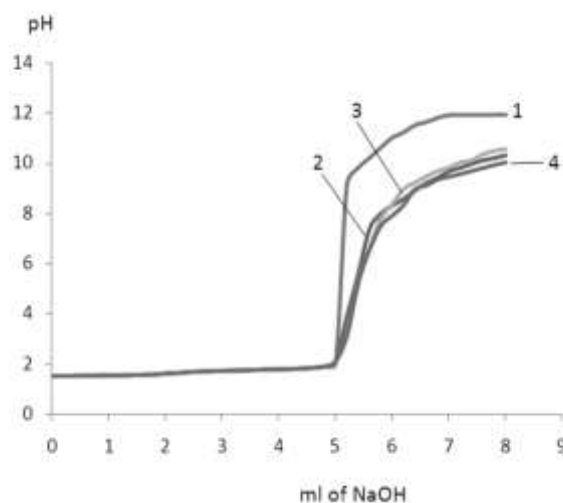
Fig.1.pH against volume of 0.10 mol dm^{-3} NaOH at

I = 0.1M at $(30\pm0.1)°C$; 1 = Acid curve, 2, 3 and 4 are the curves of ligands L^4 L^5& L^6.

3. RESULTS AND DISCUSSION

The Ligands L^4 $L^5$and L^6used in the present investigation contains only one dissociable proton from hydroxyl group. In general ligands can be represented as HL and dissociated as.

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

$$K' = \frac{[H^+][L^-]}{[HL]}$$

The proton-ligand formation number $\bar{n}_A$ was calculated by Irving Rossotti expression. The proton ligand stability constant pK were calculated from formation curves by point wise calculation method & half integral method. From formation curves drawn from $\bar{n}_A$ Vs. pH (half integral method) by nothing pH at which $\bar{n}_A$ =0.5. showing fig-1. The accurate values of pK were determined by point wise calculation method. The $\bar{n}_A$ values were calculated with the help of following equation (1)

$$\bar{\eta}_A = \gamma - \left[\frac{(E^0 + N)(V_2 - V_1)}{(V_0 + V_1)T_L^0} \right] \qquad .... (1)$$

$$\bar{\eta} = \left[\frac{(E^0 + N)(V_3 - V_2)}{(V_0 + V_2)T^0 m} \right] \qquad .... (2)$$

Where γ is number of dissociable proton.
N is concentration of NaOH (0.1 moldm^{-3})
E^0 is resultant concentration of acid.
T^0_L is resultant concentration of ligand.
V^o is initial volume of the reaction mixture.
V_1 and V_2 are volume of alkali added in acid, ligand titration and metal titration.
T^o_m is concentration of the metal ion in the reaction mixture.

Similarly metal ligand formation number $\bar{n}$ values was calculated by using equation (2) and metal ligand stability constants were determined from formation curves by point wise calculation method and half integral method mentioned in Table -2.

During titration process there is a color change of solution. In La(III) titration color becomes off white or yellowish .For Pr(III), light green color of solution gets darken & for Sm (III) color changes from yellow to orange. This color change during titration confirms 1:1 complex formation due to replaceble H$^+$ from –OH group. Due to formation of coordination bond at N site ,there is formation of 1:2 complex.

The deviation of metal titration curve from ligand curve commenced from p^H 2.7 for La, p^H 2.6 for Pr and p^H 2.9 for Sm. The significant departure of ligand curve from acid curve indicates chelate formation between metal ion & ligand gets confirmed. As solutions used are very dilute possibility of formation of polynuclear species is very less.
There is no specific trend in proton-ligand stability constant. This is due to variation in polar nature of solvents and solvent-solvent interactions.

In the present investigation there is no specific trend in metal-ligand stability constants as in table-2. This may be due to the fact that (i) difference in redox potentials E^0 values of La, Pr & Sm is very less. Hence though they have strong tendency to lose electron and undergo oxidation, the reducing power of La, Pr & Sm differs to very less extent. (ii) For trivalent lanthanide ions, increase in ionic size, increases the stability of complexes . This is due to lanthanide contraction[23]. But the variation in results may be due to metal solvent interactions.

Table 2: Metal ligand stability constants of complexes La(III), Pr(III) and Sm(III) with ligand L^4 ,L^{5}and L^6 in 70% Ethanol-water medium.

Medium	System	Constants	Method	
			Half integral	**Point wise calculation**
70% Ethanol-water	La(III)-L^4	Log K$_1$	4.5	4.38
		Log K$_2$	7.10	7.26
	Pr(III)-L^4	Log K$_1$	3.20	3.30
		Log K$_2$	6.0	5.72
	Sm(III)-L^4	Log K$_1$	3.5	3.30
		Log K$_2$	5.7	5.72
70% Ethanol-water	La(III)-L^5	Log K$_1$	3.5	4.85
		Log K$_2$	6.60	7.94
	Pr(III)-L^5	Log K$_1$	3.05	3.89
		Log K$_2$	5.5	7.13
	Sm(III)-L^5	Log K$_1$	3.10	3.410

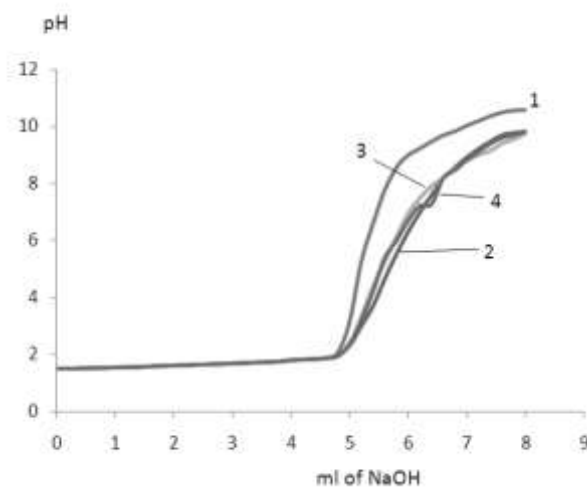|		Log K_2	5.7	5.72
70% Ethanol –water	La(III)-L[6]	Log K_1	5.5	5.53
		Log K_2	8.9	8.9
	Pr(III)-L[6]	Log K_1	4.5	4.5
		Log K_2	8.1	7.9
	Sm(III)-L[6]	Log K_1	5.2	4.6
		Log K_2	8.30	8.26

Fig. 2 pH against volume of 0.10 mol dm^{-3}NaOH at

I = 0.1 M at $(30\pm0.1)^oC$; 1= ligand curve, 2, 3 and 4 are metal curves of La(III), Pr(III) & Sm(III) respectively.

4. CONCLUSION
From the data presented in table-2.it can be concluded that there is stepwise complex formation between trivalent lanthanide ions and thiazolyl substituted schiff's bases. From the stability constants of complexes it can be concluded that for trivalent lanthanide metal ions basicity decreases with decrease in ionic radius. This results in decrease in complexes formation tendency in case of hydrated ions.

The metal-ligand stability constant has significance in determination of thermodynamic parameter in thermochemistry.

5. ACKNOWLEDGEMENTS

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