

## Stability constant of rare earth metals with substituted Thiazoles at 298.15K

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**Abstract.** The stability constant on complexation of rare earth metal ions Eu(III), Gd (III), Nd(III) and Tb(III) with substituted thiazole in 70% Dioxane (Dx)-water mixture have been determined by a pH and spectrophotometric method at 298.15K and ionic strength  $0.1\text{mol}\cdot\text{dm}^{-3}$  (sodium perchlorate).

At constant temperature, the stability constant of the formed complexes decreases in the order Tb (III), Gd(III), Eu (III), Nd (III). The dissociation process is non-spontaneous, endothermic and entropically unfavorable while formation of metal complexes has been found to be spontaneous, endothermic and entropically favorable.

### Introduction

Heterocyclic compounds have been major interest of research due to oxygen, nitrogen and sulphur<sup>[1]</sup>. Thiazoles have become the focus of interest in the recent past on account of their medicinal, biological and agrochemical activities<sup>[2-4]</sup>. There are large number of synthetic compounds with thiazole nucleus having application as anticancer<sup>[5]</sup>, analgesic<sup>[6]</sup>, antitubercular<sup>[7]</sup>, antidiabetic<sup>[8]</sup> etc. Many of the heterocyclic compounds that can affect the biological and ecological behavior of the lanthanide ions<sup>[9]</sup>. Studies on complex formation by tripositive rare earth ions with biologically active ligands are in progress because of their role in biochemical processes. The metal complexes with some heterocyclic compounds in aqueous solution has been determined by various authors<sup>[10-12]</sup>.

The present work is the continuation of our earlier of metal complexation<sup>[13-14]</sup>. The complexation of substituted thiazoles with rare earth metal ions in the 1:1 ratio at 298.15K. The ionic strength is maintained by addition of sodium perchlorate solution. Since the ligand is insoluble in water, hence 70% dioxane-water (Dx-water) mixture used as solvent.

### Materials and method:

The rare earth metal ions (Sigma Aldrich), sodium perchlorate, hydroxy thiazole (Hi-media), perchloric acid (Qualigen), sodium hydroxide (Thomes Baker) (DMF) of AnalR grade used without purification. The ligand solutions were prepared by dissolving an accurate amount in an organic-aqueous mixture in standard flask with airtight caps and the mass measurement were performed using high precision digital balance (Shimadzu, Japan accuracy  $\pm 0.1$  mg). Dilute perchloric acid solution, standard sodium hydroxide and nitrates of rare earth metal ions ( $1.0 \times 10^{-2} \text{mol}\cdot\text{dm}^{-3}$ ) standardised by literature method<sup>[15-17]</sup>.

A pH meter (827, Metrohm, Switzerland) was used for pH measurements. The pH meter has a sensitivity of 0.01 units and all measurements were carried out at 298.15K. The ionic strength was maintained by addition of sodium perchlorate. The instrument was calibrated before each titration with an aqueous standard buffer solution of pH 4.20, 7.00 and 9.10. The solution were prepared (total volume  $25 \text{cm}^3$ ); a) perchloric acid ( $2.0 \times 10^{-2} \text{mol dm}^{-3}$ , 2.5 ml) + sodium perchlorate ( $2.0 \times 10^{-2} \text{mol dm}^{-3}$ , 2.5 ml), b) solution a + ligand ( $1.0 \times 10^{-2} \text{mol dm}^{-3}$ , 5 ml) and c) solution b + metal

ion ( $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ , 1 ml). The ligand was acidified with perchloric acid in a 70% D<sub>x</sub>-water medium. The ligand was titrated against standard sodium hydroxide using Calvin-Wilson-Bjerrum pH titration techniques<sup>[18,19]</sup>.

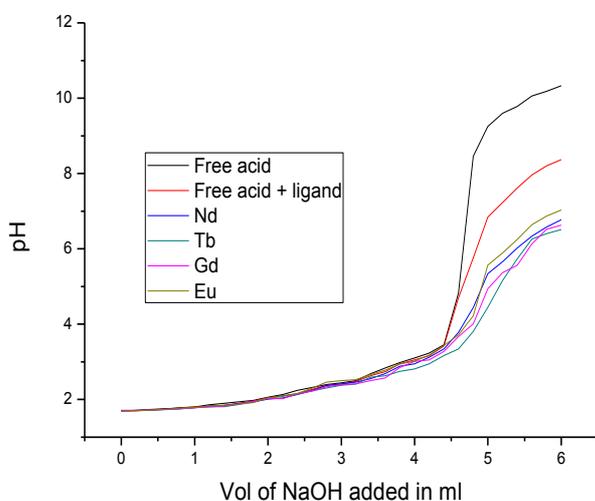


Fig.1 pH vs vol of NaOH,  $\mu = 0.1 \text{ mol.dm}^{-3}$  at 298.15K

The spectrophotometric measurements were performed by Job's method<sup>[20]</sup> on a UV-VIS spectrophotometer (Model 1800, Shimadzu, Japan) accuracy  $\pm 0.005$  with spectral range 180-1100nm. The equimolar solution of ligand and rare earth metal ions; Eu(III), Gd (III) and Tb(III) were mixed in different proportions with the pH range 2-3 and  $\mu = 0.1$  maintained by addition of sodium hydroxide and sodium perchlorate respectively. The concentration of the complex is at a maximum when reagents are in the ratio of their stoichiometric proportions in the complex.

## Results and Discussion

Figure 1 shows the nature of the acid curve and ligand curve. In the initial stages of titration the pH values of the ligand curve slightly higher than the corresponding values of acid curve at the same volume of alkali added. This is due to formation of cation of thiazole resulting in the decrease in  $\text{H}^+$  ion concentration of the reaction mixture. In the present study, the proton ligand stability constants for thiazole and the metal-ligand stability constants for the complexes of Eu(III), Gd(III), Nd(III) and Tb(III) with thiazole were determined by carrying out the acid, ligand and metal titrations at 298.15K by maintaining the ionic strength. Fig 1. Exhibits a set of acid, ligand and four metal titration curves at  $\mu = 0.1 \text{ mol.dm}^{-3}$  and  $T = 298.15\text{K}$ . At higher volumes of alkali added, the relatively large drop in pH in metal titrations with respect to the ligand titration curve and the formation of metal complex<sup>[21]</sup>.

The extent of deviation is due to dissociation of hydroxyl group completely. The proton-ligand dissociation constant and metal stability constants of HL with Eu(III), Gd (III), Nd (III) and Tb (III) have been determined pH and spectrophotometrically. The pH metric study were carried out in 0.1M  $\text{NaClO}_4$  at constant temperature. The proton ligand formation was calculated by Irving Rossotti method<sup>[22, 23]</sup>.

The accurate pK values of complexes were calculated by half integral method and concordance with pointwise calculation method. The pK values of ligand by half integral method and pointwise calculation method are found to be 8.40 and  $8.51 \pm 0.03$  respectively. There is good agreement obtained by the methods. The proton ligand formation number  $\bar{n}_A$  were calculated from the following equation;

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

Where  $\gamma$  denotes the number of dissociable protons, N is the concentration of sodium hydroxide,  $V_2$  and  $V_1$  are the volume of alkali added to reach the same pH reading,  $(V_2 - V_1)$  is the displacement values of ligand curve relative to acid curve,  $V^0$  is the initial volume of the reaction mixture,  $E^0$  and  $T_L^0$  are the resultant concentration of sodium perchlorate and concentration of ligand respectively. In the present study pH titration curve shows only one inflection point indicated that there is only one acid acidic group.

The metal-ligand stability constants determined by following equation;

$$n = \frac{(V_3 - V_2)(E^0 + N)}{(V^0 + V_2)T_m^0}$$

Where N,  $E^0$ ,  $V^0$  and  $V_2$  have the same significance as in above eq,  $V_3$  is the volume of alkali added in the metal titration to attain the pH reading and  $T_m^0$  is the concentration of the metal ion in the reaction mixture. The stability constants calculated for the systems have been calculated and tabulated in Table 1. Metal-ligand stability constants of the complexes from the table showed that there is no appreciable difference between  $\log K_1$  and  $\log K_2$  values, that indicates the formation of complexes simultaneously.

Table 1 Metal stability constants of thiazole complexes at constant ionic strength in 70% Dx-water at 298.15K

System	pH metric (log K)		Spectrophotometric (log K)
	Half Integral	Pointwise calculation	
Nd (III)-L	$\log K_1 = 7.40$ $\log K_2 = 5.29$	$\log K_1 = 7.68$ $\log K_2 = 5.22$	$\log K_1 = 7.57$ $\log K_2 = 5.44$
Eu (III)-L	$\log K_1 = 7.60$ $\log K_2 = 5.37$	$\log K_1 = 6.35$ $\log K_2 = 5.39$	$\log K_1 = 6.70$ $\log K_2 = 5.49$
Gd (III)-L	$\log K_1 = 7.78$ $\log K_2 = 5.49$	$\log K_1 = 7.26$ $\log K_2 = 5.41$	$\log K_1 = 7.83$ $\log K_2 = 5.54$
Tb (III)-L	$\log K_1 = 7.95$ $\log K_2 = 5.57$	$\log K_1 = 7.53$ $\log K_2 = 5.49$	$\log K_1 = 7.97$ $\log K_2 = 5.69$

**Spectrophotometric studies:** Using the continuous variations method, the determination of absorbance of solution of metal ion with thiazole of concentration. The conditional metal-ligand stability constants calculated using following expression;

$$K = \frac{x}{(a-x)(b-x)}$$

Where K = Conditional metal-ligand stability constant,  $x$  = concentration of complex,  $a$  and  $b$  = concentration of metal ion and ligand.

The conditional stability constants are found to be slightly greater than the real stability. It may be due to the concentration of free acid at particular pH was not taken into account and variation in temperature. The agreement between the values obtained from the both techniques is fairly good.

## Conclusion

The metal-ligand formation value of  $\tilde{n}$  was  $\approx 2$ , indicating formation of 1:1 and 1:2 complex only. The metal ion solution used in the present work was very dilute therefore there is mere possibility of the formation of polynuclear complexes. At constant temperature the stability of the ligand increases in the order Nd(III) > Eu(III) > Gd(III) > Tb(III). This order largely reflects that the stability of Nd(III) complexes is larger than those of other metals. The conditional stability constants are found to be slightly greater than the real stability.

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