

# Thermodynamic Stability and Parameter of Formation of Quaternary Complexes of Some Lanthanones

## Abstract

Complexation of La<sup>(III)</sup>, Pr<sup>(III)</sup>, Nd<sup>(III)</sup>, Gd<sup>(III)</sup> and Dy<sup>(III)</sup> with tetrapotassium salt of diethylene triamine pentaacetic acid (K<sub>4</sub>DTPA), furan-2-carboxylic acid (FA), pyridine-2, 6- dicarboxylic acid (PDA), malonic acid (MALO) and tartaric acid (TAR) has been investigated potentiometrically. The stability constants of quaternary complexes have been determined in aqueous solution at 40±1°C and at a fixed ionic strength ( $\mu=0.1M$  KNO<sub>3</sub>). The relative order of stability, has been observed to be La<sup>(III)</sup> < Pr<sup>(III)</sup> < Nd<sup>(III)</sup> < Gd<sup>(III)</sup> < Dy<sup>(III)</sup>. The change in thermodynamic parameter (free energy change,  $\Delta G^\circ$ ) for the formation of 1:1:1:1, quaternary complexes has also been evaluated.

**Keywords:** Diethylene triamine Pentaacetic acid, Furan-2-Carboxylic Acid, PH-Metric Study, Stability of Complexes.

## Introduction

Although the interaction of various ligands with lanthanides ion has been the subject of numerous studies<sup>1-5</sup>, while quaternary metal complexes in which DTPA and other heteroligand and carboxylic acid are present simultaneously in the co-ordination sphere of lanthanide ion have not been studied so far. Hence, in the present investigation, we have carried out a study on the relative stabilities of these complexes. It has been found that the stability of these complexes is affected by the size of the chelate ring formed and by the position and nature of the donor group<sup>6,7</sup>. The stabilities of the lanthanide complexes were studied as a function of ionisation potential, ionic radius, atomic number, electronegativity of the metal ion, expansion of their co-ordination number, basic character of ligands and chelate effect. Soft-soft or hard-hard acid base interaction also favours the greater stability of the resulting species<sup>8</sup>.

## Aim of the Study

Lanthanides quaternary complexes formation to resolve the metal poisoning by the stable metal complexes with used ligands.

## Experimental

All the reagents used were of AR/GR grade. Solution of metal ions and ligands were prepared in double-distilled water. Stock solutions of lanthanides metals were prepared from the respective metal nitrates and standardised by using appropriate method<sup>9,10</sup>. Solution of tetrapotassium salt of diethyl triamine pentaacetic acid (K<sub>4</sub>DTPA) was prepared by the dissolving their calculated and weighed amounts in the requisite volume of standard potassium hydroxide solution. Solution of furan-2-carboxylic acid (FA), pyridine-2,6-dicarboxylic acid (PDA), malonic acid (MALO), tartaric acid (TAR), potassium nitrate and potassium hydrogen phthalate were prepared by direct weighing method in freshly prepared conductivity water.

The experimental work for pH-metric titrations were made on ELICO (LI-613) digital pH-meter having a combined glass-calomel electrode assembly after calibrating with potassium hydrogen phthalate solution (pH=4) and standard buffer tablets solution (pH=9). Each titration was repeated at least twice against (0.1M) KOH solution at 40±1°C to gain the reproducibility of result, keeping the ionic strength at 0.1 M KNO<sub>3</sub>, total volume (50 ml) constant in beginning of each titration. The measured pH values were plotted against the moles (m) of base (KOH) added per mole of metal ion or ligand as depicted in the figs. 1, 2, and 3.

## Results and Discussion

The acid dissociation constants of the used ligands were determined by the method of Chaberek and Martell<sup>11</sup>. These values (table-1) were calculated from titration curves by using the formula for mono and dibasic ligands.

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$$K = \frac{[H^+][aC_A + [H^+] - [OH^-]]}{C_A - [aC_A + [H^+] - [OH^-]]}$$

[for monobasic ligand]

$$K_1 = \frac{[H^+][aC_A + [H^+]]}{C_A - [aC_A + [H^+]]}$$

$$K_2 = \frac{[H^+][(a-1)C_A - [OH^-]]}{C_A - [(a-1)C_A - [OH^-]]}$$

[for di basic ligand]

Where  $K_1$  and  $K_2$  are the first and second dissociation constants,

$C_A$  = total concentration of ligands,

$a$  = number of moles of alkali added per mole of ligand.

Table - 1

Ligand	pK <sub>1</sub>	pK <sub>2</sub>
DTPA	10.43	-
FA	3.68	-
PDA	2.50	5.28
MALO	2.91	5.78
TAR	2.80	4.12

The stability constants (Table-2.) of the mixed ligand complexes were obtained by the method of Ramamoorthy and Santappa<sup>12</sup> for the simultaneous chelation of the ligands to the metal ion. The values of

stability constants were calculated by the following expression.

$$K_{MLL'L}^M = \frac{T_M - \frac{1}{3}[A]X}{\left(\frac{1}{3}\right)^4 \cdot A^4 \cdot X}$$

$$A = \frac{4T_M - T_{OH} - [H^+]}{\frac{2[H^+]^2}{k_1 k_2} + \frac{3[H^+]}{k_1 + k_1' + k_1''}}$$

$$X = 1 + \frac{[H^+]^2}{k_1' k_2''} + \frac{3[H^+]}{k_1 + k_1' + k_1''}$$

Where  $T_M$  is the total metal ion concentration,  $k_1$ ,  $k_1'$  and  $k_1''$  are the first dissociation constants of the three ligands where as  $k_2$  is the second dissociation constant of dibasic ligand. The stability constants lie in the order of La<sup>(III)</sup> < Pr<sup>(III)</sup> < Nd<sup>(III)</sup> < Gd<sup>(III)</sup> < Dy<sup>(III)</sup>. Which is the order of increasing occupancy of the 4f orbitals of metal ions I3-IS accompanied by a gradual decrease in their ionic radius.<sup>13-15</sup>

The average value of evaluated stability constants were used to calculate the overall change in free energy ( $\Delta G^\circ$ ) by the Van't Hoff's isotherm. These values (Table-2) have been found to be negative in all system, indicating that the reaction between metal ions and the ligands is favoured in aqueous solution.

Table - 2  
Consolidated Values of LogK<sup>M<sub>MLL'L</sub></sup> and  $\Delta G^\circ$  for the 1:1:1:1, Quaternary Complexes [ $\mu=0.1$ MKNO<sub>3</sub>, Temp. = 40±1°C]

Systems	Properties	Lanthanides				
		La <sup>(III)</sup>	Pr <sup>(III)</sup>	Nd <sup>(III)</sup>	Gd <sup>(III)</sup>	Dy <sup>(III)</sup>
1. Ln <sup>3+</sup> -DTPA-FA-PDA	Log K <sup>M<sub>MLL'L</sub></sup>	15.9876	16.3311	16.4943	16.5697	16.7792
	$-\Delta G^\circ$	22.8992	23.3911	23.6249	23.7329	24.0330
2. Ln <sup>3+</sup> -DTPA-FA-MALO	Log K <sup>M<sub>MLL'L</sub></sup>	17.1578	17.2350	17.4429	17.7341	17.9295
	$-\Delta G^\circ$	24.5752	24.6858	24.9836	25.4007	25.6805
3. Ln <sup>3+</sup> -DTPA-FA-TAR	Log K <sup>M<sub>MLL'L</sub></sup>	12.5871	12.7746	13.5840	13.5951	13.8377
	$-\Delta G^\circ$	18.0286	18.2971	19.4565	19.4724	19.8198

### Conclusion

The order of stabilities of quaternary complexes with respect to metal ion is La<sup>(III)</sup> < Pr<sup>(III)</sup> < Nd<sup>(III)</sup> < Gd<sup>(III)</sup> < Dy<sup>(III)</sup>. This can be attributed to the decreasing size and increasing ionic potential (charge/radius) of lanthanides ions. A large value of charge/radius ratio for central ions means that the central ion will be forming more stable complexes. Calculated  $\Delta G^\circ$  values have been found to be negative in all the systems which indicates that the process of formation of complexes is spontaneous. More the negative value of  $\Delta G^\circ$ , hence a more stable the complex is formed.

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