

Study of Thermodynamic Parameters and Thermodynamic stability of Quaternary Complexes of some rare earth metals

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Abstract

Investigation of potentiometric studies have been carried on complexation of lanthanides viz. La^(III), Pr^(III), Nd^(III), Gd^(III) and Dy^(III) with N-hydroxyethyl ethylene diamine triacetic acid (HEDTA), Furan – 2 – carboxylic acid (FCA), thiophene – 2 – carboxylic acid (TCA), Pyridine – 2, 6 – dicarboxylic acid (PDA) and phthalic acid (PA). The stability constants of quaternary complexes and the dissociation constants of used ligands has been determined in aqueous solution at 40±1 °C and at a fixed ionic strength ($\mu=0.1$ M KNO₃). The relative order of stability has been observed to be La^(III) < Pr^(III) < Nd^(III) < Gd^(III) < Dy^(III). The change in thermodynamic parameter (free energy change, ΔG°) for the formation of 1:1:1:1 quaternary complexes has also been evaluated. The order of stabilization in the quaternary complexes has been explained on the basis of increasing value of ionic potential ($\phi \rightarrow$ charge/radius ratio)

Keywords: N-Hydroxyethyl ethylene-diamine triacetic acid, pH- Metric Study, Stability of Quaternary complexes, Lanthanides

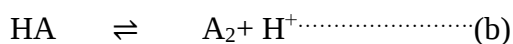
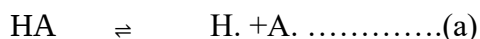
Introduction: Lanthanides are owing to non availability of orbitals for binding and large size of their common cations form few complexes with O, S or N donor ligands. An attempt has been made to study of stability constants of some Lanthanons¹⁻⁵. The best characterization of stability of complexes of HEDTA, FCA, TCA, PDA and PA formed in the solution equilibria can be made by evaluating their stability constants and other thermodynamic parameters. The stability constants of hetero ligands complexes have importance to rationalizes the understanding towards the behaviour of metal complexes in solution.

Present communication describes determination of the stability constants of the $[L_n^{(iii)}-L-L'-L'']^{n\pm}$ complexes by pH-metric titration method at 40±1°C at the fixed ionic strength $\mu=0.1$ M KNO₃

Experimental : All the reagents used were of AG/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 standardized by using appropriate method^{6,7}. Solution of N-hydroxyethyl ethylene diamine triacetic acid (HEDTA) was prepared in requisite volume of KOH. The solution of thiophene-2-carboxylic acid (TCA), Furan-2-Carboxylic acid (FCA), Pyridine-2,6-dicarboxylic acid (PDA), phthalic acid (PA), 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 Atleast twice against (0.1M) KOH solution at $40\pm 1^\circ\text{C}$ to gain the reproducibility of results , keeping the ionic strength at 0.1M KNO_3 and total volume (50ml) constant in beginning of each titration. The results pH values were plotted against the moles (m) of base (KOH) added per mole of metal ion or ligand .

Results and Discussion:- the acid dissociation constants of the used ligands were determined by the method of chaberk and Martell⁸ . These values (table-1) were calculated from titration curves by using the formula for mono and dibasic ligands.



The constant K, K_1 and K_2 were calculated by the following expressions.

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

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

[for monobasic ligand]

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

[for dibasic ligand]

Table -1

Ligand	pK ₁	pK ₂
HEDTA	10.48	-
TCA	03.63	-
FCA	03.68	-
PDA	02.50	5.28
PA	02.66	4.28

Table-2-Stability constants and free energy change of quaternary complexes

[$\mu=0.1 \text{ M KNO}_3$, Temp.= $40\pm 1^\circ\text{C}$]

	System	Properties	Metal Ion
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			La ⁽ⁱⁱⁱ⁾	Pr ⁽ⁱⁱⁱ⁾	Nd ⁽ⁱⁱⁱ⁾	Gd ⁽ⁱⁱⁱ⁾	Dy ⁽ⁱⁱⁱ⁾
1	La ³⁺ -HEDTA-TCA-PA	logK ^M _{MLL'L''} -ΔG°	12.5210 17.7953	12.6910 18.1774	12.9456 18.5421	13.3858 19.1726	13.4515 19.2667
2	La ³⁺ -HEDTA-FCA-PA	logK ^M _{MLL'L''} -ΔG°	12.1013 17.2232	12.4082 17.7724	12.8094 18.3470	12.8246 18.3668	12.9172 18.5014
3	La ³⁺ -HEDTA-PDA-PA	logK ^M _{MLL'L''} -ΔG°	11.8614 17.2546	12.4574 17.8430	12.7920 18.3221	12.8567 18.4147	13.1674 18.8598

Where C_A represents the total ligand concentration and A stands for number of moles of alkali added per mole of ligand.

The method of Ramamoorthy and Santappa⁹ is employed to calculate the stability constants (Table-2) by the following expressions.

System-1:1:1:1 Metal ion-monobasic (L)-mono basic (L') dibasic(L'').

The stability constant K_{MLL'L''} For this quaternary species were calculated by the following expression.

$$K = \frac{T_M - \frac{1}{3} \cdot A \cdot X}{\left(\frac{1}{3}\right)^4 \cdot A^4 \cdot X}$$

Where

$$A = \frac{4T_M - T_{OH} - [H^+]}{\frac{2[H^+]^2}{K_1 \cdot K_2} + \frac{3[H^+]}{K_1 + K_1' + K_1}} = 1 + \frac{[H^+]^2}{K_1 \cdot K_2} + \frac{3[H^+]}{K_1 + K_1' + K_1}$$

Where T_M total metal ion concentration and K₁, K'₁ K^M₁ and are the first dissociation constants of the three ligands where as K₂ is the second dissociation constant of the dibasic ligand.

System-1:1:1:1 metal ion-dibasic (L)-mono basic (L') dibasic (L'').

The stability constant K_{MLL'L''} for the quaternary species were calculated by following relation.

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

Where

$$A = \frac{5T_M - T_{OH} - [H^+]}{\frac{2[H^+]^2}{K_1 \cdot K_2} + \frac{3[H^+]}{K_1 + K_1' + K_1''}}$$

And

$$X = 1 + \frac{2[H^+]^2}{K_1' \cdot K_2' + K_1' \cdot K_2''} + \frac{3[H^+]}{K_1 + K_1' + K_1''}$$

Where K_1 , K_1' , K_1'' are the first dissociation constants of the monobasic acid (L) and dibasic acids (L' and L''), K_2' , K_2'' are the second dissociation constants of the dibasic acids (L' and L'').

The order of stability of quaternary complexes in terms of metal ion : $\text{La}^{(iii)} < \text{Pr}^{(iii)} < \text{Nd}^{(iii)} < \text{Gd}^{(iii)} < \text{Dy}^{(iii)}$ has been observed which is in the accordance with the increasing polarisability of the metal ions due to their decrease in size and increasing ionic potential ($\phi = \text{charge/radius ratio}$). Free energy change (ΔG°) has been calculated and found to be negative (table-2) in all the system, supporting the stabilization of complex¹⁰⁻¹¹.

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