Potentiometric Study Of Formation Of Quaternary Complexes Of Some Lanthanones With Multidentate Ligands

[1]Dr. Mahesh Pal Singh

[1]Associate Professor, Deptt. of Chemistry, Govt. P.G. College, Khair Aligarh, Uttar Pradesh

Abstract

Quaternary complex formation of La^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+} and Py^{3+} with pentadentate chelating ligand diethylene triamine pentacetic acid (K_4DTPA), 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 ± 1^0C and at a fixed ionic strength (m=0.1M KNO_3). 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^0 for the formation of 1:1:1:1, quaternary complexes has also been evaluated.

Keywords :- Diethylene Tramine Pentaacetic Acid, Pyridine 2, 6 Dicarboxylic Acid, Lanthanides, Quaternary Complexes, Stability Constants, Dissociation Constants, Free Energy Change, Potentiometric Titrotions

Introduction

Quaternary metal complexes in which DTPA and other heteroligand and corboxylic acid are present simultaneously in the co-odination 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 as 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 donar group[1,2]. 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[3].

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[4,5]. Solution of tetrapotassium salt of diethyl triamine pentaacetic acid (K_4DTPA) 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), molonic acid (MALO), tartaric acid (TAR), potassium nitrate and potassium hydrogen phthalate were prepared by direct weighing method in freshly prepared conductivity water.[6-10]

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 tablates solution (pH=9).Each titration was repeated atleast twice against (0.1M) KOH solution at $40\pm1°C$ to gain the reproducibility of result, keeping the

ionic strength at 0.1 M KNO_3, 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.

Results And Discussion :

The acid dissociation constants of the used ligands were determined by the method of Chaberck and Martell. These values (table-1) were calculated from titration curves by, using the formula for mono and dibasic ligands

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

$$K_1 = \frac{[H^+][aC_A + [H^+]]}{C_A - [aC_A + [H^+]]}, \quad K_2 = \frac{[H^+][(a-1)C_A - [OH^-]]}{C_A - [(a-1)C_A - [OH^-]]}$$ [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$_1$	pK$_2$
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[12] for the simultaneous chelation of the ligands to the metal ion. The values of stability constants were calculated by the following expression.

$$K^M_{MLLL''} = \frac{T_M - \frac{1}{3}[A].X}{\left(\frac{1}{3}\right)^4 . A^4 . X}$$

When   st dissociation constants of the three   sic ligand. The stability constants lie   s the order of increasing occupancy o   in their ionic radius.

$$A = \frac{4T_M - T_{OH} - [H^+]}{\frac{2[H^+]^2}{k_1''k_2} + \frac{3[H^+]}{k_1 + k_1' + k_1''}}, \quad X = 1 + \frac{[H^+]^2}{k_1''k_2} + \frac{3[H^+]}{k_1 + k_1' + k_1''}$$

The   ate the overall change in free energy (een 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 value of $\log K^M_{MLL'L''}$ and ΔG^0 for the 1:1:1:1 quaternary complexes [μ = $0.1MKNO_3$, Temp = 40 ± 1^0C]

Systems	Properties	Lanthanides				
		La(III)	Pr(III)	Nd(III)	Gd(III)	Dy(III)

1. LN^{3+} -DTPA-FA-PDA	$logK^M_{MLL'L''}$ $-\Delta G^0$	15.9876 22.8992	16.3311 23.3911	16.4943 23.6249	16.5697 23.7329	16.7792 24.0330
2. LN^{3+} -DTPA-FA-MALO	$logK^M_{MLL'L''}$ $-\Delta G^0$	17.1578 24.5752	17.2350 24.6858	17.4429 24.9836	17.7341 25.4007	17.9295 25.6805
3. LN^{3+} -DTPA-FA-TAR	$logK^M_{MLL'L''}$ $-\Delta G^0$	12.5871 18.0286	12.7746 18.2971	13.5840 19.4565	13.5951 19.4724	13.8377 19.8198

Conclusion : -

The order of stabilities of quaternary complexes with respect to metal ion is $La^{(III)} < Pr^{(III)} < Nd^{(III)} < Gd^{(III)} < Dy^{(III)}$. This can be atributed 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 $\Delta G°$ 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 $\Delta G°$, hence a more stable the complex is formed.

References :

1. Nair, M.S.; Arasu, P.T.; Pillai, M.S. and Nataranjan, C; J. Chem. Soc. Dalton Trans, 917 (1993), Talanta 40, 1993, 1411.
2. Neelkantan, M.A.; Indian J. Chem. 33A, 1994, 429.
3. Basolo, F. and Pearson, R.G. "Mechanism of Inorganic Reaction, A study of metal complexes in solution" wiley Eastern Pvt. Ltd. 11 ed, 1973, 23.
4. West, W.S. "Complexometry with EDTA and Related Reagents" Broglia Press, London, 1969.
5. Tishchenko, M.A. Zheltvii, I.I., and Poluektov, N.S., Zhur. Neorg. Khim. 19,1974,1793.
6. Singh, MP, Rawat, M.K., Journal of the Indian council of chemistry, 20(1), 27(2003)
7. Singh MP, Acta ciencia Indica, XXIX C, 4, 295 (2003)
8. Singh MP, Oriental journal of chemistry, 20(2); 407 (2004)
9. Singh MP, Goyal SC, Rawat MK, council, chan, 20(2), 84(2004)
10. Singh MP, IJARMS, 01 (1), 2018