eISSN 2581-8996
[Date]
THE INTERNATIONAL JOURNAL OF ADVANCED RESEARCH IN MULTIDISCIPLINARY SCIENCES (IJARMS)
A BI-ANNUAL, OPEN ACCESS, PEER REVIEWED (REFEREED) JOURNAL
Vol. 1, Issue 01, Jan 2018

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

[1]Dr. M.P. Singh

[1]Associate Professor (Chemistry), Govt. P.G. College, Khair (Aligarh)

Received: 01 Jan 2018, Accepted: 15 Jan 2018 ; Published on line: 31 Jan 2018

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 (μ=0.1 M 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^o) 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 (ø →= charge/radius ratio)

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

Introduction: lanthides are owing to non availaibility of orbitals for binding and large size of their common cations from few complexes with O, S or N donor ligants. An attempt has been made to study of stability constants of some Lanthanons[1-5.] 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^{0}C at the fixed ionic strength μ=0.1MKNO_3

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-dicarboxiylic acid (PDA), phthalic acid(PA), potassium nitrate and potassium hydrogen phthalate were prepared by direct weighing method in freshly prepared conductivity water .

eISSN 2581-8996
[Date]
THE INTERNATIONAL JOURNAL OF ADVANCED RESEARCH IN MULTIDISCIPLINARY SCIENCES (IJARMS)
A BI-ANNUAL, OPEN ACCESS, PEER REVIEWED (REFEREED) JOURNAL
Vol. 1, Issue 01, Jan 2018

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 standerd buffer tablets solution (pH=9) . Each titration was repeated Atleast twice against (0.1M) KOH solution at 40 ± 1^0c 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 Disscussion:- the acid dissociation constants of the used ligands were determind by the method of chaberck and Martell[8] . These values (table-1) were calculated from titration curves by using the formula for mono and dibasic ligands.

$HA \rightleftharpoons H. + A.$ ……(a)

$H_2A \rightleftharpoons HA + H^+$

$HA \rightleftharpoons A_2 + H^+$ ……(b)

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

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

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

$$[for\ monobasic\ ligand$$

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

$$[for\ diabasic\ ligand$$

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

[μ=0.1 M KNO_3 , Temp.=40±1°C]

	System	Properties	Metal Ion

eISSN 2581-8996
[Date]
THE INTERNATIONAL JOURNAL OF ADVANCED RESEARCH IN MULTIDISCIPLINARY SCIENCES (IJARMS)
A BI-ANNUAL, OPEN ACCESS, PEER REVIEWED (REFEREED) JOURNAL
Vol. 1, Issue 01, Jan 2018

			$La^{(iii)}$	$Pr^{(iii)}$	$Nd^{(iii)}$	$Gd^{(iii)}$	$Dy^{(iii)}$
1	La^{3+} -HEDTA-TCA-PA	$logK^{M}{}_{MLL'L''}$ $-\Delta G^{o}$	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	$logK^{M}{}_{MLL'L''}$ $-\Delta G^{o}$	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	$logK^{M}{}_{MLL'L''}$ $-\Delta G^{o}$	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 Santappa[9] is employed to calculate the stability constants (Table-2) by the following expressions.

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

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

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

Where

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

Where T_M total metal ion concentration and K_1 ,K'_1 $K^M{}_1$ and are the frist dissociation constants of the three ligands where as K_2 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.

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

Where

eISSN 2581-8996
[Date]
THE INTERNATIONAL JOURNAL OF ADVANCED RESEARCH IN MULTIDISCIPLINARY SCIENCES (IJARMS)
A BI-ANNUAL, OPEN ACCESS, PEER REVIEWED (REFEREED) JOURNAL
Vol. 1, Issue 01, Jan 2018

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

And

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

Where K_1, K'_1, K''_1 are the frist 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 :$La^{(iii)}$ <$Pr^{(iii)}$ <$Nd^{(iii)}$ <$Gd^{(iii)}$ <$Dy^{(iii)}$ 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 (ø=charge/radius ratio). Free energy change (Δ G^o) has been calculated and found to be negative (table-2) in all the system, supporting the stabilization of comlex[10-11].

REFERENCES

01. Agrawal, R.K., Goel, N. and Sharma, A. K., J. Indian Chem Soc., 78, 2001, 39.
02. Dwivedi, K. and Ahuja, R.;Indian J. Chem., 30A, 1991, 614.
03. Singh M. P. and Rawat, M.K.; J.Ind. C.C., 20(1), 2003, 27.
04. Nagar, R., Dwivedi, P.C. and Sharma, R.C., Indian J. Chem. 28A, 1989, 722.
05. Limaya, S.N. Verma S. and Saxena, M.C., Indian J. Chem., 32A, 1993; 545.
06. Vogel A I , A Text book of quantitative inorganic analysis , ELBS , London (1961).
07.Tishchenko, M.A.;Zheltvii,1.1 and Poluektov, N.S.; Zhur.Neorg.Khim.;19,1974,1793.
08.Chaberck,S.and Martell,A.E.;J.Am.Chem.Soc.,74,1952,5052.
09.Ramamoorthy S and Santappa M, Indian J Chem,9,381 (1971),33,1775 (1971).
10.Singh m.p. and rawat m.k. j.Ind. Council Chem. Vol.20,(1),2003,30.
11.Singh m.p.,Acta ciencia In