

Experimental Determination Of Stability Constant And Thermodynamical Parameter Of Quaternary Complexes Of Some Lanthanides

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Abstract

Quaternary complexes of some lanthanones viz, La^(III), Pr^(III), Nd^(III), Gd^(III) and Dy^(III) have been investigated potentiometrically with tripotassium salt of Ethylenediamine-N,N,N',N' - tetraacetic acid (K₃EDTA), Thiophene-2-carboxylic acid (TCA), Furan-2- Carboxylic acid (FA) and dibasic acid such as oxalic acid (ox), Succinic acid (SUC) in aqueous solution at 40±1°C and at an ionic strength of 0.1 mol dm⁻³. (KNO₃). The stability constants of these 1:1:1:1, quaternary complexes, have been evaluated by various computational methods. The relative order of stability in terms of La^(III) < Pr^(III) < Nd^(III) < Gd^(III) < Dy^(III) metal ion has been observed, which is almost in accordance with the increasing (Φ)=charge/radius ratio. The change in thermodynamic parameter (free energy change, ΔG°) has also been calculated under the same conditions.

Keywords :- Ethylene diamine tetracetic acid, Furan 2 –carboxylic acid, Lanthanides, stability constant, free energy change, potentiometric titration.

Introduction

The lanthanides are attractive for complex studies due to their high charge and their large and variable coordination number. The ligands have been chosen because of their ability to forming complex with metal ion'. A Considerable work on binary and ternary complexes of transition metal^{2,3,4} and inner transition metals^{5,6,7} has been reported, but work on quaternary complexes is rather scanty. Interligand hydrophobic and stacking interactions in complexes depend on the extent of overlap between the non-coordinated side groups of the ligands bound to metal ions⁸. Besides the geometric coordination requirements of the metal ions, the polydentate character of the ligand, leading to different orientation of the side group, also influence such interactions⁹.

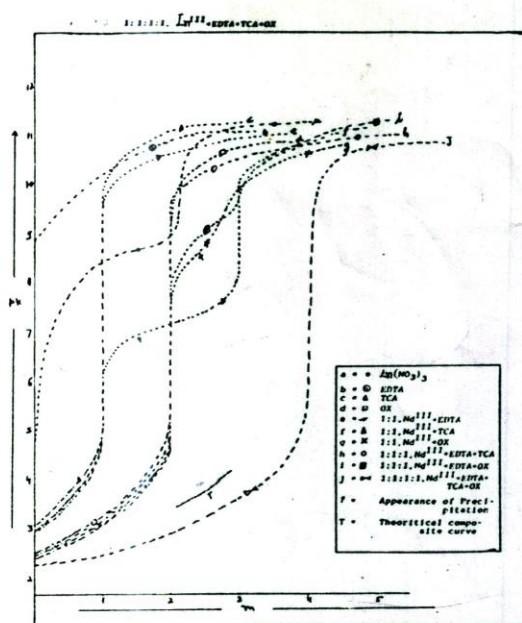
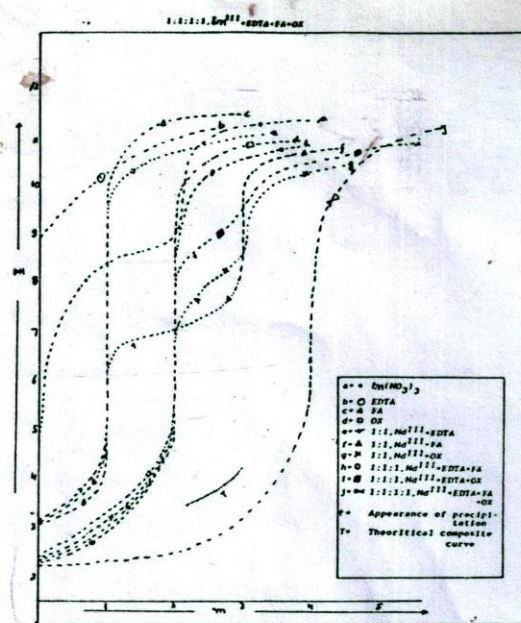
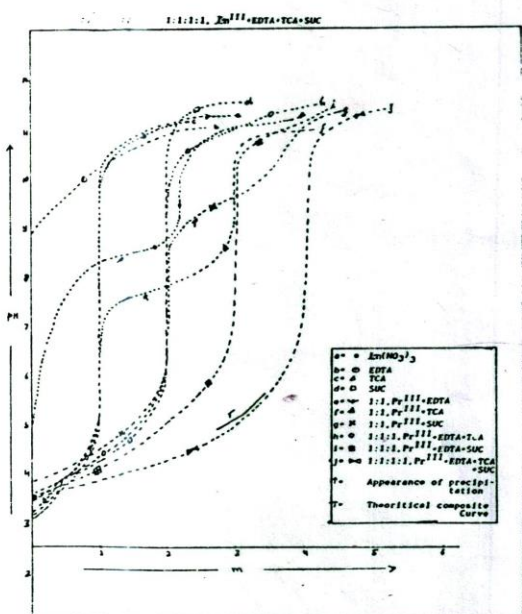
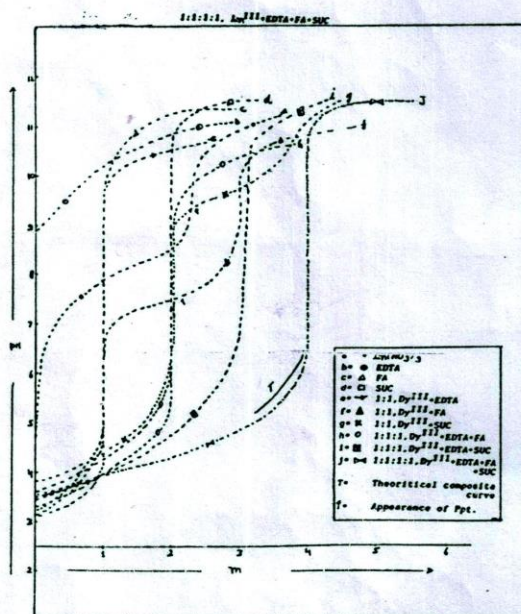
Experimental :-

All the reagents used were of AR, BDH grade. The solution of all the chemicals were prepared in doubly distilled water. Solution of Lanthanide nitrates were prepared and standardized by the oxalate method¹⁰. Ethylene diamine, N, N, N', N'- tetraacetic acid was used in their monoprotated form and prepared in calculated volume of KOH.

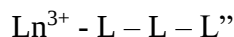
The solutions of TCA, FA, SUC, OX, KNO₃ and potassium hydrogen phthalate were prepared by direct weighing method and solution of KOH were prepared by standardization method.

pH - metric titration were carried out by ELICO (LI-613) pH-meter fitted with a combined glass - calomel electrodes assembly, used for entire pH-range (0 to 14) having an accuracy of ± 0.01 pH unit. The instruments was standardized against potassium hydrogen phthalate solution (0.05M) for pH-4 and standard Buffer tablates solution (pH-9). Each Titration was repeated at least twice against (0.1 M)

potassium hydroxide solution at $40 \pm 1^\circ\text{C}$ to ensure the reproducibility of result, keeping the ionic strength at 0.1 mole dm^{-3} (KNO_3) and total volume (50 ml) constant in the 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. 1,2,3 and 4 being the representation curves for lanthanides and ligands in the systems

Fig.-1, System- Ln^{3+} -EDTA-TCA-OXFig.-2, System- Ln^{3+} -EDTA-FA-OXFig.-3, System- Ln^{3+} -EDTA-TCA-SUCFig.-4, System- Ln^{3+} -EDTA-FA-SUC

Where $\text{Ln}^{3+} = \text{La}(\text{III}), \text{Pr}(\text{III}), \text{Nd}(\text{III}), \text{Gd}(\text{III}), \& \text{Dy}(\text{III})$



Where $\text{Ln}^{3+} = \text{La}^{(\text{III})}, \text{Pr}^{(\text{III})}, \text{Nd}^{(\text{III})}, \text{Gd}^{(\text{III})}$ and $\text{Dy}^{(\text{III})}$

$\text{L} = \text{EDTA}, \text{L}' = \text{TCA/FA}, \text{L}'' = \text{OX/SUC}$

The dissociation constant (Table-1) of TCA, FA, K₃EDTA, SUC, OX were calculated by the method of chaberck and martell". Stability constants ($\log K_{\text{MLL}'\text{L}''}^{\text{M}}$) for quaternary Mixed ligand Complexes were calculated by the method of Ramamoorthy and santappa¹² for the simultaneous complexation of ligands to the metal ion and in stepwise addition of the ligand to metal ion the method of Thompson and Loraas¹³ was used. The average ($\log K_{\text{MLL}'\text{L}''}^{\text{M}}$) values were used to calculated the free energy change (ΔG°) from the van't Hoff's isotherm. The data are listed in Table-2.

Table-1

Ligand	PK ₁	PK ₂
K ₃ EDTA	9.78	
TCA	3.63	
FA	3.68	
SUC	4.54	5.96
OX	2.07	3.94

Results and discussion:

Potentiometric titration have been carried out to determine the stability constants of quaternary Complexes of the type $\text{M} + \text{L} + \text{L}' + \text{L}'' \rightleftharpoons \text{MLL}'\text{L}''$. The value of stability constants are recorded in table-2, lie in order $\text{La}^{(\text{III})} < \text{Pr}^{(\text{III})} < \text{Nd}^{(\text{III})} < \text{Gd}^{(\text{III})} < \text{Dy}^{(\text{III})}$ can be correlated in terms of increasing ionic potential (Φ) of the metal ion¹⁴. The value of free energy change (ΔG°) of the resulting quaternary complexes are recorded in table-2, calculated ΔG° Values have been found to be negative in all the systems, indicating the spontaneity of complex formation¹⁵⁻¹⁹.

Table No. 02 – Stability constants and free energy change of quaternary complexes [$\mu = 0.1 \text{ mol dm}^{-3} (\text{KNO}_3)$, Temp = $40 \pm 1^\circ\text{C}$]

Systems	Properties	Lanthanides				
		$\text{La}^{(\text{III})}$	$\text{Pr}^{(\text{III})}$	$\text{Nd}^{(\text{III})}$	$\text{Gd}^{(\text{III})}$	$\text{Dy}^{(\text{III})}$
$\text{Ln}^{3+} - \text{EDTA-TCA-OX}$	$(\log K_{\text{MLL}'\text{L}''}^{\text{M}})$	10.7194	10.9676	11.1900	11.3684	11.7200
	$-\Delta G^\circ$	15.3535	15.7089	16.0275	16.2830	16.7866
$\text{Ln}^{3+} - \text{EDTA-FA-OX}$	$(\log K_{\text{MLL}'\text{L}''}^{\text{M}})$	12.3052	12.5079	12.7186	12.7886	12.9126
	$-\Delta G^\circ$	17.6248	17.9152	18.2169	18.3172	18.4948
$\text{Ln}^{3+} - \text{EDTA-TCA-SUC}$	$(\log K_{\text{MLL}'\text{L}''}^{\text{M}})$	12.5306	12.5449	12.7372	12.7568	13.1286
	$-\Delta G^\circ$	17.9477	17.9681	18.2436	18.2717	18.8042

LN ³⁺ -EDTA-FA-SUC	(logK _{MLL'L''} ^M) -ΔG ⁰	12.3388	12.5814	12.7325	12.9216	13.2952
		17.6729	18.0204	18.2368	18.5077	19.0428

References:-

1. S.N. Limaye and M.C. Saxena, J. Indian chem. Soc., 62, (1985), 353, 67 (1990) 162; S.K. Shak and C.M. Gupta, Talanta, 27, (1980) 823.
2. R. Nagar, R.K. Parashar and R.C. Sharma, Bull Electrochem. 4, (1988) 405.
3. R.C. Sharma, and R. Nagar J. Indian chem. soc. 65, (1988) 240.
4. M.S. Nair and M.A. Neelakantan, J. Indian, chem, soc. 77 (2000) 394.
5. G.K. Chaturvedi, R.C. Sharma and R. Kumar; J inorg, nucl, chem, 43, (1981) 2503.
6. H.S. Rana and J.P. Tondon, Indian J. Chem., 14 (1976) 428.
7. S.D. Naikwade, P.S. Mane and T.K. chondhekar, J. Indian chem, soc. 78 (2001) 41.
8. C. Telene & G. Lancelot, Prog. Biophys, Mol. Biol, 39, (1982)1.
9. P. Amico, R.P. Bonomo, R. Coli, V. Cucinotta, P.G. Daniele, G. Ostacoli and E. Rizzarelli, Inorg chem. 28, (1989) 3555.
10. M.A. Tishchenko I.I. Zheltvoi and N.S. Polucktov, Zneogy Khim, 19 (1974) 1793.
11. S. Chaberek and A.E. Martell; J. Am. Chem. soc. 74, (1952) 5052.
12. S. Ramamoorthy and M. Santappa, Indian J. Chem. 9 (1971), 381.
13. L.C. Thompson and J.A. Loraas Inorg, chem. 2 (1963) 89.
14. D.B. Ingle and D.D. Khandkar, J. Indian chem. Soc. 50, (1973) 190.
15. Singh, MP, Rawat, M.K., Journal of the Indian council of chemistry, 20(1), 27(2003)
16. Singh MP, Acta ciencia Indica, XXIX C, 4, 295 (2003)
17. Singh MP, Oriental journal of chemistry, 20(2); 407 (2004)
18. Singh MP, Goyal SC, Rawat MK, council, chan, 20(2), 84(2004)
19. Singh MP, IJARMS, 01 (1), 2018