

pH-METRIC STUDIES ON THE QUATERNARY COMPLEXES OF SOME RARE EARTHS

P.S. Rajpoot

Associate Professor

Department of Chemistry,

Govt. P.G. College, Chharra, Aligarh (U.P.)

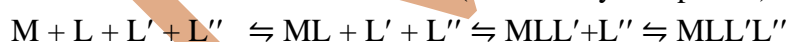
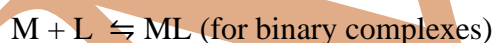
INTRODUCTION

The Metal complexes are formed by the combination of one or different type of complexing agents with central metal ion resulting in the formation of mixed ligand complexes. These are further divided as Binary, Ternary and quaternary complexes depending on the type of ligands.

Andoreg et.al.¹ and ozer² reported an expanded co-ordination number of rare earths, usually Lanthanons show a tendency to expand their normal co-ordination number beyond six³⁻⁴. Ternary complexes of the Lanthanons with basic ligands have been investigated⁵⁻⁶. Recently Sharma et.al.⁷⁻¹² have reported some quaternary complexes of some transition as well as rare earths metals electrometrically.

The stability/constant and free energy of quaternary complexes with various combination of the system 1:1:1:1, M(III)-NTA-TCA-IMDA, have been measured pH-metrically in this paper. (Where M(III)=La(III), Pr(III) and Nd(III) NTA- Nitrilotriacetic Acid, TCA=Thiopine-2-Corboxylic acid, IMDA=Iminodiacetic acid.

The quaternary complexes formation can take place by step-wise co-ordination of ligands to the metal ion as-



The increasing order of stability constants of quaternary species¹³ in terms of metal ion has been found to be La(III) < Pr(III) < Nd(III). It may be explained on the basis of decreasing size and increasing ionization potential (Charge/radius ratio) of the metal ions.

EXPERIMENTAL

The chemicals were used of Analar (BDH) and GR (E.Merck/Fluka) grades, all the solutions needed were prepared in conductivity water. Stock solutions of rare earth metal ions were prepared by dissolving Nitrate(M). The desired solution of Potassium Nitrate(M), Potassium hydroxide (0.1M)

and Potassium hydrogen Phthalate (0.05M) were prepared by dissolving their calculated amounts in conductivity water.

All the amino-poly carboxylic acids were used in their mono protonated forms. The solution of dipotassium salt of Nitrilotri-acetic acid was prepared by dissolving their calculated amount in required volume of standard potassium hydroxide solution. IMDA and TCA solutions were prepared by direct weighing method and dissolved in conductivity water.

The pH-metric titrations were carried out against (0.1M) Potassium hydroxide solution with Toshniwal pH-meter (C.L.46) using a combined electrode assembly. The Temp. was maintained at $25 \pm 1^{\circ}\text{C}$ with the help of an electrically controlled thermostat. At the beginning of each titration, the instrument was standardized with the help of ($5 \times 10^{-2}\text{M}$) Potassium hydrogen phthalate solution before starting the titration of the total volume (50 ml) and the ionic strength were kept constant. The obtained pH-value were plotted against the moles of base (KOH) added per mole of metal or/and ligand/s.

RESULTS AND DISCUSSIONS

The pk values of the ligands (Table-1) were determined pH-metrically by the method of Chaberk and Mertell 14 for dibasic ligands-

$$K_1 = \frac{[\text{H}^+][\text{aC}_A + \text{H}^+]}{\text{C}_A - [\text{aC}_A + (\text{H}^+)]} \quad \text{----(1) In lower buffer region in higher pH-range}$$

$$K_2 = \frac{[\text{H}^+][(\text{a}-1)\text{C}_A - [\text{OH}^-]]}{\text{C}_A - [(\text{a}-1)\text{C}_A - [\text{OH}^-]]} \quad \text{----(2)}$$

Since K_1 , K_2 each dissociation step is considered separately.

The dissociation constant of the monobasic acids can be determined by the method of Albert and sergeat¹⁵.

$$K = \frac{[\text{H}^+][\text{aC}_A + [\text{H}^+] - [\text{OH}^-]]}{\text{C}_A - [\text{aC}_A + [\text{H}^+] - [\text{OH}^-]]} \quad \text{----(3)}$$

Where C_A – is the total ligand concentration.

a – stand for number of moles of alkali added per mole of ligand.

**Table-1 pK values of the ligands at
 $25 \pm ^{\circ}\text{C}$**

Ligand	pK ₁
K ₂ NTA	9.84
TCA	3.25
IMDA	9.05

Formation constants of the mixed ligand complexes

The calculations of the formation constant for the resulting hetro-legand species could only be made in soluble systems in the region of mixed ligand complex formation by the method of Thompson and Lorass¹⁶ in case of step-wise addition of ligand to the metal ions.

$$K_{MLL'L''} = \frac{C_B - \left[(B) \left(\frac{H^+}{K_1} + 1 \right) \right]}{(B) \left[C_m - C_B + (B) \left(\frac{H^+}{K_1} + 1 \right) \right]} \quad \text{----(4)}$$

Where

$$B = \frac{(1-a)C_B - (H^+) + (OH^-)}{\left[\frac{H^+}{K_1} \right]} \quad \text{----(5)}$$

C_m = Total concentration of metal ion.

a = Number of moles of alkali added per mole of ligand present.

C_B = Total concentration of ligand.

B = Free ligand concentration.

$K_{MLL'L''}$ Formation constant of quaternary complexes.

Free Energies of Formation:

The free energies of formation (ΔG^0) for the resulting mixed ligand complexes were calculated by the expression-

$$\Delta G^0 = -RT \ln K_1 \quad \text{----(6)}$$

$$= -2.303 RT \log K_1 \quad \text{----(7)}$$

Where ' K^1 ' is the formation constant of the quaternary complexes.

R = gas constant,

T = absolute Temperature

ΔG^0 = Free energy of formation obtained in K. Cal./mole

Results of stability constant and free energies of quaternary complexes of rare earth metal given in Table-3.

SYSTEM - 1:1:1:1 M(III) – NTA – TCA – IMDA

Where M = La (III), Pr (III) and Nd (III)

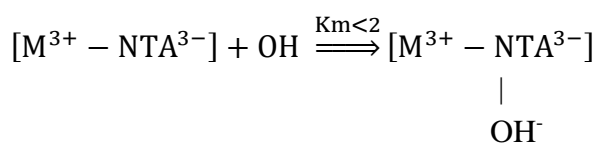
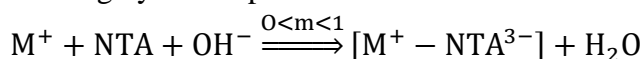
Curve 'a' (Fig.1-3) representing the pH-metric titration of metal ions, exhibits an inflection at $m \sim 2.5$, which may be attributed to the basic salt formation and is in earlier observation of Britton¹⁷.

Curve 'b' (Fig.1-3) depicts the Titration of dipotassium salt of Nitrilotriacetic acid (K_2 NTA), a weak inflection at $m=1$, on the curve attributes the labile nature of remaining carboxylic proton of acid salt at high pH.

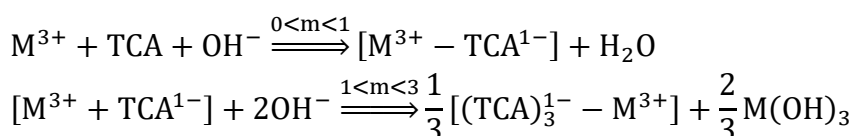
Curve 'c' (Fig.1-3) showing the Titration of Thiophene-2 carboxylic acid (TCA), which exhibits a single well defined inflection at $m=1$, attributing the titration of the carboxylic proton of the acid.

Curve 'd' (Fig.1-3) represent the titration of IMDA, an ill-defined inflection at $m\sim 4$, which may be correlated to the titration of the carboxylic group forming acid salt of the dibasic acid.

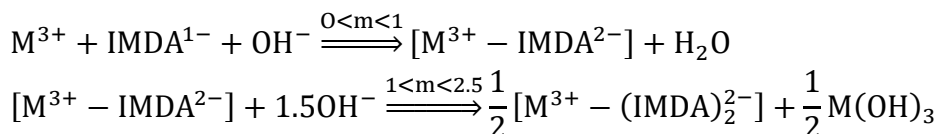
BINARY SYSTEM – Curve 'e' (Fig.1-3) describes the titration of 1:1, M(III)-NTA binary system. A sharp inflection at $m=1$, is due to the formation of 1:1, M(III)-NTA binary complex¹⁸. Another poor inflection at $m=2$, indicates the addition of one more OH⁻ group to the initially formed complex forming hydroxo species.



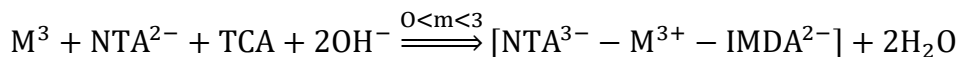
Curve 'f' (Fig.1-3) corresponds the titration of 1:1, M(III)-TCA binary system. The lowering in the initial pH as compared to the curve 'c' followed by an inflection at $m=1$, may be ascribed to the formation of 1:1, M(III)-TCA complex. Another inflection at $m=3.0$, in this system may, however, be correlated to the disproportionation of the initially formed 1:1 complex into 1:3 M(III)-TCA soluble species with the simultaneous precipitation of the remaining metal as its hydroxide in the higher buffer region.



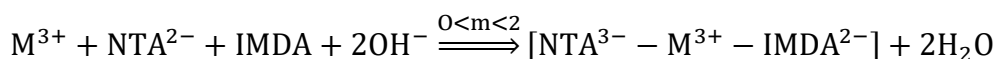
Curve 'g' (Fig.1-3) depicts the titration of 1:1, equimolar mixture of metal nitrate and ligand IMDA. An initial lowering in the pH followed by an inflection at $m=1$, may be attributed to the formation 1:1, M(III)-IMDA complex. Another inflection at $m\sim 2.5$ and the appearance of a white gelatinous precipitate at $m > 1$, may be ascribed to the disproportionation of the initially formed 1:1, species into 1:2, M(III)-IDMA complex and the remaining metal is precipitated as metal hydroxide.



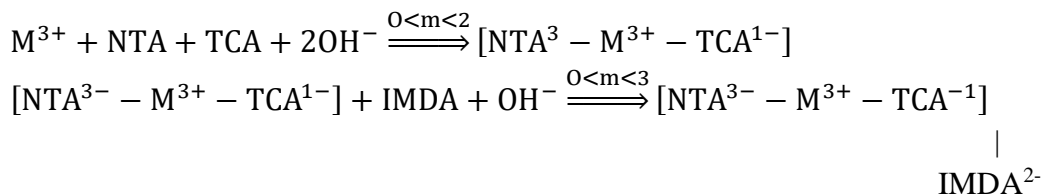
TERNARY SYSTEM – Curve ‘h’ (Fig. 1-3) describes the titration of 1:1:1, M(III)-NTA-TCA. The initial lowering in pH in comparison to the curve ‘f’ (for 1:1, M(III)-TCA, binary complex) and two inflections at m=2 and m=3 are obtained on the curve ‘h’, The first inflection at m=2 shows the formation of 1:1, m=(III)-NTA in lower pH range whereas second one at m=3 indicates the addition of TCA lateron.



1:1:1, M(III)-NTA-IMDA Ternary system is represented by the curve ‘i’ which gives single sharp inflection at m=2 and indicates the simultaneous chelation of both the ligands (NTA and IMDA) to the metal ion.



QUATERNARY SYSTEM – Curve ‘j’ (Fig.1-3) describes the titration of 1:1:1:1, M(III)-NTA-TCA-IMDA. This curve runs parallel to the curve ‘h’ for 1:1:1, M(III)-NTA-TCA Ternary System. An appreciable lowering in the initial pH of this curve ‘j’ as compared to the curves representing the titrations of Binary and Ternary systems and inflection at m=2, on this curve shows the formation of 1:1:1, M(III)-NTA-TCA Ternary species in the beginning. The occurrence of one more inflection at about m=3, shows the step-wise formation of 1:1:1:1, M(III)-initially 1:1:1, Ternary complexes in the higher buffer region.



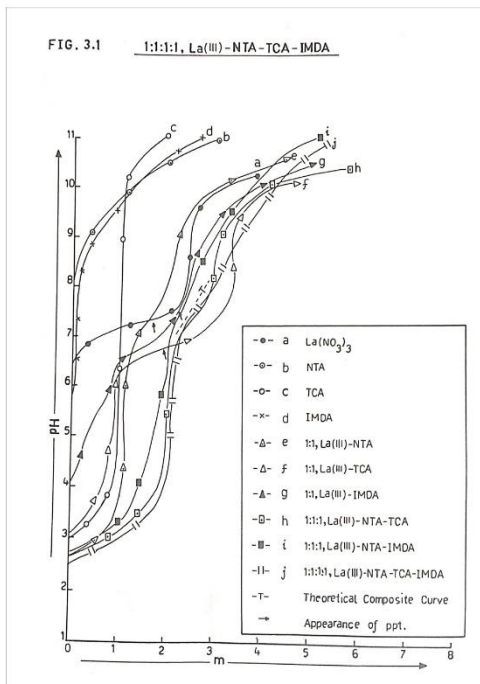


Fig-1

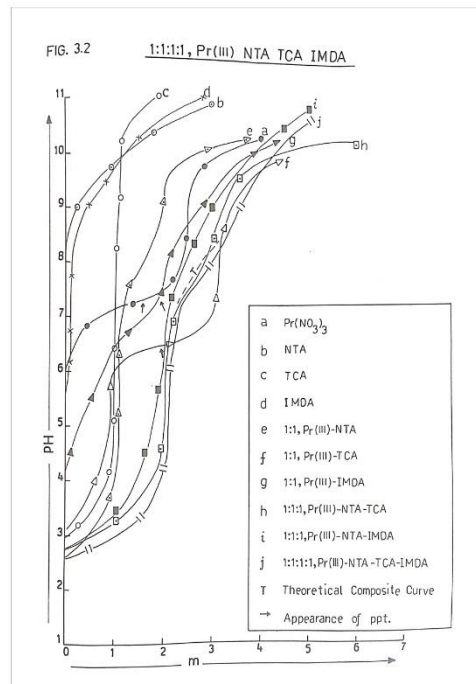


Fig-2

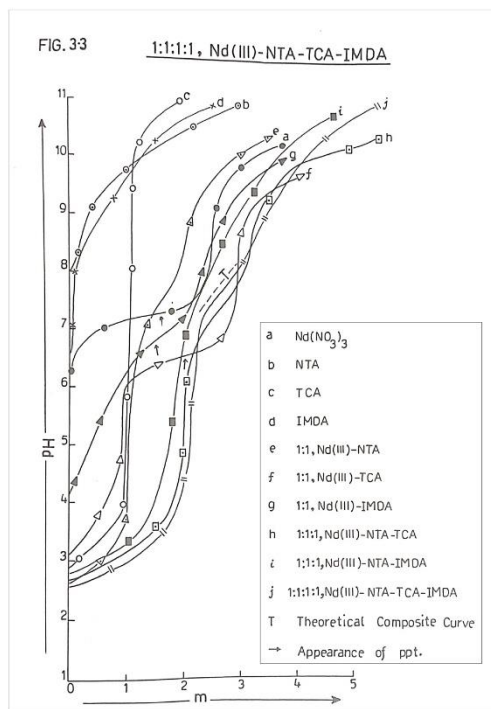


Fig-3

The formation of above mixed ligand quaternary complexes in solution is further supported by the following facts.

- (i) The non-appearance of any solid phase in the region of quaternary complex formation.
- (ii) By the constancy observed in the calculated values of stability constants.
- (iii) Non-superimposable nature of the theoretical composite curve (T) with the experimental curve 'j' representing the quaternary systems.
- (iv) The lowering in pH of the Titration curves representing the quaternary systems as compared to the curves for Binary and Ternary Systems.

The calculated values of the stability constants ($\log K_{MLL'L''}$) and free energies of the quaternary species at $25 \pm 1^\circ\text{C}$ are recorded in Table (2)

Table-2– System: 1:1:1:1, M(III)-NTA-TCA-IMDA Quaternary System-

(Where M(III) = La(III), Pr(III), Nd(III))

Temperature = $25 \pm 1^\circ\text{C}$, $\mu = 0.1 \text{ M KNO}_3$, $\text{KOH} = 0.1 \text{ M}$

Concentration = $\text{M(III)} = \text{NTA} = \text{TCA} = \text{IMDA} = 5 \times 10^{-3} \text{ M}$

S.No.	m	<u>La(III)-NTA-TCA-</u> <u>-IMDA</u>		<u>Pr(III)-NTA-TCA-</u> <u>-IMDA</u>		<u>Nd(III)-NTA-TCA-</u> <u>-IMDA</u>	
		pH	Log $K_{MLL'L''}$	pH	Log $K_{MLL'L''}$	pH	Log $K_{MLL'L''}$
1.	0.1	4.50	-	4.52	-	4.55	-
2.	0.2	6.53	-	6.72	3.96*	6.64	4.02
3.	0.3	6.70	4.14	7.26	4.18	6.93	4.22
4.	0.4	7.21	4.19	7.38	4.21	7.15	4.30
5.	0.5	7.36	4.22	7.42	4.23	7.35	4.34
6.	0.6	7.45	4.26	7.50	4.28	7.55	4.39
7.	0.7	7.67	4.31	7.70	4.34	7.78	4.41
8.	0.8	7.78	4.36	7.84	4.49	7.86	4.61
9.	0.9	7.94	4.54	7.96	4.96*	8.01	5.01*

$\log K_{MLL'L''}$	$\log K_{MLL'L''}$	$\log K_{MLL'L''}$
$= 4.29 \pm .20$	$= 4.31 \pm .15$	$= 4.37 \pm .19$
$\Delta G^0 = -5.85 \text{ K.Cal/mole}$	$\Delta G^0 = -5.87 \text{ K.Cal/mole}$	$\Delta G^0 = -5.95 \text{ K.Cal/mole}$

* Values Omitted.

The relative order of stability of quaternary species in terms of metal ions has been found to be in the increasing order La(III) < Pr(III) < Nd(III). Which may be explained on the basis of decreasing size and increasing ionization potential (Charge/radius ratio) of the metal ions.

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