

'Formation Studies of Some Hetroligand Complexes of Rare – Earth Metals'**R. S. Saxena* and S. S. Yadav****ABSTRACT**

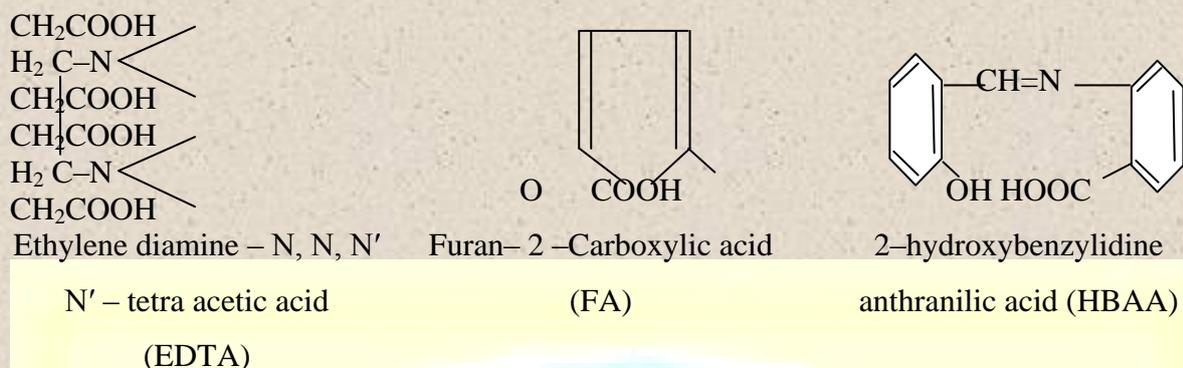
Potentiometric evidences have been cited for the formation of 1:1:1:1, MLL'L'' quaternary complexes [where M (III) = La (III), Pr (III) and Nd (III), L = ethylene diamine – N, N, N'N' – tetra acetic acid (EDTA), L' = furan – 2 – carboxylic acid (FA) and L'' = 2 – hydroxybenzylidene anthranilic acid (HBAA)] have been studied potentiometrically with a view to determine their formation constants, thermodynamic parameters and to explore and confirm the possibilities of their expanded coordination number [1, 2]. The formation constants $\log K_{MLL'L''}$ and $\log K_{MLL'L''}$ for the resulting ternary and quaternary complexes at constant ionic strength ($\mu = 0.1 \text{ M KNO}_3$) and four different temperatures ($15 \pm 0.1^\circ\text{C}$, $25 \pm 0.1^\circ\text{C}$, $35 \pm 0.1^\circ\text{C}$ and $45 \pm 0.1^\circ\text{C}$) have been evaluated. The order of formation constants in terms of metal ions has been found both in ternary and quaternary complexes as: La (III) < Pr (III) < Nd (III) and in terms of Complex species as: ternary < quaternary. These orders have been explained in terms of increased number of fused rings [3]. The obtained negative values of ΔG° indicated the spontaneous nature of the reaction and the bond formation in the resulting complexes. The obtained negative values of ΔH° and positive values of ΔS° indicated that both enthalpy and entropy favours the complex formation.

(Key Words: Stability Constants / Lanthanides / Ternary Complexes/ Quaternary Complexes)

INTRODUCTION:

In recent years, the chemistry of ternary complexes of lanthanides [4 – 6] has been developed considerably but comparatively less work has been reported on quaternary complexes of lanthanide ions [7]. A survey of literature reveals that lanthanide ions expand their coordination number in mixed – ligand complex formation. This idea led us to investigate some more 1: 1: 1: 1, quaternary systems of lanthanides potentiometrically to find out the formation of their quaternary mixed – ligand complexes. In the present paper, we report pH – metric studies on 1: 1: 1: 1, M (III) – EDTA – FA – HBAA quaternary systems with a comparison of their stability with those of the corresponding 1: 1: 1, M (III) – EDTA – FA / HBAA ternary complexes.

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EXPERIMENTAL:**MATERIAL AND METHODS:****Fig. 1. Structure of Ligands Used**

The solutions of all the chemicals (AR, BDH, GR, or E. Merck) used, were prepared in conductivity water. Standard Solutions of lanthanide nitrates were prepared and standardised by their usual methods [8,9]. EDTA was used in the form of its tripotassium salt. The solutions of 2 – furoic acid, potassium nitrate and potassium hydrogenphthalate were prepared by direct weighing method. The solution of HBAA was prepared in commercially available alcohol. The concentrations of above solutions were further checked by pH – metric titrations against 0.05 M KOH solution.

INSTRUMENT AND TECHNIQUE:

pH – measurements were carried out with a Toshniwal pH-meter (CL-46) using a combined glass and calomel electrode assembly. The instrument was standardized against 0.05M potassium hydrogenphthalate solution (pH=4) before starting each titration. The total volume (50ml) and ionic strength ($\mu=0.05\text{MKNO}_3$) also kept constant in the beginning of each titration.

CALCULATIONS:

- (a) **Formation Constants :** The dissociation constants of tripotassium ethylene diamine- N, N, N', N'-tetra acetate (K_3EDTA) ($\text{p}k=9.65 \pm 0.04$), 2-furoic acid (FA) ($\text{p}k=3.32 \pm 0.12$) and 2-hydroxybenzalidine antheranilic acid (HBAA) ($\text{p}k_1=5.57$)

± 0.08 , $\text{pk}_2 = 11.40 \pm 0.07$) were evaluated by the method of Chaberek and Martell [10]. The formation constants ($\log K_{\text{MLL}'}$, $\log K_{\text{MLL}''}$ and $\log K_{\text{MLL'L}''}$) of the ternary and quaternary complexes were calculated by the method of Ramaoorthy and Santappa (11) from the expression;

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

Where the total free ligand concentration

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

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

In all the above expression, T_M is total metal ion concentration K_1 , K_1' , and K_1'' are the first dissociation constants of three ligands whereas K_2 is the second dissociation constant of the dibasic ligand.

(b) Thermodynamic parameters:

Thermodynamic parameters; free energy of formation (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), changes were calculated as follows :

(i) Free energies of formation:

Free energies of formation (ΔG^0), obtained in K.Cal. /mol. were evaluated by putting the values of formation constants in the equation given below :

$$\Delta G^0 = RT \log K.$$

Where R = gas constant (1.987 Cal/mol/deg.), T = temperature in absolute degrees.

(ii) Enthalpy or heat change:

Following equation is given to evaluate the enthalpy change in K.Cal / mol. during complex formation:

$$\Delta H^0 = \frac{2.303 R T_1 T_2 (\log \beta_2 - \log \beta_1)}{T_2 - T_1}$$

Where β_1 and β_2 are the formation constants at the temperature T_1 and T_2 respectively.

(iii) Entropy Change:

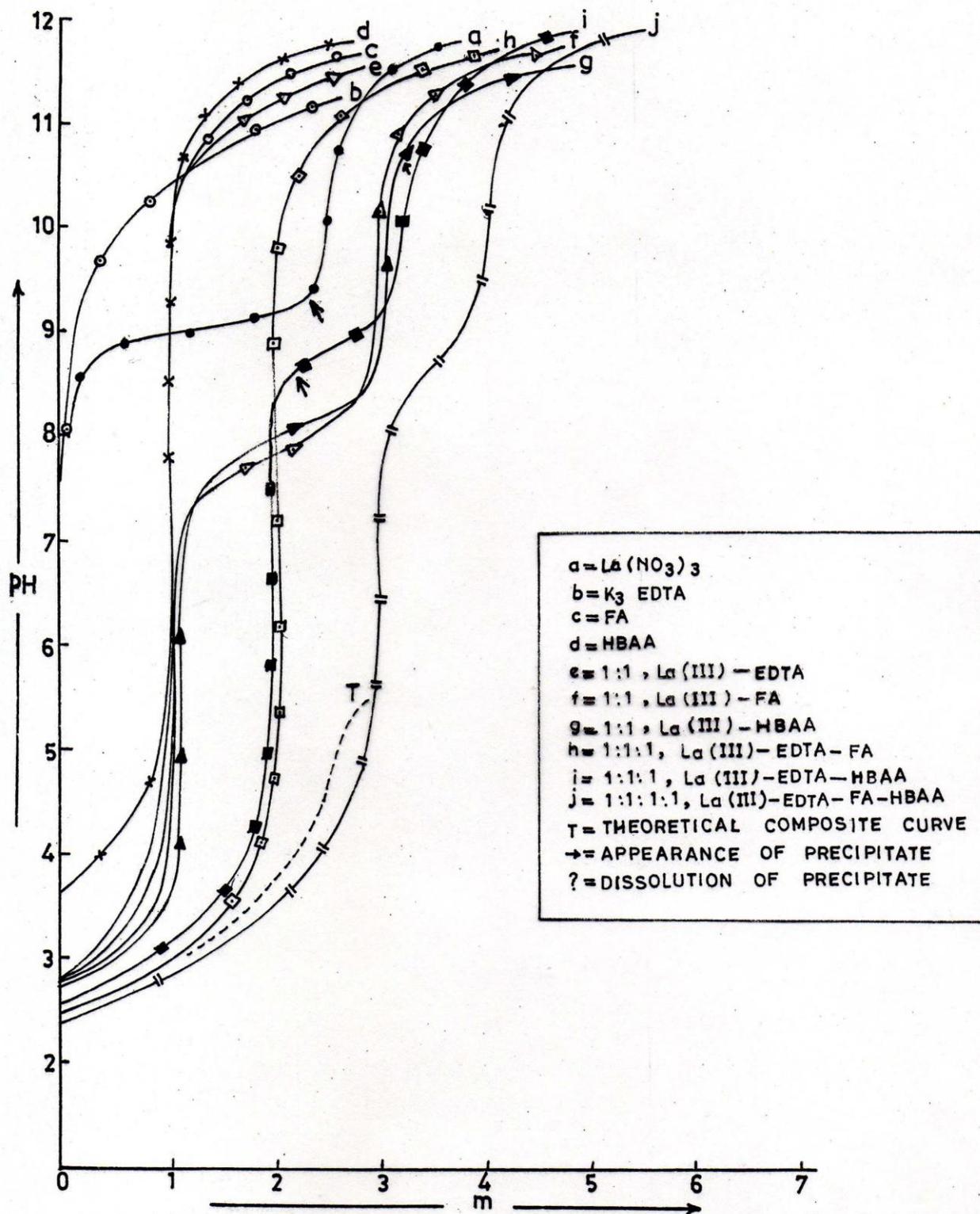
The value of entropy (ΔS^0) in cal./deg. was evaluated by the equation given as below:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

RESULTS AND DISCUSSION:

The corresponding curves obtained in all systems of different metal ions at four different temperatures were identical hence for the sake of brevity, the curves for 1:1:1:1, La (III) – EDTA – FA – HBAA have only been discussed.

FIG. 2 SYSTEM 1:1:1:1, La (III) - EDTA - FA - HBAA



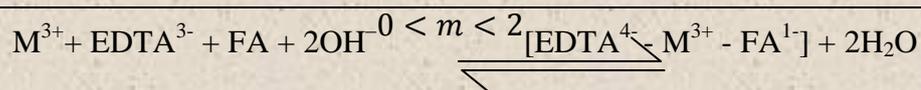
A well-defined inflection ($M \approx 2.6$) before $m = 3$ on the curve 'a' (Fig. 2) indicates the basic salt formation (12) of metal ions and is in conformity with the observations of Britton (13) ($m =$ moles of alkali added per mole of the metal ion or the ligand). Curve 'b' (Fig. 2) for tripotassium salt of EDTA may be ascribed to then non titrable nature of the remaining carboxylic proton of the amino polycarboxylic acid. Curve 'C' represents the pH-metric titration of 2-furoic acid (FA). A single sharp inflection at $m=1$ indicates the titration of only carboxylic proton present in this acid and curve 'd' represents the potentiometric titration of 2-hydroxy benzalidine anthranitic acid (HBAA). A sharp inflection at $m=1$ on this curve depicts the titration of the only carboxylic proton present in this acid.

BINARY SYSTEMS:

Curve 'e' (Fig. 2) illustrates the titration of 1:1, La (III)-EDTA. An extensive lowering in the initial pH as compared to the curve 'b', followed by a well-defined inflection at $m=1$ may be attributed to the formation of soluble 1:1, La (III)-EDTA species [14]. Curve 'f' illustrates the titration of 1:1, M (III)-FA binary species. An inflection at $m=1$ may be due to the formation of 1:1, La (III)-FA complex. Another inflection at $m \approx 3$ may be attributed to the simultaneous formation of metal hydroxide and 1:3, metal-ligand complex. It is further evidenced by the appearance of solid phase at $m>1$. Curve 'g' (Fig. 2) represents the titration of 1:1, M (III)-HBAA in 1:1 ratio. A well-defined inflection at $m=1$ may be due to the formation of 1:1, M (III)-HBAA species due to the titration of the carboxylic proton of the ligand. Another inflection at $m \approx 3$ may be attributed to the simultaneous formation of metal hydroxide and 1:3, metal-ligand complex in higher buffer region. It is further evidenced by the appearance of precipitate at $m>3$.

TERNARY SYSTEM:

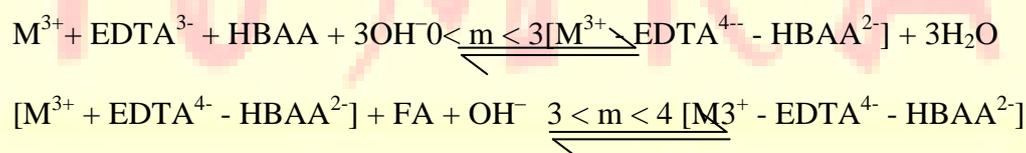
Curve 'h' (Fig. 2) representing the titration of 1:1:1, M (III)-EDTA-FA ternary system. An inflection at $m = 2$ may be due to the titration of the $-COOH$ group of tripotassium salt of EDTA and FA simultaneously forming 1:1:1, M (III)-EDTA-FA ternary complex:



During the titration of 1:1:1, M (III) – EDTA- HBAA ternary system, Curve ‘i’ depicts an ill-defined inflection at $m \approx 2$ due to the formation of 1:1, M (III)-EDTA binary complex in lower buffer region. Another inflection at $m \approx 3.5$ can probably be ascribed to the complexation of HBAA to the initially formed species in higher buffer region forming 1:1:1, M (III) – EDTA – HBAA ternary complex.

QUATERNARY SYSTEM:

Curve ‘j’ (Fig. 2) illustrates the pH-metric titration of 1:1:1:1, M (III)-EDTA-FA-HBAA quaternary system. An initial lowering in the pH of this curve as compared to the curves representing the binary and ternary species (curves e, f, g, h, and i) followed by an inflection at $m = 3$ may be correlated to the simultaneous chelation of EDTA and HBAA to the metal ion forming 1:1:1, M (III)-EDTA-HBAA ternary species in the beginning. Another inflection at $m \approx 4$ may be ascribed to the addition of the remaining ligand (FA) in higher pH-range forming 1:1:1:1, M (III)-EDTA-FA-HBAA quaternary complex. The absence of any precipitate during the titration and non-super imposable nature of the theoretical composite curve ‘T’ [15] (drawn by adding horizontal distances of curves ‘e’ and ‘i’ to the curve ‘j’ in the region of mixed-ligand complex formation) lend additional support to the above quaternary complex formation:



The formation of above mixed ligand complex is further supported by the following facts:

- (i) Non-appearance of any solid phase in the region of quaternary complex formation.
- (ii) Non-superimposable nature of the theoretical composite curve T with the experimental curve ‘j’ representing the quaternary system in the region of triligand complex formation.

- (iii) By the constancy of calculated values of stability constants observed [16] in the region of quaternary complex formation.

FORMATION CONSTANTS OF MIXED-LIGAND SPECIES:

The value of formation constants and thermodynamic parameters have given in Table 1. The relative order of stabilities for ternary and quaternary species ($\log K_{MLL'}$, $\log K_{MLL''}$ and $\log K_{MLL'L''}$ respectively) in terms of metal ions at four different temperatures ($15 \pm 0.1^\circ$, $25 \pm 0.1^\circ$, $35 \pm 0.1^\circ$ and $45 \pm 0.1^\circ$ C) have been found to be: La (III) < Pr (III) < Nd (III) and may be explained on the basis of decreasing size and increasing ionic potential (charge/radius ratio) of the metal ions. In terms of quaternary and ternary complexes, the observed trend as, quaternary > ternary. It may be due to the increased number of fused chelate rings [17] and extra-stabilization caused by ligand-ligand interactions in quaternary complexes. The value of stability constants decreases with an increase in temperature which refer that the lower temperature favours the formation of complexes. This is further supported by an increase in ionisation constants of the ligands with size in temperature.

Table-1: Formation Constants of Mixed-Ligand Complexes at different temperatures

System	$\log K_{MLL'L''}$ at temperature			
	$15 \pm 0.1^\circ\text{C}$	$25 \pm 0.1^\circ\text{C}$	$35 \pm 0.1^\circ\text{C}$	$45 \pm 0.1^\circ\text{C}$
La(III)-EDTA-FA-HBAA	10.98	10.22	9.96	9.82
Pr(III)-EDTA-FA-HBAA	11.10	10.94	10.16	9.91
Nd(III)-EDTA-FA-HBAA	11.93	11.23	10.57	10.11

Table-2 : Values of free energy of formation (ΔG°) at different temperatures

System	(ΔG°) K.Cal./mole			
	$15 \pm 0.1^\circ\text{C}$	$25 \pm 0.1^\circ\text{C}$	$35 \pm 0.1^\circ\text{C}$	$45 \pm 0.1^\circ\text{C}$
La(III)-EDTA-FA-HBAA	-14.47	-13.93	-14.03	-14.28
Pr(III)-EDTA-FA-HBAA	-14.62	-14.91	-14.31	-14.42
Nd(III)-EDTA-FA-HBAA	-15.72	-15.31	-14.89	-14.71

Table-3 : Values of enthalpy (ΔH°) at different temperatures

System	ΔH° K.Cal/mole		
	ΔH_1	ΔH_2	ΔH_3
LA(III)-EDTA-FA-HBAA	-29.84	-26.92	-16.27
Pr(III)-EDTA-FA-HBAA	-26.28	-32.76	-18.20
Nd(III)-EDTA-FA-HBAA	-27.48	-27.12	-20.61

Table-4 : Values of enthalpy (ΔS°) at different temperatures

System	ΔS° Cal/mole					
	ΔS_1°		ΔS_2°		ΔS_3°	
	$15 \pm 0.1^\circ$	$25 \pm 0.1^\circ$	$25 \pm 0.1^\circ$	$35 \pm 0.1^\circ$	$35 \pm 0.1^\circ$	$45 \pm 0.1^\circ$
LA(III)-EDTA-FA-HBAA	43.71	43.38	30.10	29.75	25.19	24.18
Pr(III)-EDTA-FA-HBAA	38.95	37.95	39.89	38.95	33.09	32.12
Nd(III)-EDTA-FA-HBAA	40.83	33.89	41.64	40.87	36.57	35.55

THERMODYNAMIC PARAMETERS OF MIXED-LIGAND SPECIES:

The values of free energy of formation (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes of resulting quaternary complexes recorded in Table (1-4) calculated ΔG° values have been found to be negative in all the cases [18] which indicate that complex formation appears to be almost spontaneous in process [19,20]. The obtained negative values of ΔH° and positive values of ΔS° indicate that both enthalpy and entropy favour the complex formation. Negative values of enthalpy show the exothermic nature of the reaction and covalent character of the bonds formed between the metal ions and the donor atoms of the ligands. However, the some values of entropy at different temperatures ($15 \pm 0.1^\circ$, $25 \pm 0.1^\circ$, $35 \pm 0.1^\circ$ and $45 \pm 0.1^\circ$ C) show that the complex formation reaction remains unaffected by the change of temperature.

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