

Potentiometric Studies on Some Ternary Complexes of Yttrium(III) with Nitrilotriacetic Acid, N-Hydroxyethylethylenediaminetriacetic Acid & Ethylenediaminetetraacetic Acid as Primary Ligands

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Mixed ligand complex formation constant (K_{MAL}), where $M=Y^{3+}$; A = nitrilotriacetic acid (NTA) or N-hydroxyethylethylenediaminetriacetic acid (HEDTA) or ethylenediaminetetraacetic acid (EDTA) and L = 8-hydroxyquinoline (OX), acetylacetonone (acac), benzoylacetonone (Bzac), protocatechualdehyde (PCAD) or kojic acid (KA) have been determined using modified Irving-Rossotti technique at three different temperatures and $\mu=0.2M$ (KNO_3). Studies in the case of PCAD, 8-hydroxyquinoline and benzoylacetonone were done in 25% (v/v) aqueous-ethanol media. The values of $\log K_{MAL}^{MA}$ have been found in the order, $\log K_{MAL}^{NTA} > \log K_{MAL}^{HEDTA} > \log K_{MAL}^{EDTA}$. Trends in the formation constants are discussed. The data also indicate that the Y(III) ion expands its coordination number larger than six in some of these complexes.

IN continuation of our earlier work¹⁻³ on the application of Irving-Rossotti titration technique⁴ for the study of ternary complex of Y(III), the results of study of the system MAL where $M=Y(III)$, A = nitrilotriacetic acid (NTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA) or ethylenediaminetetraacetic acid (EDTA) and L = 8-hydroxyquinoline (OX), acetylacetonone (acac), benzoylacetonone (Bzac), protocatechualdehyde (PCAD) or kojic acid (KA) are presented in this paper. The chelate of yttrium(III) with A has high stability constants^{5,6}. Hence, these are suitable for being used as primary ligands. Secondary ligands were chosen on the basis that the stability of secondary ligand complex with metal is less than primary complex.

Materials and Methods

A stock solution of $Y(NO_3)_3 \cdot 6H_2O$ (BDH) was prepared in a calculated quantity of nitric acid and its metal content estimated by complexometric titration with EDTA, using bromopyrogallol red as an indicator⁷. The stock solution of 0.01M NTA (BDH), 0.01M EDTA (BDH) and 0.01M HEDTA (Sigma Chemical Co.), 0.02M KA (BDH), 0.02M acac (BDH) were prepared in double distilled water. The stock solution of 0.01M PCAD (Fluka AG), 0.02M Bzac (Fluka AG) and 0.02M OX (BDH) were prepared in purified ethanol. All these solutions which were freshly prepared were standardized potentiometrically. Care was taken to avoid their oxidation. Carbonate free sodium hydroxide was prepared by standard technique⁸ and standardized potentiometrically against potassium hydrogenphthalate. Other reagent solution, i.e. potassium nitrate, and nitric acid were prepared from their AR sample.

An expanded scale pH-meter, with an accuracy ± 0.02 pH units, having a glass calomel electrode

assembly was used. The saturated calomel electrode was connected to the cell by means of an agar-agar bridge, saturated with KNO_3 to prevent the formation of chloro complexes. The design of the cell was such that it allowed flushing of nitrogen through the solution and also enabled measurements to be carried out in an atmosphere of nitrogen. The temperature was maintained with an accuracy $\pm 0.1^\circ$.

Procedure — For the study of ternary complexes following four mixtures (total volume 100 ml, $\mu=2M$, KNO_3) were prepared and titrated against 1.22M NaOH: (i) $1.0 \times 10^{-2}M$ nitric acid; (ii) $1.0 \times 10^{-2}M$ nitric acid + $2.0 \times 10^{-3}M$ secondary ligand; (iii) $1.0 \times 10^{-2}M$ nitric acid + $2.0 \times 10^{-3}M$ primary ligand + $2.0 \times 10^{-3}M$ Y(III) solution; and (iv) $1.0 \times 10^{-2}M$ nitric acid + $2.0 \times 10^{-3}M$ primary ligand + $2.0 \times 10^{-3}M$ secondary ligand + $2.0 \times 10^{-3}M$ Y(III) solution.

In the case of PCAD, Bzac and OX 25% (v/v) aqueous-ethanol media was maintained. In each case the ratio between M:A:L was kept 1:1:1. The four titration curves are referred to as (a) acid titration curve, (b) secondary ligand titration curve, (c) primary complex titration curve, and (d) mixed ligand titration curve.

Results

A typical plot of pH against volume of NaOH is represented in Fig. 1 for $[Y(III)(NTA)(KA)]$ system. The nature of the curves are similar in other systems also.

Proton-ligand stability constants for the secondary ligands were calculated from the acid ligand titration curves using Irving-Rossotti technique. The "practical" stability constants of the proton complexes were obtained from two computational methods: (A) interpolation at half \bar{n}_A values and (B) interpolation at various \bar{n}_A values at each temperature

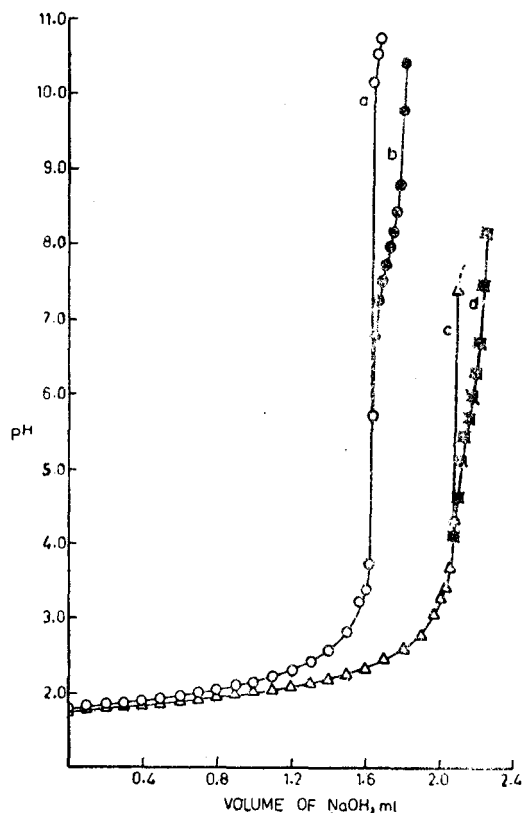


Fig. 1 — Titration curves for Y(III)(NTA)(KA) system at $\mu=0.2M$ [Curve (a) Acid titration curve; (b) secondary ligand titration curve; (c) primary complex titration curve; and (d) ternary complex titration curve]

and these values have been taken into account for the formation constants of ternary complexes. The values obtained for "practical" proton-ligand stability constants with error limits of ± 0.05 are summarized in Table 1.

Stability constants of ternary complexes — An observation of mixed ligand system shows that the pH of the precipitation of mixed ligand system is more than the pH of the precipitation in the single ligand systems. Secondly, the interaction between

primary complex and secondary ligand shows that the mixed ligand curve has displaced from primary complex in pH range ~ 5.5 to 9.5 . The nature of the complex equilibrium whether stepwise or simultaneous was investigated according to the method suggested by Carey and Martell⁹. The calculation of \bar{n} shows that 1:1 primary complex formation is complete up to $pH \sim 4.0$. [Y(III)-(HEDTA)(OH)_n] or [Y(III)(EDTA)(OH)_n] could not form up to $pH \sim 10.0$ which indicates that primary complex formed at low pH is quite stable. However, in the case Y(III)-NTA, the calculation of \bar{n} shows that the complex formation takes place up to $pH 4.5$ and after $pH 6.8$ the \bar{n} value increases rapidly and the precipitation of metal hydroxy complex takes place.

Primary curve (c) and mixed complex curve (d) overlap each other at low pH . This indicates that in this pH range where primary ligand combines with metal, combination of secondary ligand does not take place. Since the dissociation of KA, Bzac, acac, OX and PCAD is negligible at low pH , the curves (c) and (d) overlap. In the case of these ligands, curve (d) diverges from curve (c) after $pH 5.5$. In this range, combination of secondary ligand with primary complex starts.

In the case of OX curve (d) separates from curve (c) at lower pH due to self-dissociation of protonated group. Since, the dissociation of primary complex does not take place in the range of dissociation of secondary ligand, it can be considered that the secondary ligand combines with primary complex just as it does with $[M(aq)_n^{3+}]$ in binary systems. In the presence of secondary ligands, formation of [Y(III)(A)(OH)_n] is suppressed. The horizontal distance between curve (A) and curve (B) can be measured (V_2) and subtracted from the difference (V_3) between curves (c) and (d). As is clear the V_2 indicates the protons released due to the self-dissociation of the secondary ligand and V_3 denotes the release of protons due to the self dissociation of secondary ligands plus the release of protons due to the formation of mixed complex. The $(V_3 - V_2)$ therefore accounts for the total protons released due to the formation of mixed ligand complex only. It is then used for the calculation of \bar{n} , where \bar{n}

TABLE 1 — STEPWISE PROTONATION CONSTANT OF THE SECONDARY LIGAND AT VARIOUS TEMPERATURES ($\mu=0.2$)

Ligands	Constants	25°		35°		45°	
		A	B	A	B	A	B
PCAD*	$\log K_1^H$	11.40	11.23	11.20	11.15	11.00	11.09
	$\log K_2^H$	7.90	7.92	7.70	7.71	7.58	7.57
OX*	$\log K_1^H$	10.35	10.41	10.25	10.28	10.10	10.13
	$\log K_2^H$	5.00	5.01	4.82	4.83	4.65	4.69
Bzac*	$\log K_1^H$	9.24	9.32	9.16	9.22	9.08	9.14
acac	$\log K_1^H$	9.15	9.15	9.05	9.06	8.94	8.97
KA	$\log K_1^H$	7.85	7.84	7.75	7.73	7.63	7.62

*Experiment in 25% ethanol.

is the average number of secondary ligand molecules associated with primary complex (Eq. 1).

$$\bar{n} = \frac{(V_3 - V_2)[N + E^\circ + T_{CL}^\circ(Y - \bar{n}_A)]}{(V_0 + V_2)\bar{n}_A T_{CM}^\circ} \quad \dots(1)$$

Now substituting

$$Y - \bar{n}_A = \frac{(V_2 - V_1)(N + E^\circ)}{(V_0 + V_1)T_{CL}^\circ} \quad \dots(2)$$

in Eq. (1) we get final equation,

$$\bar{n} = \frac{(V_3 - V_2)(N + E^\circ)}{(V_0 + V_1)\bar{n}_A T_{CM}^\circ} \quad \dots(3)$$

where T_{CM}° is the concentration of primary complex which is the concentration of Y(III). V_0 is the initial volume of each mixture, V_1 is the volume of NaOH required in titration of mixture (i). The other terms have their usual meaning. \bar{n} and pL values were calculated at various pH in aqueous medium. In the case of water-organic solvent media, for the calculation of pL , the 'B' values were used instead of pH values, where 'B' denotes the pH -meter reading only and not the actual pH , as the pH -meter is calibrated with aqueous buffer. Also the values of proton ligand stability constants are termed as "practical" proton ligand stability constants. These constants are convenient intermediates if the stability constants of only metal complexes are required. The use of pH -meter reading 'B' instead of the pH values does not make any difference in the calculation of pL , as proved by several workers^{4,10,11}.

Typical plots for \bar{n} against pL for [Y(III)(NTA)(KA)] system at different temperatures are shown in Fig. 2. From the values of pL at $\bar{n}=0.5$, $\log K_{MAL}^{MA}$ can be calculated. The values obtained by the method of interpolation at various \bar{n} values were also calculated. These values are given in Table 2.

Discussion

When Y(III) is bound by chelating agent (NTA) having four donor groups, completion of its coordination requirements with supplementary ligands to satisfy a characteristic coordination number of

six, greatly enhances the stability of the chelate and decreases the tendency of chelate compound [Y(III)(NTA)] to hydrolyse and consequently increases its tendency to form mixed ligand chelate compounds.

It is observed that the values of $\log K_{MAL}^{NTA}$ are lower than the value of $\log K_{ML}$. This is understandable, since in the mixed ligand complex formation, the secondary ligand (L) has to approach a neutral primary chelate species (MA) and the number of coordination positions vacant for the coordination of secondary ligand are also less. Whereas in case of binary system, ligand anion has to approach the positively charged Y(III) ion, and more coordination positions are vacant for its

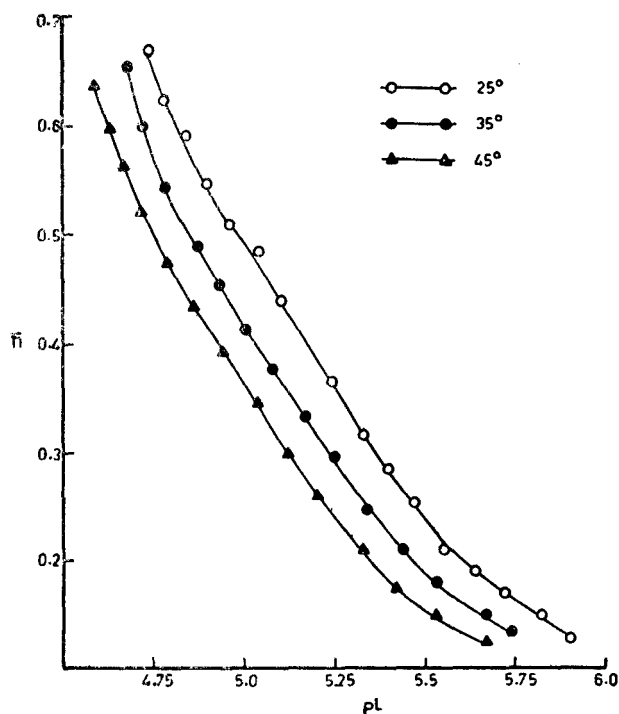


Fig. 2 — Formation curves for [Y(III)(NTA)(KA)] system

TABLE 2 — STABILITY CONSTANTS (LOG K_{MAL}^{MA}) OF MIXED LIGAND CHELATES OF Y(III) AT VARIOUS TEMPERATURES ($\mu=0.2$)

System	25°		35°		45°	
	A	B	A	B	A	B
Y(III)(NTA)(PCAD)*	8.12	8.26	7.92	8.07	7.78	7.92
Y(III)(HEDTA)(PCAD)*	6.88	6.90	6.58	6.70	6.38	6.49
Y(III)(EDTA)(PCAD)*	6.32	6.34	6.08	6.13	5.92	5.98
Y(III)(HEDTA)(OX)*	5.42	5.49	5.27	5.32	5.16	5.22
Y(III)(EDTA)(OX)*	4.85	4.85	4.70	4.68	4.60	4.56
Y(III)(NTA)(KA)	4.98	5.01	4.84	4.87	4.74	4.77
Y(III)(HEDTA)(KA)	4.32	4.33	4.23	4.24	4.15	4.16
Y(III)(EDTA)(KA)	3.85	3.86	3.73	3.74	3.63	3.62
Y(III)(NTA)(Bzac)*	4.96	4.98	4.82	4.80	4.72	4.68
Y(III)(HEDTA)(Bzac)*	4.19	4.14	4.09	4.04	3.85	3.95
Y(III)(EDTA)(Bzac)*	3.52	3.59	3.42	3.47	3.34	3.38
Y(III)(NTA)(acac)	4.57	4.60	4.47	4.52	4.40	4.41
Y(III)(HEDTA)(acac)	3.95	3.94	3.85	3.83	3.78	3.75
Y(III)(EDTA)(acac)	3.36	3.12	3.32	3.06	3.29	3.03

*Experiment in 25% ethanol.

attachment. This results in lowering of stability constant of mixed ligand complexes. The second factor which influences the stability of mixed ligand complexes is the steric hindrance caused due to the primary ligand which is already attached with Y(III). Although [Y(III)(HEDTA)] chelate is also neutral, HEDTA occupies only five coordination positions. Hence Y(III) has to expand its coordination number greater than six to form the mixed ligand complex with secondary ligand and this results in $\log K_{MAL}^{NTA}$ values higher than $\log K_{MAL}^{HEDTA}$. The $\log K_{MAL}^{EDTA}$ values are lower than $\log K_{MAL}^{HEDTA}$, because [Y(III)(EDTA)] chelate exerts an electrostatic force of repulsion on approaching negatively charged secondary ligand and also the Y(III) has to expand its coordination number from 6 to 8.

Not much generalizations are possible in comparing the stabilities of mixed chelates. The stabilities of mixed chelates are also dependent on the basicity of ligand. The order of stability constant of mixed ligand complexes (in 25% ethanol) with change in secondary ligand is PCAD > OX > Bzac. Although the basicity of ligands is one of the factors responsible for stability of the mixed ligand complex, still acac forms less stable complex than kojic acid. This is only because of acac forms six-membered

ring whereas kojic acid forms stable five-membered ring with Y(III).

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References

1. PUJARI, A. M. & MUNSHI, K. N., *Indian J. Chem.*, **13** (1975), 397.
2. PUJARI, A. M. & MUNSHI, K. N., *Indian J. Chem.*, **14A** (1976), 192.
3. PUJARI, A. M. & MUNSHI, K. N., *J. Indian chem. Soc.*, (in press).
4. IRVING, H. M. & ROSSOTTI, H. S., *J. chem. Soc.*, (1954), 2904.
5. MOELLER, T. & FERRUS, R., *Inorg. Chem.*, **1** (1962), 55.
6. SILLEN, L. C., *Stability constants of metal-ion complexes: Special publication No. 17* (Chemical Society, London), 1964, 511.
7. JENICKOVA, J., SUK, V. & MALAT, M., *Chem. Listy*, **50** (1956), 760; *Chem. Abstr.*, **50** (1956), 10595.
8. VOGEL, A. I., *Quantitative inorganic analysis* (Longmans, Green, London), 1961, 433.
9. CAREY, G. H. & MARTELL, A. E., *J. Am. chem. Soc.*, **89** (1967), 2859.
10. VAN UITERT, L. G. & HASS, C. G., *J. Am. chem. Soc.*, **75** (1953), 451.
11. VAN UITERT, L. G., FERNELIUS, W. C. & DOUGLAS, B. E., *J. Am. chem. Soc.*, **75** (1953), 3577.