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Ternary Complexes of Y(III) with Nitrilotriacetic Acid, EDTA or N-Hydroxyethylethylenediaminetriacetic Acid as Primary Ligands & Picolinic Acid or Pyrocatechol Violet as Secondary Ligands

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1:1 Chelates of Y(III) with nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and N-hydroxyethylethylenediaminetriacetic acid (HEDTA) form mixed ligand (1:1:1) chelates with pyrocatechol violet (PCV) and picolinic acid (PA). Mixed ligand complexes of NTA are more stable than those of EDTA and HEDTA. Formation constants of ternary complexes have been determined at different temperatures.

STUDIES on the ternary complexes of lanthanides including yttrium have shown that these metals have their coordination number greater than six[1-3]. In the present paper the study of K^{MA}_{MAL} of the systems [where M = Y(III), A=nitrilotriacetic acid (NTA) or ethylendiaminetetraacetic acid (EDTA) or N-hydroxyethylethylenediaminetriacetic acid (HEDTA) as primary ligands and L=picolinic acid (PA) or pyrocatechol violet (PCV) as secondary ligands] have been reported by the modified form of Irving-Rossotti titration technique[4]. The stability constants are correlated with the vacant coordination sites after reaction with primary ligands. The studies on binary complexes formed between Y(III) and these primary ligands have already been reported by earlier workers[5,6].

Materials and Methods

A stock solution of $Y(NO_3)_3 6H_2O$(BDH) was prepared in a known quantity of nitric acid, added to prevent the hydrolysis. The metal content was estimated by complexometric titration[7]. The stock solutions of 0·01*M* NTA (BDH), 0·01*M* disodium salt of EDTA (BDH) and 0·01*M* HEDTA (Sigma) were prepared in doubly distilled water. 0·01*M* PA (Sigma) and 0·005*M* PCV (BDH) were also prepared and all these solutions were standardized potentiometrically. Other reagents like sodium hydroxide, potassium nitrate, nitric acid and potassium hydrogen phthalate were prepared from their AR grade samples.

Expanded *p*H-meter (accuracy ±0·02 *p*H unit) of (Electronic Corporation of India Ltd) fitted with glass-calomel electrode assembly was used to measure $[H^+]$ of solution. The saturated calomel electrode was connected externally by means of an agar-agar bridge saturated with KNO_3 to prevent the formation of chloro complexes[8]. Different temperatures were maintained with an accuracy of 0±0·1°.

Procedure — Solutions containing Y(III) ions, NTA (EDTA or HEDTA) and the secondary ligands PCV (or PA) were prepared for the study of ternary systems.

In each case, 0·2*M* ionic strength was maintained by adding required quantity of potassium nitrate solution and total volume of the system was made up to 100 ml. Titration was carried out with standard sodium hydroxide solution. The ratio of Y(III)-primary ligand-secondary ligand was always kept 1:1:1 in each system. Typical plots of *p*H against alkali added have been represented for mixed ligand complex study of pyrocatechol violet system in Fig. 1. Similar plots were obtained for other systems also. Titration with 1:1:2 (Y: A: L:) have also been performed but in all the cases it has been found that the nature of curves tally exactly with that of 1:1:1 titrations, indicating that further expansion of coordination number of Y(III) is not possible.

Y(III)-secondary ligand stability constant values have already been reported from these laboratories[9,10].

Results

Proton-ligand stability constant — The values of $\bar{n}_A$ have been calculated at various *p*H and at three different temperatures (25°, 35° and 45°) at a fixed ionic strength (0·2*M*). These values of protonation constants have been taken into account for the calculation of the formation constant of ternary systems. All these values are given in Table 1.

TABLE 1 — PROTON-LIGAND STABILITY CONSTANT OF SECONDARY LIGANDS AT DIFFERENT TEMPERATURES

System	log *K* at			
	25°	35°	45°	
PCV-H	8·80	8·70	8·48	(K_1^H)
	5·45	5·25	5·00	(K^H)
PA-H	5·29	5·23	5·06	(K^H_1)

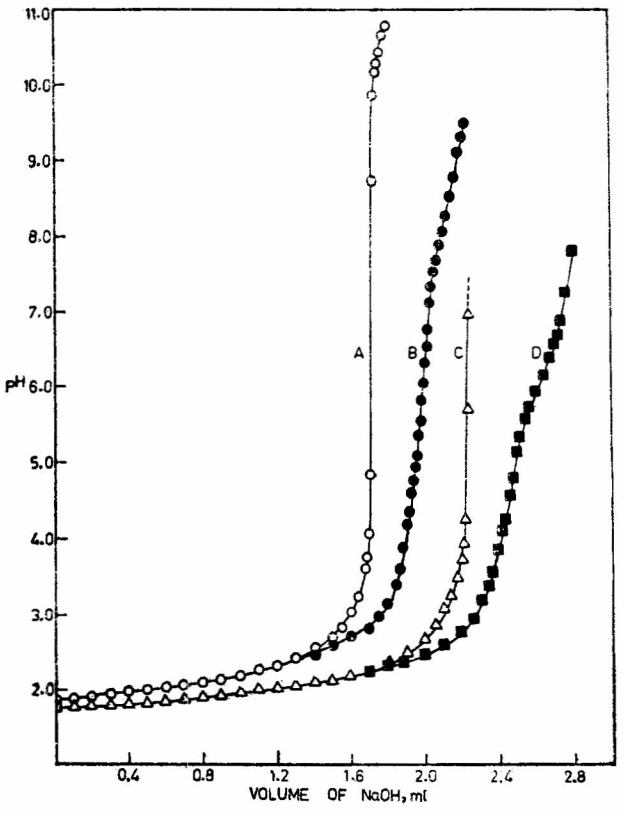

Fig. 1 — Titration curves for the Y(III)-NTA-PCV mixed ligand complex at 25° and $\mu = 0{\cdot}2M$ (KNO_3) [Curve A, $1{\cdot}955\times10^{-2}$ M nitric acid; curve B, $1{\cdot}955\times10^{-2}M$ nitric acid + $2\times10^{-3}M$ PCV; curve C, $1{\cdot}955\times10^{-2}M$ nitric acid + $2\times10^{-3}M$ NTA + $2\times10^{-3}M$ Y(III); curve D·95, $15\times10^{-2}M$ nitric acid + $2\times10^{-3}M$ NTA + $2\times10^{-3}M$ PCV + $2\times10^{-3}M$ Y(III)]

Mixed ligand complex — It is observed that the primary complex formation (curve C) of Y(III)-NTA, takes place at very low *p*H. The value of $\bar{n}=1{\cdot}0$ shows that 1:1 complex formation is complete at *p*H 4·0. This value of $\bar{n}$-remains almost constant upto *p*H 7·0 after which it increases rapidly and turbidity at about *p*H 7·0 develops into a precipitate at about *p*H 8·0 and settles. This precipitate remains insoluble even up to *p*H 11·5. However, when HEDTA and EDTA are used as primary ligands, the precipitation does not occur even up to *p*H 10·0.

Primary complex curve (C) and mixed complex, Y(III)-NTA-PCV, curve (D), overlap each other at lower *p*H values, i.e. *p*H 2-2·3. This indicates that in this range where NTA combines with Y(III) (*p*H ~1·8) attachment of secondary ligands does not take place. The mixed complex curve (D) however separates from primary complex curve (C) at *p*H ~2·3 due to the self-dissociation of the PCV at low *p*H. After *p*H 4·0 to 4·5 mixed complex curve indicates attachment of secondary ligand, (PCV) with Y(III). When PA is used for ternary complex system, the primary complex curve is found to overlap the mixed complex curve upto *p*H 3·8, indicating the negligible dissociation of PA at lower *p*H values. Similar curves have been obtained with HEDTA and EDTA as primary ligands.

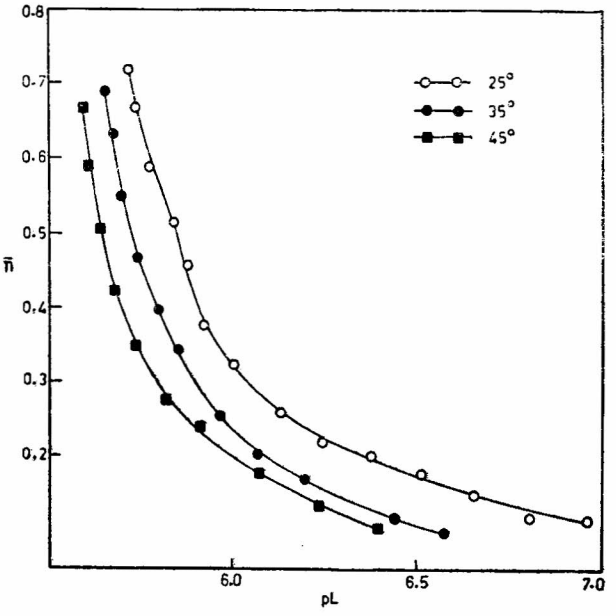

Fig. 2 — Formation curves of [Y(III) (A) (PCV)] at different temperatures

The general reactions (1 and 2) can be written for NTA or HEDTA and (3) and (4) for EDTA as primary ligands:

$$Y^{3+} + H_3A \leftrightharpoons [Y(A)] + 3H^+ \quad ...(1)$$

$$[Y(A)] + HPA \leftrightharpoons [Y(A)(PA)]^- + H^+ \text{ and}$$
$$[Y(A)] + H_3PCV \leftrightharpoons [Y(A)(HPCV)]^{2+} + 2H^+ \quad ...(2)$$

$$Y^{3+} + H_2EDTA^{2-} \leftrightharpoons [Y(EDTA)]^- + 2H^+ \quad ...(3)$$

$$[Y(EDTA)]^- + HPA \leftrightharpoons [Y(EDTA)(PA)]^{2-} + H^+ \text{ and}$$
$$[Y(EDTA)]^- + H_3PCV \leftrightharpoons [Y(EDTA)(HPCV)]^{3-} + 2H^+ \quad ...(4)$$

Since, the dissociation of Y-A (A = NTA or HEDTA) does not take place in the range of dissociation of the secondary ligand, it can be considered that secondary ligands combine with Y(III). In the presence of secondary ligand, the formation of hydroxo complex, Y(III)-A $(OH)_n$ is also suppressed. The $\bar{n}$ values were calculated by finding out the differences from curves at various *p*H values where $\bar{n}$ is average number of secondary ligand molecule associated with one Y(A). The values of $\bar{n}$ were calculated from Eq. (5)

$$\bar{n} = \frac{(V_3 - V_2)(N+E)}{(V_0+V_1)\bar{n}_A T^\circ_{CM}} \quad ...(5)$$

where T°_{CM} is the concentration of Y(III)-A which is the concentration of Y(III). $\bar{n}$ and pL were calculated at different *p*H. At $\bar{n} = 0{\cdot}5$ in the formation curve $pL = \log K^{MA}_{MAL}$. A typical plot of $\bar{n}$ against pL for Y(III)-NTA-PCV system is shown in Fig. 2. Other systems also gave similar plots. The values of log K^{MA}_{MAL} have been summarized in Table 2. The error limits are of $\pm 0{\cdot}03$ log units.

Thermodynamic parameters — The value of overall changes in free energy (ΔG) enthalpy (ΔH), and entropy (ΔS) have been calculated at three different temperatures and at ionic strength $0{\cdot}2M$ (KNO_3) for ternary complex formation, with the help of the temperature coefficients and Gibb's-Helmholtz, equation. The values are summarized in Table 2.

TABLE 2 — STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF SOME MIXED LIGANDS COMPLEXES OF Y(III)

Sytem	K^{MA}_{MAL} at			ΔH kcal mole^{-1}	ΔS cal/ deg^{-1} mole^{-1}
	25°	35°	45°		
Y(III)-NTA-PCV	5·85	5·72	5·65	−4·3	+12
Y(III)-HEDTA-PCV	4·84	4·67	4·47	−7·9	−4
Y(III)-EDTA-PCV	4·25	4·15	4·00	−5·3	+2
Y(III)-NTA-PA	3·69	3·57	3·42	−6·0	−3
Y(III)-HEDTA-PA	3·46	3·43	3·41	−1·1	+12
Y(III)-EDTA-PA	3·28	3·26	3·24	−0·9	+12

Discussion

The order of the formation constants (Table 1) of ternary systems, with change in primary ligand is NTA > HEDTA > EDTA, which can be explained on the basis of the vacant coordination sites after reaction with primary ligands, as both the secondary ligand used here are bidentate. NTA occupies only four positions of the coordination sphere of Y(III) and Y(NTA) chelate has a lower electrostatic repulsion for the incoming secondary ligand (PA or PCV) because of its neutral nature. Although Y(HEDTA) chelate is electrically neutral, it occupies five coordination positions, and thus for a bidentate secondary ligand to attach Y(III) must expand its coordination number beyond six. In the case of Y(EDTA), it occupies six coordination positions of Y(III) and thus unless the expansion of coordination number from 6 to 8 is assumed, a secondary bidentate ligand cannot attach itself to it. Also as $[Y(EDTA)]^-$ is a negatively charged species, it will repel the approaching negatively charged secondary ligands. With similar primary ligands the stabilities of ternary complexes of PA are less than those of PCV, because PCV is more basic than PA.

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