

important to add that the values of $\log \beta_{MAL}$ for ternary complexes are higher than the mean of $\log K_{MA_2}$ and $\log K_{ML_2}$, indicating the higher stability of mixed complexes.

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Studies on the Stability of Trivalent Lanthanum Complexes with Catechol

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THE complexation reactions of catechol with La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III) and Y(III) have been studied potentiometrically at $25 \pm 0.5^\circ$ in aqueous solution with potassium nitrate as supporting electrolyte. The thermodynamic stability constants have been evaluated. The trend in the stability of these complexes has also been discussed.

A survey of the literature revealed that some studies¹⁻³ have been made on the complex formation ability of catechol with trivalent lanthanide ions. However, no attempt appears to have been made to determine the thermodynamic stability constants of the complexes of catechol with Ln(III). In view of the above, the present study deals with the determination of thermodynamic stability constants of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III) and Y(III) complexes with catechol by extrapolating the determined formation constants at different ionic strengths (0.05, 0.2 and 0.35M, 25°) to zero ionic strength. The experimental technique used was that of Calvin and Bjerrum^{4,5} as modified by Irving and Rossotti⁶.

Experimental

Materials: The lanthanide nitrates (Indian Rare Earths Ltd.) were dissolved in double distilled water and standardized by oxalate method⁷. All other reagents used were of AR grade.

Apparatus: A Philips pH meter (PR 9405M) fitted with glass and calomel electrodes was used

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for measuring pH. The instrument was standardized by using BDH buffer tablets of pH 4 and 9.2.

Procedure: Three solutions (total volume 50 ml in each case) of following compositions were prepared: $3.91 \times 10^{-3}M$ nitric acid, $3.91 \times 10^{-3}M$ nitric acid + $3.0 \times 10^{-3}M$ ligand, and $3.91 \times 10^{-3}M$ nitric acid + $3.0 \times 10^{-3}M$ ligand + $5.0 \times 10^{-4}M$ metal. Appropriate amounts of potassium nitrate (2M) were added to maintain the desired ionic strengths.

The mixtures were thermostated at $25 \pm 0.5^\circ$ and were titrated pH metrically against a standard sodium hydroxide solution (0.6993M). For the sake of brevity titration curves obtained at $\mu = .05M$ ($25 \pm 0.5^\circ$) for La(III)-catechol system have only been given in Fig. 1 [the acid titration curve (A), ligand titration curve (B) and complex titration curve (C)].

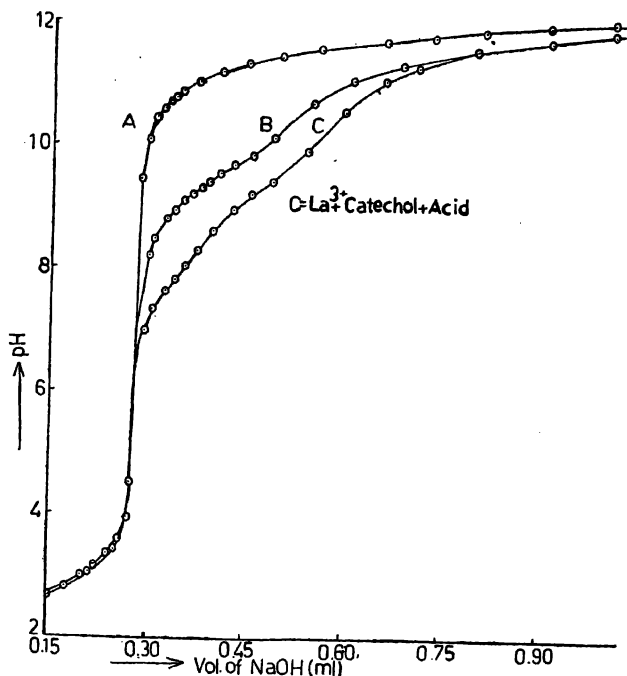


Fig. 1. pH titration curves: A—Acid, B—Ligand, C—Complex titration curves; $\mu = 0.05M$ (KNO_3), 25° .

Results and Discussion

The protonation constants of the ligand and stepwise stability constants of metal ligand complexes were calculated as follows:

The \bar{n}_A values calculated at various pH values from acid and ligand titration curves using Irving and Rossotti equation⁶ were plotted against the values of pH. From the formation curves, the values of protonation constants obtained at half \bar{n}_A values were computed using computational techniques^{8,9}, viz., Pointwise calculation method, Correction term method and Curve fitting method. The mean values are given in Table 1.

The stepwise metal-ligand stability constants were calculated using ligand and complex titration

curves. The values were computed using the above computational techniques and the mean values are presented in Table 1. The metal-ligand stability constants decrease with an increase in the ionic strength of the media is in accordance with Hückel's theory¹⁰.

TABLE 1—VALUES OF STABILITY CONSTANTS OF Ln(III) COMPLEXES AT 25° AND DIFFERENT IONIC STRENGTHS

Cations	log K ₁	$\mu=0.35M$	$\mu=0.2M$	$\mu=0.05M$	$\mu=0.00M$
H ⁺	log K ₁ ^H	11.46±0.06	11.59±0.04	11.80±0.08	—
La ³⁺	log K ₁ ^H	9.27±0.03	9.29±0.03	9.45±0.08	—
	log K ₁	8.05±0.05	8.42±0.03	9.12±0.03	9.60
Ce ³⁺	log K ₁	7.51±0.06	7.46±0.02	8.20±0.09	8.60
	log K ₂	9.18±0.01	9.68±0.02	9.96±0.02	10.40
Pr ³⁺	log K ₁	8.25±0.05	8.46±0.03	9.09±0.05	9.50
	log K ₂	8.63±0.02	8.99±0.01	9.65±0.02	10.20
Nd ³⁺	log K ₁	7.93±0.02	8.04±0.06	8.74±0.01	9.25
	log K ₂	9.07±0.07	9.49±0.01	10.00±0.04	10.58
Sm ³⁺	log K ₁	8.10±0.04	8.26±0.03	9.01±0.05	8.60
	log K ₂	9.41±0.05	9.99±0.04	10.36±0.04	11.00
Gd ³⁺	log K ₁	8.59±0.06	9.11±0.02	9.44±0.02	9.90
	log K ₂	9.21±0.03	9.70±0.01	10.36±0.04	10.98
Tb ³⁺	log K ₁	8.50±0.00	8.55±0.03	9.26±0.02	9.73
	log K ₂	9.58±0.05	9.89±0.03	10.50±0.04	11.11
Dy ³⁺	log K ₁	8.84±0.04	9.31±0.06	9.78±0.05	10.20
	log K ₂	9.46±0.04	9.93±0.05	10.39±0.07	10.95
Ho ³⁺	log K ₁	8.77±0.04	9.23±0.03	9.61±0.05	10.00
	log K ₂	9.61±0.05	10.26±0.04	10.54±0.05	11.20
Y ³⁺	log K ₁	9.00±0.05	9.41±0.06	9.80±0.05	10.30
	log K ₂	9.11±0.05	9.69±0.07	10.37±0.03	11.08
	log K ₃	8.45±0.05	8.89±0.05	9.56±0.01	10.11

Linear plots were observed when log K_n values were plotted against $\sqrt{\mu}$. Thermodynamic step stability constants (Table 1) were obtained by extrapolating the experimentally determined stability constants to zero ionic strength. A more or less increasing trend of stability constants was observed with decreasing ionic radii for lighter lanthanides. The only exception was with Ce(III), and this anomalous behaviour is probably due to the tendency of cerium towards quadrivalency. Stability order shows a break at or very near Gd³⁺ ion which has been interpreted as corresponding to either the stability of the half-filled (4f⁷) arrangement for Gd³⁺ ion or the change in ionic radii centering at the Gd³⁺ ion which allows a change in the coordination number of the cation^{1,12}. The heavier lanthanides do not show a regular trend as has been observed in a number of systems¹².

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Formation Constants of the Chelates of 2-Hydroxy-1-Naphthalidine-*p*-Acetylaminoaniline with Some Bivalent Metal Ions

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POTENTIOMETRIC studies have been carried out on metal complexes of Cu²⁺, Zn²⁺, Ni²⁺, Co²⁺ and Mg²⁺ with 2-hydroxy-1-naphthalidine-*p*-acetylaminoaniline. The dissociation constants of the ligand and formation constants of its metal chelates have been determined by Bjerrum's method at 25±0.1°, and at ionic strength 0.1M NaClO₄ in 75:25 (v/v) dioxan-water medium. The order of stability of chelates is found to be Cu>Zn>Co>Ni>Mg.

Experimental

The ligand 2-hydroxy-1-naphthalidine-*p*-acetylaminoaniline was prepared by adding an equimolar quantity of *p*-acetylaminoaniline to 10 gm of 2-hydroxy-1-naphthaldehyde dissolved in 50 ml of ethanol and refluxing the reaction mixture on a water bath for an hour. After cooling, the solution was filtered to give the crude product which was repeatedly crystallised from alcohol to get an analytically pure compound having m.p. 139° (observed). (Found: C, 74.10; H, 5.20; N, 9.05 per cent. Calcd. for C₁₆H₁₆N₂O₃; C, 74.02; H, 5.19; N, 9.09 per cent) and C=N stretching frequency, 1624 cm⁻¹.

The experimental techniques used in the present investigation were the same as reported earlier^{1,2}.

Results and Discussion

It may be mentioned here that the ligand does not undergo hydrolysis under the experimental conditions described. This was indicated by the rapid attainment of equilibrium during the titrations and