Stability of some Ln(III) chelates of pyrogallol

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Abstract. The complexation reactions of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) ions with pyrogallol have been studied by potentiometric method at various ionic strengths and temperatures. In acidic solutions, the formation of monopyrogallolate derivative of these metal ions has been indicated even in the presence of large excess of pyrogallol. The thermodynamic stability contants and thermodynamic parameters are also reported.

Keywords. Pyrogallol; lanthanides; potentiometric study.

1. Introduction

The complexation reaction of pyrogallol has been studied earlier (Halmekoski 1959; Dubey and Mehrotra 1967; Agarwal and Mehrotra 1965; Soni and Bartusek 1971; Bartusek and Stejskal 1973; Pujari and Munshi 1977). Literature survey revealed that no previous work has been reported on the potentiometric studies of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) chelates of pyrogallol. The present work deals with the potentiometric determination of stability constants and related thermodynamic parameters of some tervalent lanthanide-pyrogallol chelates.

2. Experimental

2·1 Materials

Lanthanide nitrates (India Rare Earths Limited) were dissolved in double-distilled water. The solutions were standardised gravimetrically by precipitating the metal oxalates and subsequent ignition and weighing as metal oxides. The solutions of required strength were then prepared by suitable dilution. Sodium hydroxide (BDH AR grade) was dissolved in a pyrex flask. The carbondioxide layer on sodium hydroxide pellets was washed away previously. The solution was

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standardised potentiometrically against the standard oxalic acid. Stock solutions of nitric acid and potassium nitrate were prepared by dissolving AR grade reagents in double-distilled water. Freshly prepared solution of pyrogallol (BDH AR grade) in oxygen-free double-distilled water was used.

2·2. *Apparatus*

A pH meter (Philips PV 9405M) with a glass and calomel electrode assembly was employed for pH determination. The instrument was calibrated before and after titration by a 0·05 M solution of potassium hydrogen phthalate.

2·3. *Conditions of study*

The experiments were performed in a double-walled beaker in an atmosphere of nitrogen gas bubbled through the solution. The pH measurements were made at $25 \pm 0·5°$ and $35 \pm 0·5°$ using a thermostat bath. The following three solutions were prepared and titrated against standard alkali (0·4 M) using the titration technique (Calvin and Wilson 1945; Bjerrum 1941) as modified by Irving and Rossotti (1954).

(i) 5 ml of $3·96 \times 10^{-2}$ M HNO_3. (ii) 5 ml of $3·96 \times 10^{-2}$ M HNO_3 + 30 ml of $5·0 \times 10^{-3}$ M pyrogallol, (iii) 5 ml of $3·96 \times 10^{-2}$ M HNO_3 + 30 ml of $5·0 \times 10^{-3}$ M pyrogallol + 5 ml of $5·0 \times 10^{-3}$ M metal ion solutions.

The total volume was kept at 50 ml and an appropriate amount of potassium nitrate (2 M) was added to maintain the desired ionic strengths.

3. Results and discussion

The proton-ligand stability constants ($\log K_1^H$ and $\log K_2^H$) of pyrogallol were obtained for the plot of pH versus $\bar{n}_A$. The $\bar{n}_A$ values do not go below 1 even at pH 11 indicating that the third proton does not dissociate. Thus pyrogallol behaves like a weak dibasic acid. The values of $\log K_1^H$ and $\log K_2^H$ were calculated and computed by the following techniques (Irving and Rossotti 1953, 1954) (i) the interpolation of half $\bar{n}$ values, (ii) the correction term method, (iii) the curve fitting method, and (iv) the pointwise calculation method. The final values are given in table 1.

The metal-ligand formation constants ($\log K_1$) were calculated from the plot of $\bar{n}$ versus pA values, the values were further refined by the above mentioned techniques. The final values are given in table 1. The second step-formation constants ($\log K_2$) for Ln (III) chelates could not be evaluated as the precipitation starts after $\bar{n} = 1·0$. In the case of heavier lanthanides even the $\log K_1$ values could not be determined as precipitation starts from the beginning of separation points between ligand and complex titration curves. The stability order was found to be La < Ce $\approx$ Pr < Nd < Sm. The increase in stability at Ce(III) is probably due to its tendency towards quadrivalency.

The thermodynamic stability constants or the standard state of zero ionic strength were calculated by extrapolating the determined stability constants to zero ionic strength. The standard free energies of chelation were calculated from the expre-

Table 1. Stability and thermodynamic parameters of ln(III)-pyrogallol chelates

Metal ion	$25° \pm 0.5°$ C					$35° \pm 0.5°$ C		
	$\mu = 0.05$	$\mu = 0.1$	$\mu = 0.15$	$\mu = 0.0$	$\mu = 0.1$	$-\triangle G°$ kcal/mol	$-\triangle H$ kcal/mol	$\triangle S$eU
$H^+ \log K_1^H$	11.24 ±0.06	11.14 ±0.04	11.03 ±0.04	11.35	10.76 ±0.05	—	—	—
$\log K_2^H$	9.16 ±0.01	9.13 ±0.01	9.07 ±0.03	9.25	8.84 ±0.01	—	—	—
$La^{3+} \log K_1$	9.24 ±0.01	9.16 ±0.01	8.85 ±0.01	9.40	9.18 ±0.02	12.82	+0.84	44.03
$Ce^{3+} \log K_1$	10.10 ±0.03	9.96 ±0.02	9.68 ±0.01	10.32	9.97 ±0.01	14.08	+0.42	46.2
$Pr^{3+} \log K_1$	10.08 ±0.02	9.79 ±0.02	9.59 ±0.01	10.30	9.73 ±0.03	14.05	2.50	35.74
$Nd^{3+} \log K_1$	10.26 ±0.02	10.01 ±0.02	9.84 ±0.01	10.50	9.76 ±0.01	14.34	10.50	10.93
$Sm^{3+} \log K_1$	10.53 ±0.01	10.41 ±0.02	9.27 ±0.01	10.67	10.12 ±0.03	14.56	12.18	6.69

ssion $\triangle G° = -RT \ln K^{\mu=0}$. The other thermodynamic parameters were calculated from standard equations (Vasil'ev and Yatsimirskii 1960) and the values are given in table 1. Within the limits of experimental determination of thermodynamic parameters, it has been observed that the metal-ligand interaction become more exothermic as the atomic number increases. The entropy change was found to be positive and thus favourable for complex formation in all the cases.

Acknowledgements

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