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pH-metric Studies on Some Ternary Complexes of Lanthanones

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With 3 Figures

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Stepwise mixed ligand complex formation has been cited for the formation of 1 : 1 : 1, *Ln*(III)—*NTA*—catechol ternary complexes potentiometrically [where *Ln*(III) = La(III), Pr(III) or Nd(III)]. The results of titration curves indicate the formation of 1 : 1, *Ln*(III)—*NTA* complexes in beginning and the addition of catechol, takes place later on in the higher buffer region. The relative stability of these ternary complexes in terms of metal ion has been reported as La(III) < < Pr(III) < Nd(III).

Introduction

In earlier communications[1–3] from these laboratories, pH-metric evidences have been cited for the formation of 1 : 1 : 1, *Ln*(III)—*NTA*—dicarboxylic acids/hydroxy acids/*HQ*/*HQS*/*PIC* ternary complexes (where *NTA* = nitrilotriacetic acid, dicarboxylic acids = oxalic, malonic, phthalic, maleic, citraconic acids; *HQ* = 8-hydroxyquinoline, *HQS* = 8-hydroxyquinoline-5-sulphonic acid and *PIC* = α-picolinic acid). A survey of the literature reveals that the systems, *Ln*(III)—*NTA*—catechol have not been studied so far. It was, therefore, considered worthwhile to investigate these systems potentiometrically. The results of such studies have been presented in this communication.

Experimental

Material and Method

All the chemicals used were either AnalaR BDH or E. Merck grade and their solutions were prepared in double distilled water.

Stock solutions of lanthanone nitrates were prepared and standardised by titrating their oxalates with standard $KMnO_4$ solution[4], and also complexometrically[5] with *EDTA*. A desired solution of di-potassium nitrilotriacetate (K_2*NTA*) was prepared by dissolving the free acid (*NTA*) in calculated amount of 0.1*M*-KOH solution. Solutions of catechol, KNO_3 and K hydrogen-phthalate were prepared by direct weighing method.

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pH-metric studies were conducted with Philips pH-meter (RP 9405) calibrated with $0.05M$-K hydrogen-phthalate solution for pH = 4. The total volume (50 ml), ionic strength ($\mu = 0.1M$ KNO_3) and temperature (25 °C) were maintained constant. Following systems were titrated with $0.1M$-KOH solution repeatedly to ensure the reproducibility of results.

Systems. *Ln*(III)—*NTA*—catechol
[where *Ln*(III) = La(III), Pr(III) or Nd(III)]

(i) 10 ml $0.025M$-metal nitrate (Curve a)
(ii) 10 ml $0.025M$-K_2*NTA* (Curve b)
(iii) 10 ml ($0.025M$-metal nitrate + + 10 ml $0.025M$-*NTA* [*Ln*(III)—*NTA*, 1 : 1) (Curve c)
(iv) 10 ml $0.025M$-catechol (Curve d)
(v) 10 ml $0.025M$-metal nitrate + + 10 ml $0.025M$-catechol [*Ln*(III)—catechol, 1 : 1] (Curve e)
(vi) 10 ml $0.025M$-metal nitrate + 10 ml $0.025M$-*NTA* + + 10 ml $0.025M$-catechol [*Ln*(III)—*NTA*—catechol, 1 : 1 : 1) (Curve f)

Calculations

First ionisation constant ($pK_1 = 9.34$) of the secondary ligand (catechol) was calculated by the method of *Chaberek* and *Martell*[6] and the value of second ionisation constant ($pK_2 = 12.8$) was taken from the literature[7]. The formation constants ($\log K_{MAB}$) of the resulting mixed ligand complexes were determined by the method of *Thompson* and *Loraas*[8] and the free energies of formation ($\Delta F°$) from the equation:

$$\Delta F° = -2.303\, RT \log K_{MAB}.$$

Results and Discussion

Curve a (Figs. 1–3) represents the potentiometric titration of metal nitrate. A well-defined inflection at $m \approx 2.5$ (where m = moles of alkali added per mole of metal atom or ligand) indicates the basic-salt formation[9] of the metal and is in conformity with the earlier observation of *Britton*[10].

Curve b (Figs. 1–3) depicts titration of dipotassium nitrilotriacetate, giving an ill-defined inflection at $m = 1$, indicating that the carboxylic proton of the acid-salt is titrable at high pH ($\approx$ 10.7). Curve c (Figs. 1–3) showing the titration 1 : 1 *Ln*(III)—*NTA* binary mixture, gives two inflections at $m = 1$ and $m \approx 2$. The lowering in initial pH and a sharp inflection at $m = 1$ may be due to the formation of 1 : 1, *Ln*(III)—*NTA* complex whereas the second inflection at $m \approx 2$ is probably due to the formation of 1 : 1, *Ln*(III)—*NTA*—hydroxo complex[11].

Curve d (Figs. 1–3) attributes the titration of catechol. A single ill-defined inflection at $m = 1$ indicates the titration of only one phenolic proton in alkaline medium (pH $\approx$ 10.2).

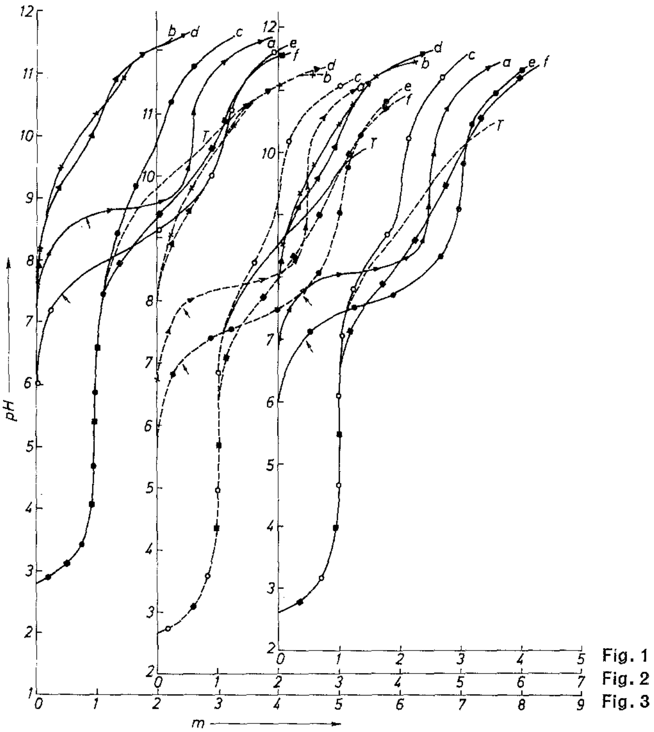
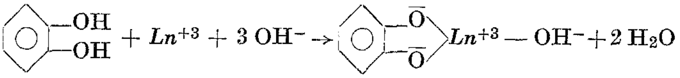


Fig. 1. La(III)—*NTA*—catechol. Curve a = La(III), b = K_2*NTA*, c = La(III)—*NTA*, d = catechol, e = La(III)—catechol, f = La(III)—*NTA*—catechol, T = theoretical composite curve. → = Appearance of ppt

Fig. 2. Pr(III)—*NTA*—catechol. Curve a = Pr(III), b = K_2*NTA*, c = Pr(III)—*NTA*, d = catechol, e = Pr(III)—catechol, f = Pr(III)—*NTA*—catechol, T = theoretical composite curve. → = Appearance of ppt

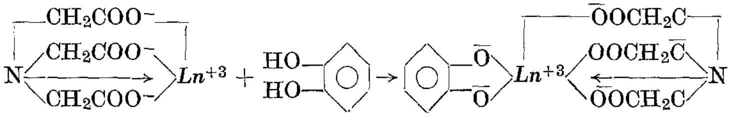
Fig. 3. Nd(III)—*NTA*—catechol. Curve a = Nd(III), b = K_2*NTA*, c = Nd(III)—*NTA*, d = catechol, e = Nd(III)—catechol, f = Nd(III)—*NTA*—catechol, T = theoretical composite curve. → = Appearance of ppt

Curve e (Figs. 1–3) represents the titration 1 : 1, *Ln*(III)—catechol binary system. The appearance of green solid almost from the beginning of the titration and a single inflection at $m \approx 3$ may be attributed to the formation of a neutral 1 : 1, *Ln*(III)—catechol—hydroxo complex:



(where Ln^{+3} = La^{+3}, Pr^{+3}, Nd^{+3})

Curve f (Figs. 1–3) depicts the titration of 1:1:1, *Ln*(III)—*NTA*—catechol ternary system. The initial superimposable nature of this curve with the curve c and a sharp inflection at $m = 1$ possibly indicate the formation of *Ln*(III)—*NTA* binary complex at the beginning. Another inflection at $m = 3$ is probably due to the further addition of catechol to the initially formed 1 : 1, *Ln*(III)—*NTA* complex finally resulting in the formation, 1 : 1 : 1, *Ln*(III)—*NTA*—catechol ternary species.



(where Ln^{+3} = La^{+3}, Pr^{+3}, Nd^{+3})

The formation of above mixed ligand complexes is further supported by the absence of a solid phase and the lowering of this curve (f) to the theoretical composite curve (T) [drawn by adding the horizontal distance of the secondary ligand (catechol) to the curve (c) for 1 : 1, *Ln*(III)—*NTA* at the same pH] in the region to ternary conplex formation.

Formation Constant of the Ternary Complexes

The values of stability constant ($\log K_{MAB}$) and free energies of formation ($\Delta F°$) given in the following table indicate the order of stability in terms of metal ion as La(III) < Pr(III) < Nd(III) which is in conformity with the earlier observations of *Sharma* and *Tandon*[12] as reported in the case of *Ln*(III)—*HEDTA*—dicarboxylic acid ternary complexes.

Table 1. *Formation Constants and the Free Energies of Formation of Mixed Ligand Complexes at 25 ± 0.1 °C*

System	Stability constant	$\Delta F°$ kcals/mole
La(III)—*NTA*—catechol	6.99 ± 0.075	— 9.52
Pr(III)—*NTA*—catechol	7.43 ± 0.13	— 10.12
Nd(III)—*NTA*—catechol	7.63 ± 0.14	— 10.39

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