Formation Studies on Quaternary Complexes of Some Rare Earth Metals

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Lanthanides are highly electropositive in character and hydrolytic in nature and hence have little tendency to form complexes - particularly with N and S donor ligands. Only few references [1,2] have been reported on their quaternary complexes in which these metal ions not only form stable complexes but also expand their coordination number beyond six [3-7].

In present paper, we report the pH-metric studies on 1:1:1 Ln(III)-IMDA-TDA/FA ternary and 1:1:1:1 Ln(III)-IMDA-TDA-FA quaternary complexes with an aim to compare their formation and stabilities.

EXPERIMENTAL

Materials

The chemicals used were either AR, BDH or GR, E.Merck samples. Double distilled water was used to prepare solutions. Standard solutions of metal nitrates were prepared using lanthanide nitrate, praseodimium nitrate and neodimium nitrate and standardized by the usual methods [8,9]. Solution of iminodiacetic acid (IMDA), thiodiacetic acid (TDA) and furan-2-carboxylic acid (FA) were prepared by direct wighing. The concentration of the ligand and metal solutions were further checked by pH metric titrations against 0.1 M KOH solution.

General Procedure

The pH-metric titrations were carried out in a thermostat at 28 ±1° C using a Toshniwal pH-meter (CI-46) and a combined electrode assembly. The instrument was standardized against 0.05 M potassium hydrogen phthalate solution (pH=4) before each titration. The total volume at the beginning of each titration was 50 ml and ionic strength was maintained with 0.1 M KNO_3. Titrations in clear solutions were used for deriving inferences.

Calculation

The dissociation constants of iminodiacetic acid (IMDA) (pK_1 - 2.83 ± 0.007, pK_2 = 8.90 ± 0.06), thiodiacetic acid (TDA) (pK_1 = 3.09 ± 0.04, pK_2 = 4.21 ± 0.08) and furan-2-carboxylic acid (FA) (pK = 3.36 ± 0.02) were calculated by the method of Chaberek and Martel [10]. The formation constants of quaternary complexes formed by the simultaneous co-ordination of all the ligands to the metal ion (log $K_{MLL'L''}$) were calculated by the method of Ramamoorthy and Santappa [11] from the following expression:

$$K_{MLL'L''} = \frac{T_M - 1/3\ A\ X}{(1/3)^4\ A^4\ X}$$

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with total ligand concentration A and X are given by

$$A = \frac{5T_N - T_{OH} - [H^+]}{\frac{4[H^+]^2}{K_1'K_2' + K_1''K_2''} + \frac{3[H^+]}{K_1+K_1'+K_1''}}$$

$$X = 1 + \frac{2[H^+]^2}{K_1'K_2' + K_1''K_2''} + \frac{3[H^+]}{K_1+K_1'+K_1''}$$

where K_1, K_1' and K_1'' are the first dissociation constants of monobasic acid (L) and dibasic acids (L' and L"). K_2' and K_2'' are the second dissociation constants of dibasic acids (L' and L").

Free energies of formation (ΔG°) for mixed-ligand quaternary species were also calculated by putting the values of formation constants in the expression.

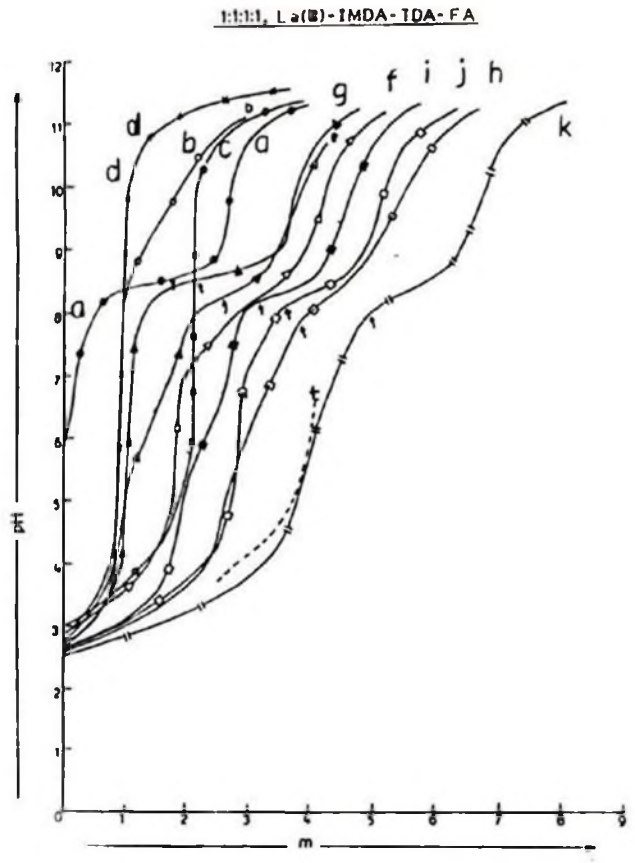
$$\Delta G^\circ = -2.303\ RT \log K$$

where R is gas constant (1.987 cal/mole/deg), T is absolute temperature (t° C + 273).

RESULT AND DISCUSSION

Titration curves in case of all the three lanthanides were similar, hence only the curves for 1:1:1:1 La(III)-IMDA-TDA-FA have been discussed to explain the formation of ternary and quaternary complexes.

Curve a (Fig. 1) represents the pH-metric titration of lanthanum nitrates. Appearance of an inflection at m=2.5 (m-moles of alkali added per mole of the metal ion or ligand) on this curve may be attributed to the basic-salt



- a – $La(NO_3)_3$
- b – IMDA
- c – TDA
- d – FA
- e – 1:1, La(III)-IMDA
- f – 1:1, La(III)-TDA
- g – 1:1, La(III)-FA
- h – 1:1:1, La(III)-IMDA-TDA
- i – 1:1:1, La(III)-IMDA-FA
- j – 1:1:1, La(III)-TDA-FA
- k – 1:1:1:1, La(III)-IMDA-TDA-FA
- T – Theoretical Composite Curve
- → Appearace of ppt

formation [12] and is in confirmity with the earlier observations of Britton [13].

Curve b (Fig.1) shows the titration of iminodiacetic acid (IMDA). A well-defined inflection at m = 1 may be correlated to the titration of one of the carboxylic group of the acid forming its acid-salt. Curve c for thiodiacetic acid (TDA) gives sharp inflection at m=2 which leads to the simultaneous titration of both the protons of the two involved carboxylic groups of the dibasic acid. Curve 'd' represents the pH-metric titration of 2-furoic acid (FA). A single sharp inflection at m=1 indicates the titration of only carboxylic proton present in 2-furoic acid.

Binary Systems

Curve e (Fig.1) describes the titration of 1:1 M(III)-IMDA binary system. A sufficient lowering in the initial pH followed by an inflection at m=1 may be correlated to the formation of 1:1 M(III)-IMDA complex. Another inflection at m = 2.5 and an appearance of a white gelatinous precipitate at m>1 may be ascribed to the disproportionation of the initially formed complex into 1:2 complex and the metal hydroxide.

Curve f depicts the titration of 1:1 M(III)-TDA. The lowering in initial pH followed by an inflection at m=2 may be due to formation of 1:1 M(III)-TDA species. Another inflection at m=3.5 with the appearance of solid phase at m=2 may be correlated to the disproportionation of initially formed 1:1 complex into 1:2 M(III)-TDA species with the simultaneous precipitation of the remaining metal as hydroxide in the higher buffer region.

Curve g (Fig.1) representing the titration of 1:1 M(III)-FA system, gives an inflection at m=1 which may be due to the formation of 1:1 M(III)-FA species. Another inflection at m=3 followed by precipitation may be attributed to the formation of 1:3 M(III)-FA complex and the simultaneous precipitation of metal hydroxide.

Ternary Systems

Curve 'h' (Fig.1) for 1:1:1:1 M(III) -IMDA-TDA species gives a well defined inflection at m=4 which can be correlated to the simultaneous chelation of both the ligands to metal ion forming 1:1:1 hetero-ligand species:

$$M^{3+} + IMDA + TDA + 4\ OH \rightleftharpoons [IMDA^{2-} - M^{3+} - TDA^{2-}] + 4H_2O.$$

Curve i for 1:1:1 M(III)-IMDA-FA shows an inflection at m=2 which may be due to the formation of 1:1 M(III)-IMDA binary complex in the begnning. Another inflection at m=3 indicates the addition of FA later on to the initially formed 1:1 complex. Similarly, curve j ascribes the titration of 1:1:1 M(III)-TDA-FA ternary system. An inflection at m=3 can be attributed to the simultaneous chelation of both the ligands to the metal ion forming 1:1:1 ternary species.

Quaternary Systems

Curve k represents the pH-metric titration of 1:1:1:1 M(III)-IMDA-TDA-FA systems. The lowering in the initial pH

followed by an inflection at m=5 may be due to the simultaneous chelation of all the three ligands to the metal ion forming 1:1:1:1 soluble quaternary species:

$$M^{3+} + IMDA + TDA + FA + 5\ OH^- \rightleftharpoons [M^{3+}\text{-}IMDA^{2-}\text{-}TDA^{2-}\text{-}FA] + 5\ H_2O$$

The above observation is further supported by the lowering of the theoretical composite curve t in comparison to the curve k representing the mixed ligand complex formation.

Formation constants

The calculated values of formation constants and free energies of formation (ΔG^0) of the ternary and quaternary species are recorded in Table 1. The relative order of stability of quaternary species in terms of metal ions have been found to be : La(III) < Pr(III) < Nd(III) and may be explained on the basis of decreasing size and increasing ionic potential (charge/radius ratio) of the metal ions.

Table 1

Formation Constants and Free Energy of formation

Metal ion - La(III), Pr(III) and Nd(III) 5.0 X 10^{-3} M
Ligands - IMDA, TDA and FA 5.0 X 10^{-3} M
Temp 28 ± 1°C; Ionic Strength 0.1 M KNO_3;
Titrant 0.1 M KOH; ΔG° in K cal/mol

Parameter	La(III)	Pr(III)	Nd(III)
1:1:1 M-IMDA-TDA Ternary System			
log $K_{MLL'}$	8.04±0.11	9.55±0.19	10.28±0.16
ΔG°	-11.0742	-13.1541	-14.1596
1:1:1 M-IMDA-FA Ternary System			
log $K_{MLL'}$	9.55±0.17	10.04±0.80	10.93±0.15
ΔG°	-13.1541	-14.3249	-15.0549
1:1:1:1 M-IMDA-TDA-FA Quaternary System			
log $K_{MLL'L''}$	11.93±0.13	12.31±0.11	13.40±0.10
ΔG°	-16.1668	-16.9687	-16.4682

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