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Mixed Ligand Chelates of Some Rare Earth Metals With Diethylenetriamine-pentaacetic Acid and Dicarboxylic Acids

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By means of potentiometric studies evidence was found for the formation of 1:1:1 ternary chelates of the type: *M*(III)—*DTPA*—dicarboxylic acids [*M*(III) = La(III), Pr(III), Nd(III), Gd(III) or Dy(III); dicarboxylic acids = phthalic acid (*PHA*) or malonic acid (*MLA*)]. The formation constants (log $K_{MLL'}$) and free energies of formation (ΔG°) have been evaluated. The order of stabilities with respect to the metal ions was La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III) and with respect to the dicarboxylic acids *MLA* < *PHA* was observed.

(Keywords: Potentiometric formation constants; Rare earth complexes; Ternary complexes)

Gemischte Chelate einiger Selten-Erd-Metalle mit Diethylentriamin-pentaessigsäure und Dicarbonsäuren

Es wurden ternäre 1:1:1-Chelate folgenden Typs mittels potentiometrischer Untersuchungen nachgewiesen: *M*(III)—*DTPA*—Dicarbonsäure [*M*(III) = La(III), Pr(III), Nd(III), Gd(III) oder Dy(III); Dicarbonsäure = Phthalsäure (*PHA*) oder Malonsäure (*MLA*)]. Die Komplexbildungskonstanten ($K_{MLL'}$) und die Bildungsenthalphien (ΔG°) wurden bestimmt. Bezüglich der Stabilität der Komplexe ergaben sich folgende Reihungen: La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III) bzw. *MLA* < *PHA*.

Introduction

Recently, the ternary systems: rare earth ions—aminopolycarboxylic acids (*NTA*, *HEDTA* or *EDTA*)—dicarboxylic acids[1–3] have been reported. The lanthanide ions are capable of showing expansion of their coordination number[2–6] during complexation. *DTPA*, an octadentate ligand, may form stable hydrolysis resistant biligand complexes with lanthanide ions in association with a number of bidentate ligands such

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as dicarboxylic acids. Survey of the literature reveals that no work was carried out on the systems: *M*(III)—Diethylenetriamine-pentaacetic acid (*DTPA*)—dicarboxylic acids. The physico-chemical studies of the above systems may lead to interesting results. The data of the potentiometric studies on the above mentioned systems are discussed in the present communication.

Experimental

Solutions of all the chemicals (AnalaR, BDH or E. Merck grade) metal nitrates, dicarboxylic acids were prepared and standardised as described earlier[1–2]. Diethylene triamine pentaacetic acid was used in its monoprotonated form. The solution of tetrapotassium salt of *DTPA* was prepared by dissolving the calculated weighed amount of the acid in calculated volume of standardised caustic potash solution. The concentration of the solution was then checked potentiometrically.

Philips pH-meter (PR 9405 M), standardised against 0.05*M*-potassium hydrogen phthalate solution at 27 ± 1 °C for pH = 4, was used for pH-measurements. The ionic strength ($\mu = 0.1M$-KNO_3) and the total volume (50 ml) of the solution were maintained constant at the beginning of the titration. The pHs were plotted against *m* (moles of base per mole of metal ion or ligand).

Calculations

The ionization constants of ligands were calculated by the method of *Chaberek* and *Martell*[7] and are shown in Table 1. The formation constants ($\log K_{MLL'}$) for the ternary species were calculated by the method of *Ramamoorthy* and *Santappa*[8] using equ. (1) and free energies of formation by equ. (2). The values of $\log K_{MLL'}$ and $\Delta G°$ are recorded in Table 2.

$$K_{MLL'} = \frac{T_M - (1/2)\,A\,X}{(1/2)^3 A^3 X} \tag{1}$$

with total free ligand concentration,

$$A = \frac{2\,T_M - T_{OH} - [H^+]}{\dfrac{2\,[H^+]}{K_1 + K_1'}}$$

T_{OH} = KOH; T_M = total metal ion concentration,
K_1 = dissociation constant of *DTPA* and
K'_1 = first dissociation constant of dicarboxylic acids (*PHA*/*MLA*) and

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

$$\Delta G° = -RT \ln K_{MLL'} \tag{2}$$

where R = gas constant; *T* = temperature in K.

Results and Discussion

Because of the identical nature of the curves obtained in the systems involving the rare earth metal ions, La(III), Pr(III), Nd(III), Gd(III) and Dy(III), the curves for the system: La(III)—*DTPA*—*PHA*/*MLA* are considered representative for all others and will be discussed extensively (see Fig. 1*a*, *b*).

Table 1. *Dissociation constants of the ligands under investigation*

Ligand	pK_1	pK_2
DTPA	10.30 ± 0.16	—
PHA	2.69 ± 0.07	5.35 ± 0.08
MLA	2.82 + 0.07	5.75 ± 0.07

Table 2. *Formation constants* (log $K_{MLL'}$) *and free energies of formation* ($\Delta G°$ *in* kcal mol^{-1} *at 27 ± 1 °C*

Metal Ion	*M*(III)—*DTPA*—*PHA*		*M*(III)—*DTPA*—*MLA*	
	log $K_{MLL'}$	$\Delta G°$ 300	log $K_{MLL'}$	$\Delta G°$ 300
La(III)	6.21 ± 0.07	—8.52	5.39 ± 0.12	—7.40
Pr(III)	6.28 ± 0.08	—8.62	5.48 ± 0.08	—7.52
Nd(III)	6.33 ± 0.10	—8.69	5.53 ± 0.08	—7.59
Gd(III)	6.47 ± 0.09	—8.87	5.68 ± 0.09	—7.80
Dy(III)	6.54 ± 0.11	—8.98	5.73 ± 0.09	—7.86

An inflection at $m = 2.5$ in the curve a (Fig. 1*a*) may be attributed to the basic salt formation[9] in confirmity with the observations of *Britton*[10].

The only carboxy proton of the tetrapotassium salt of *DTPA* remains non labile and is not titrated even at a very high pH (curve b, Fig. 1*a*).

Curve d (Figs. 1*a* and *b* respectively, for *PHA* and *MLA*) exhibits inflections at $m = 1$, $m = 2$ indicating the titration of carboxy protons of the acids in distinct steps.

Binary Systems

La(III)—DTPA: The extensive lowering in pH indicated by the curve c (Fig. 1*a*) for the 1:1 La(III)—*DTPA* system and a sharp

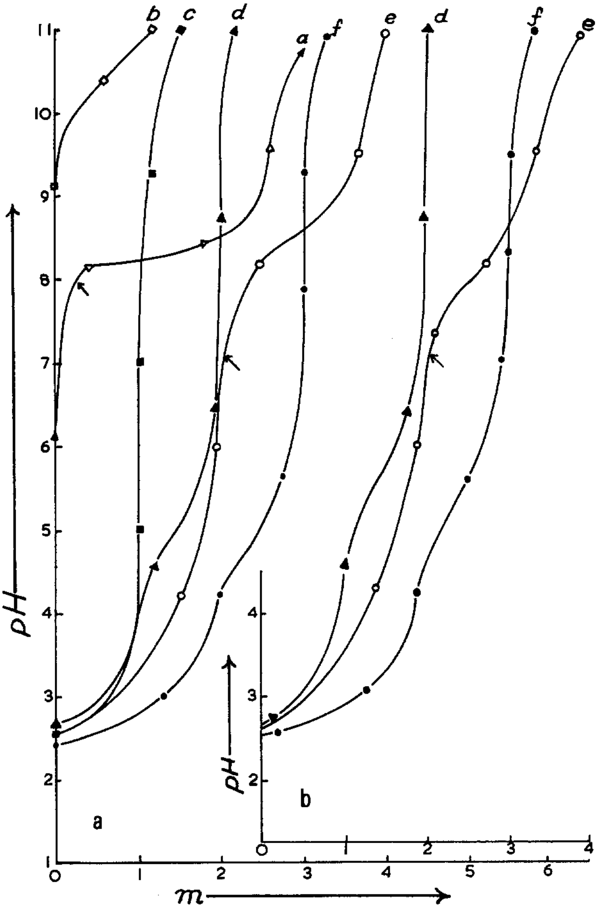


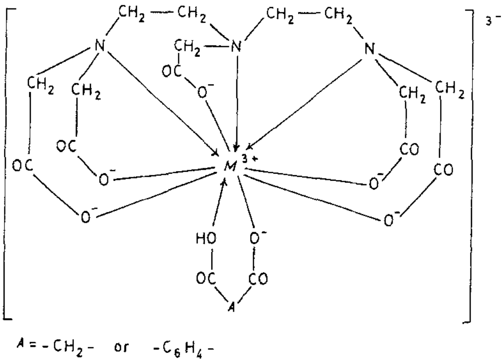
Fig. 1. *a* Curve a = La(III), b = K_4*DTPA*, c = La—*DTPA* (1:1), d = *PHA*, e = La—*PHA* (1:1), f = La—*DTPA*—*PHA* (1:1:1); *b* Curve d = *MLA*, e = La—*MLA* (1:1), f = La—*DTPA*—*MLA* (1:1:1)

inflection at $m = 1$ may be ascribed to the formation of a soluble 1:1 metal—*DTPA* chelate.

La(III)—*PHA*/*MLA*: Curve e (Figs. 1*a*, *b*) depicting the titration of La(III) in presence of an equimolar amount of *PHA* or *MLA* gives a sharp inflection at $m = 2$ which may be attributed to the formation of 1:1 La(III)—*PHA*/*MLA* complex. The binary complex, thus formed in the beginning, appears to undergo disproportionation at $m \approx 2$ (pH > 7) resulting in formation of 1:3 La(III)—*PHA*/*MLA* complex[2] and the gelatinous white metal hydroxide. The inflection observed at $m \approx 4$ may, probably, be attributed to such a disproportionation process.

Ternary Systems

La(III)—DTPA—PHA/MLA: The curve f representing the 1:1:1 La(III)—*DTPA*—*PHA* system (Fig. 1*a*) and 1:1:1 La(III)—*DTPA*—*MLA* system (Fig. 1*b*) exhibits appreciable lowering in pH from the very beginning indicating complexation. An inflection at $m = 2$ may probably be attributed to the simultaneous additions of *DTPA* and *PHA/MLA* to the metal ion resulting in the formation of a 1:1:1 protonated species (I) (one of the carboxy protons of the acids remaining intact in the process). Another sharp inflection at $m = 3$ (pH $= 6$) may be ascribed to the deprotonation of species (I).



(I)

The possibility of the formation of 1:1 La(III)—*DTPA* or 1:1 La(III)—*PHA/MLA* complexes in the initial stages may safely be ruled out. In the event of formation of binary species, the ternary complex curve f, would overlap either of the curve c (for 1:1 La(III)—*DTPA*) or curve e (for 1:1 La(III)—*PHA/MLA*) which is not observed. The simultaneous addition of both the ligands resulting in the formation of a soluble ternary species is, therefore, evidenced; this is further supported by the non appearance of the precipitate throughout the titration.

Formation Constants of Ternary Chelates

The calculated values of formation constants ($\log K_{MLL'}$) for the ternary complexes and free energies of formation (ΔG°) are recorded in Table 2. The order of stability

La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III) may be attributed to the decreasing size and increasing charge/radius ratio of the metal ion. The relative order of stability in terms of dicarboxylic acids *MLA* < *PHA* may, however, be correlated to the presence of a benzene ring in *PHA*.

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