Stability Constants of Trivalent Lanthanide and Yttrium Complexes with Ethyleneglycol-bis(2-Aminoethyl Ether)-N,N,N',N'-Tetraacetic Acid (EGTA) and Phthalic Acid— A Potentiometric Study

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Mixed ligand complexes of trivalent lanthanide and yttrium metal ions, involving ethyleneglycol-bis(2-aminoethylether)-N,N,N'N'-tetraacetic acid (EGTA) as primary ligand and phthalic acid as secondary ligand were studied potentiometrically at three different ionic strengths (0.05, 0.10 and 0.15 m) and at 25°C in aqueous solution.

INTRODUCTION

Aminopolycarboxylic acids are the biologically active chelating agents[1]. Variety of mixed ligand complexes of lanthanide(III) metal ion using aminopolycarboxylic acid as primary and phthalic acid as secondary ligand have been reported[2,3]. EGTA is an important member of aminopolycarboxylic acid series and chelating agent in biology and medicine. It is well known to form stable binary complexes with trivalent lanthanide and yttrium metal ions. However, the work reported on ternary complexes in literature about this compound is scanty[4-6]. Therefore it was considered of interest to determine the thermodynamic stability constant of ternary complexes of lanthanide and yttrium metal ions using EGTA as the primary and phthalic acid as the secondary ligand.

EXPERIMENTAL

All the chemicals used were of A.R. grade and the solutions were prepared in doubly distilled CO_2-free water. Solutions of disodium salt of EGTA (Na_2H_2 EGTA) and phthalic acid were prepared by dissolving their accurately weighed amounts. Metal nitrate solutions of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Y^{3+} were prepared by dissolving accurately weighed amounts of corresponding metal nitrate. and standardised by usual method[7]. An Elico pH meter model LI-120 (accuracy ±0.01 pH unit) fitted with glass (EN–66) and calomel (ER–70) electrodes were used. All pH measurements were taken after calibration with standard buffer solutions of pH 4.00 and 9.20. Following sets of titrations were performed under nitrogen atmosphere against 0.10 M NaOH at three different ionic strengths (μ = 0.05M, 0.10 M and 0.15 M) maintained by $NaNO_3$ at $25 \pm 1°$. The total volume in each set was kept 50 mL.

(1) HNO_3 (2.0×10^{-3} M)
(2) HNO_3 (2.0×10^{-3} M) + ligand Na_2H_2-EGTA/phthalic acid (1.0×10^{-3} M).
(3) HNO_3 (2.0×10^{-3} M) + ligand Na_2H_2-EGTA/phthalic acid (1.0×10^{-3} M) + metal ion ($1.0 \times^{-3}$ M) .

(4) HNO_3 $(2.0 \times 10^{-3} M)$ + ligand $Na_2H_2\text{-EGTA}$ $(1.10 \times 10^{-3} M)$ + ligand phthalic acid $(1.0 \times 10^{-3} M)$ + metal ion $(1.0 \times 10^{-3} M)$

RESULTS AND DISCUSSION

The proton-dissociation constants of the ligands and the stability constant of 1:1 binary and 1:1:1 ternary complexes were calculated by using the algebriac method and these values are given in Table-1.
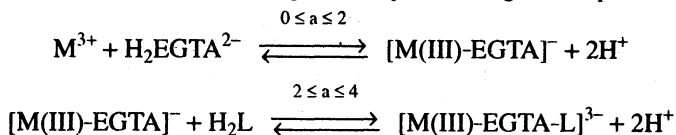
TABLE-1

THE DISSOCIATION CONSTANTS OF THE LIGANDS AND STABILITY CONSTANTS OF THE COMPLEXES

Proton dissociation constants	$\mu = 0.15$ M		$\mu = 0.10$ M		$\mu = 0.05$ M		$\mu \to 0$	
	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
H_2A	8.73	10.37	8.86	10.50	9.05	10.62	9.18	10.75
H_2L	2.75	4.94	2.84	5.07	2.96	5.25	3.19	5.51
Binary complexes	$\log K_{MA}^M$		$\log K_{MA}^M$		$\log K_{MA}^M$		$\log K_{MA}^M$	
La(III)-H_2A	15.25		15.37		15.47		15.55	
Ce(III)-H_2A	15.64		15.75		15.83		15.92	
Pr(III)-H_2A	15.73		15.85		15.93		16.02	
Nd(III)-H_2A	15.91		16.08		16.14		16.24	
Sm(III)-H_2A	16.46		16.54		16.65		16.74	
Y(III)-H_2A	16.85		16.95		17.04		17.10	
La(III)-H_2L	4.08		4.16		4.24		4.44	
Ce(III)-H_2L	4.17		4.27		4.37		4.59	
Pr(III)-H_2L	4.27		4.37		4.48		4.71	
Nd(III)-H_2L	4.45		4.55		4.64		4.86	
Sm(III)-H_2L	4.56		4.64		4.75		4.96	
Y(III)-H_2L	4.76		4.85		4.94		5.14	
Ternary complexes	$\log K_{MAL}^{MA}$		$\log K_{MAL}^{MA}$		$\log K_{MAL}^{MA}$		$\log K_{MAL}^{MA}$	
La(III)-H_2A-H_2L	3.76		3.85		3.98		4.17	
Ce(III)-H_2A-H_2L	3.87		3.97		4.04		4.24	
Pr(III)-H_2A-H_2L	3.97		4.06		4.15		4.36	
Nd(III)-H_2A-H_2L	4.06		4.15		4.25		4.46	
Sm(III)-H_2A-H_2L	4.15		4.25		4.37		4.58	
Y(III)-H_2A-H_2L	4.23		4.33		4.46		4.69	

where $H_2A = H_2EGTA^{2-}$, H_2L = Phthalic acid

Titration curve of M(III)–EGTA-phthalic acid system in 1:1:1 ratio, exhibits an inflection at a = 4 and pH ≈ 6.1. An examination of the mixed ligand titration curve reveals that this runs superimposed on the 1:1 M(III)-EGTA curve upto a = 2 and pH ≈ 3.4, thus indicating that phthalic acid does not participate in

complexation and formation of 1:1 binary M(III)- EGTA complex upto this stage. The formation of mixed ligand complex is suggested by the comparison of mixed ligand titration curve with the theoretical composition curve. The latter was drawn by the graphical addition of phthalic acid to 1:1 M(III)-EGTA curve. However at $2 \le a \le 4$ the experimental curve of mixed ligand system is displaced from the composite curve to the right indicating the liberation of extra protons and thus suggesting the formation of mixed ligand complex, throughout stepwise equilibria.

$$M^{3+} + H_2EGTA^{2-} \xrightarrow[]{0 \le a \le 2} [M(III)\text{-}EGTA]^- + 2H^+$$

$$[M(III)\text{-}EGTA]^- + H_2L \xrightarrow[]{2 \le a \le 4} [M(III)\text{-}EGTA\text{-}L]^{3-} + 2H^+$$

where H_2L = phthalic acid.

The occurrence of precipitate in 1:1 M(III)-phthalic acid system at pH 6.3, but the nonappearance of any solid phase in ternary systems further supports the formation of mixed ligand complex in solution.

Negative values of $\Delta \log K$ (-0.40 ± 0.08) and per cent of relative stabilization[10] [(%), R.S.] (-7.40 ± 1) indicate that the ternary complexes are less stable than binary complexes, *i.e.* secondary ligand $H_2 L$ binds better to aquometal ion than the $(M\text{-}EGTA)^-$ complex. It can be explained on the basis of the electrostatic repulsion between $[M\text{-}EGTA]^-$ and incoming negatively charged secondary ligands, coupled with the availability of lesser number of coordinating sites for coordination on $[M\text{-}EGTA]^-$ binary complex compared to aquated metal ions.

The formation of ternary complexes can also be evidenced by the study of the distribution of various complex species present in solution as a percentage of metal with pH is drawn, from which it is observed that upto pH $\approx$ 3.5, no mixed ligand species is formed and about 95% of total metal ion exists as in $[M\text{-}EGTA]^-$ complex. It is clearly evident that the pH $\approx$ 3.8 from which formation of M-EGTA-phthalic acid complex starts and form about 75% of the total metal ion in solution.

Stability order of binary and ternary complexes is found to be accordance with the increasing ionic potential of metal ions *viz.*, $La^{3+} < Ce^{3+} < Pr^{3+} < Nd^{3+} < Sm^{3+} < Y^{3+}$.

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