Formation Constants of La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Y(III) Ternary Chelates.

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Equilibrium studies in metal-disodium salt of ethylene glycol *bis* (2-amino ethyl ether)-N,N,N′,N′-tetraacetic acid (ligand A)—L proved the formation of ternary complexes of the type MAL. The ligands (L) used are anthranilic acid, 3-methylanthranilic acid and monosodium salt of 5-sulfoanthranilic acid. Equilibrium constants corresponding to various equilibria have been measured at 25°C and at three different ionic strengths of 0.05 M, 0.10 M and 0.15 M (NaNO₃). The metal ions taken for the present studies are La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Y(III).

INTRODUCTION

In anthranilic acid (AA) and its substituted derivatives 3-methyl anthranilic acid (MAA) and monosodium salt of 5-sulfoanthranilic acid (SAA) the presence of —NH_2 group *ortho* to —COOH group provides favourable geometry of stable chelate ring formation.

Survey of literature reveals that the binary complexes of anthranilic acid with lanthanide(III) ions have been reported[1]. pH-Metric technique has been applied to study the ternary complex formation of lanthanide(III) ions using EDTA as one ligand and anthranilic acid as the second ligand[2, 3]. Ethylene glycol *bis*(2-amino ethyl ether)-N,N,N′,N′-tetraacetic acid (EGTA) is an important member of aminopolycarboxylic acid series, but scanty work of this type has been reported.[4–7] In the present paper, we communicate the thermodynamic formation constants of 1:1:1 ternary complexes of lanthanide(III) and yttrium(III) using EGTA as one ligand and AA, MAA and SAA as the second ligand. In order to have comparative complexation studies, the 1:1 binary complexes of metal with AA, MAA and SAA have also been investigated under similar experimental conditions.

EXPERIMENTAL

Standard solutions of NaOH (0.10 M), nitric acid (0.01 M) and sodium nitrate (1.00 M) were prepared. Solution of anthranilic acid (AA), 3-methyl anthranilic

acid (MAA), monosodium salt of 5-sulfoanthranilic acid (SAA) and disodium salt of EGTA each of 0.01 M were prepared by direct weighing. Solution of Na_2H_2EGTA was prepared in aqueous medium while solutions of AA, MAA and SAA were prepared in absolute ethanol.

Lanthanum(III), cerium(III), praseodymium(III), neodymium(III), samarium (III) and yttrium(III) nitrate solutions each of 0.01M, were prepared and used after standardisation. All chemicals used in the present investigation were of analytical grade and the solutions were prepared in doubly distilled CO_2-free water.

pH-Metric measurements were made with an Elico pH-meter LI-120 (accuracy ± 0.01 pH unit) employing a glass electrode and a saturated calomel electrode. It was calibrated before and after each potentiometric titration with buffer solutions of 4.00 and 9.20 pH values. The following titration mixtures were prepared at $\mu = 0.05$ M. The ionic strength was maintained by the addition of required volume of 1.0 M $NaNO_3$ solution.

(1) HNO_3 (2.0×10^{-3} M)

(2) HNO_3 (2.0×10^{-3} M) + ligand A (1.0×10^{-3} M)

(3) HNO_3 (2.0×10^{-3} M) + ligand A (1.0×10^{-3} M)

    + metal ion (1.0×10^{-3} M)

(4) HNO_3 (2.0×10^{-3} M) + ligand L (1.0×10^{-3} M)

(5) HNO_3 (2.0×10^{-3} M) + ligand L (1.0×10^{-3} M)

    + metal ion (1.0×10^{-3} M)

(6) HNO_3 (2.0×10^{-3} M) + ligand A (1.0×10^{-3} M)

    + ligand L (1.0×10^{-3} M) + metal ion (1.0×10^{-3} M)

Similar titration mixtures were prepared at the other ionic strengths, *i.e.*, 0.10 M and 0.1 5 M ($NaNO_3$). The initial volume of each titration mixture was raised to 50.0 mL. All the solutions were allowed to attain equilibrium at $25 \pm 0.2°C$ (thermostated) and titrated with standard sodium hydroxide solution of 0.10 M. All these solutions were prepared in 20% (v/v) ethanolic-aqueous medium and appropriate corrections in pH-meter readings were made[8, 9] to get true pH values.

RESULTS AND DISCUSSION

The dissociation constants of the ligands and the stability constants of 1:1 binary complexes were calculated by algebraic method of Martell and Chaberek as modified by Dey *et al.*,[10, 11] and are recorded in Table-1 with their thermodynamic values.

In all the 1:1:1 ternary systems studied the mixed ligand titration curve overlaps with the 1:1 M-EGTA binary curve upto a = 2, pH ≈ 3.8 (where a = moles of alkali per mole of metal ions), suggesting the formation of 1:1 M-EGTA complex, it further indicates that the AA, MAA and SAA ligands do not interact with [M-EGTA]⁻ species up to this pH (Fig. 1).

TABLE-1

DISSOCIATION CONSTANTS OF THE LIGANDS AND STABILITY
CONSTANTS OF COMPLEXES.

Proton dissociation constant	$\mu = 0.15$ 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
A	8.73	10.37	8.86	10.5	9.05	10.62	9.18	10.75
L^1	4.95		5.15		7.38		8.65	
L^2	5.66		6.48		7.38		8.65	
L^3	4.95		5.00		5.18		5.30	

Binary Complexes	$\log K_{MA}^M$	$\log K_{MA}^M$	$\log K_{MA}^M$	$\log K_{MA}^M$
La(III)-A	15.25	15.37	15.47	15.55
Ce(III)-A	15.64	15.75	15.83	15.92
Pr(III)-A	15.73	15.85	15,92	16.02
Nd(III)-A	15.91	16.08	16.14	16.24
Sm(III)-A	16.46	16.54	16.65	16.74
Y(III)-A	16.85	16.95	17.04	17.10

	$\log K_{ML}^M$	$\log K_{ML}^M$	$\log K_{ML}^M$	$\log K_{ML}^M$
La(III)-L^1	3.14	3.33	3.56	3.76
Ce(III)-L^1	3.27	3.46	3.64	3.83
Pr(III)-L^1	3.35	3.56	3.74	3.93
Nd(III)-L^1	3.56	3.75	3.85	4.03
Sm(III)-L^1	3.76	3.97	4.14	4.31
Y(III)-L^1	4.07	4.22	4.43	4.59
La(III)-L^2	4.53	4.66	4.77	4.89
Ce(III)-L^2	4.62	4.79	4.85	5.10
Pr(III)-L^2	4.85	4.92	5.07	5.18
Nd(III)-L^2	4.93	5.10	5.23	5.38
Sm(III)-L^2	5.17	5.24	5.38	5.49
Y(III)-L^2	5.48	5.56	5.68	5.78
La(III)-L^3	3.10	3.23	3.40	3.55
Ce(III)-L^3	3.14	3.38	3.55	3.75
Pr(III)-L^3	3.23	3.46	3.67	3.88
Nd(III)-L^3	3.49	3.68	3.76	3.92
Sm(III)-L^3	3.67	3.81	4.01	4.19
Y(III)-L^3	3.89	4.14	4.27	4.46

$A = H_2EGTA^{2-}$,

$L = L^1$ (anthranilic acid) or L^2 (3-methyl anthranilic acid) or L^3 (monosodium salt of 5-sulfo-anthranilic acid).
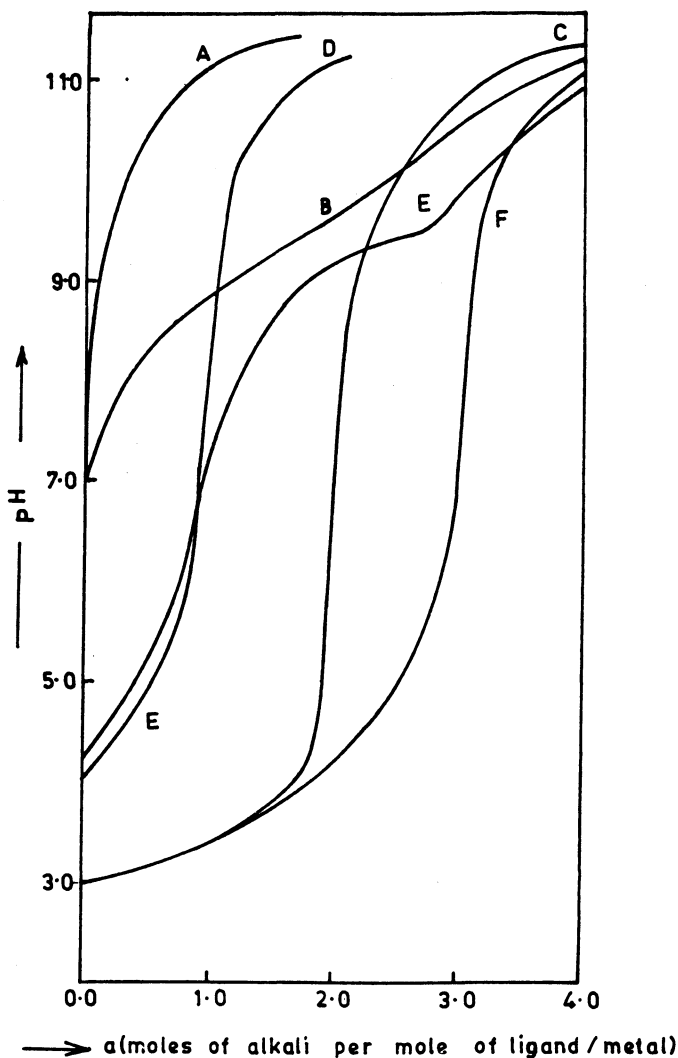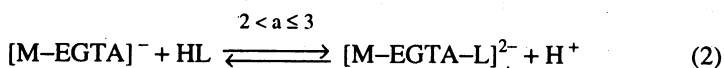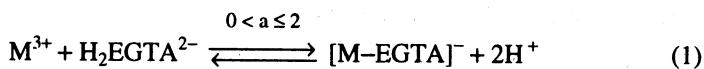
Fig. 1.   Potentiometric titration curves of M(III)-EGTA-L^1 system

The formation of mixed ligand complex is evidenced by the comparison of 1:1:1 mixed ligand titration curve with the theoretical composite curve T. The divergence of the experimental ternary complex curves at pH ≈ 3.8 and $2 < a \leq 3$ from the theoretical composite curve indicate the formation of ternary complexes through stepwise equilibria which can be represented as under:

$$0 < a \leq 2$$
$$M^{3+} + H_2EGTA^{2-} \rightleftharpoons [M-EGTA]^- + 2H^+ \tag{1}$$

$$2 < a \leq 3$$
$$[M-EGTA]^- + HL \rightleftharpoons [M-EGTA-L]^{2-} + H^+ \tag{2}$$

In case of SAA which is taken as HL$^-$, the charge on the ternary complex would be -3.

The formation of mixed ligand complex is further supported by the non-appearance of any solid phase throughout the mixed ligand titration. The concentrations of various complex species at pH values from 2.0–10.0 were obtained by analysing the mixed ligand pH-metric titration data with the aid of following mass and charge balance relations. The total concentrations of ligand H_2A^{2-}, ligand HL and the metal M^{3+} at any pH on the mixed ligand titration curve from $a = 0$ to 3, are given by the following expressions:

$$C_A = [H_2A] + [HA] + [A] + [MA] + [MAL]$$

$$C_L = [HL] + [L] + [ML] + [MAL]$$

$$C_M = [M] + [MA] + [ML] + [MAL]$$

$$aC_M = [HA] + 2[A] + 2[MA] + [L] + [ML] + 3[MAL]$$

a = moles of alkali per mole of metal ion in the ternary system (charges omitted for simplicity).

Substituting the proton-dissociation constants of the ligands and the equilibrium constants of their binary complexes, the free ligand concentrations [A] and [L] were calculated by Newton-Raphson method[11, 12]; thereby the concentrations of other species were obtained. These values were used for the calculation of equilibrium constants of the ternary complexes. The species present in solution were considered to be H_2A^{2-}, HA^{3-}, A^{4-}, HL, L$^-$, MA$^-$, ML^{2+} and MAL^{2-}. The per cent distribution of various species are presented in Fig. 2. The conditional
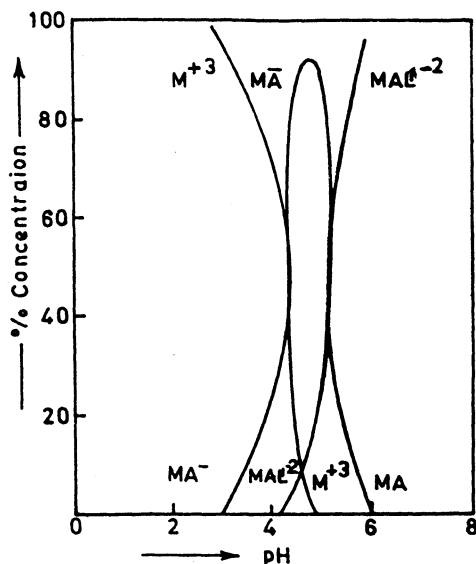

Fig. 2 Species distribution of M(III)-EGTA-L[1] system

constants obtained at different ionic strengths were used to obtain corresponding thermodynamic constants graphically by extrapolation to zero ionic strength. The formation constants of ternary complexes $\Delta \log K$ and percentage of relative stabilization are listed in Table-2. The parameter per cent relative stabilization $[(\%) \text{ R.S.}]^{13}$ for the ternary complexes describe the quantitative stabilization of ternary complexes.

TABLE-2
FORMATION CONSTANTS OF TERNARY COMPLEXES

Mixed Complex	$\log K_{MAL}^{MA}$				$\Delta \log K$	(%) R.S.
	$\mu = 0.15$ M	$\mu = 0.10$ M	$\mu = 0.05$ M	$\mu \to 0$		
La(III)-A-L^1	2.26	2.46	2.75	2.98	− 0.78	− 20.74
Ce(III)-A-L^1	2.43	2.74	2.93	3.17	− 0.66	− 17.23
Pr(III)-A-L^1	2.64	2.87	3.06	3.25	− 0.68	− 17.30
Nd(III)-A-L^1	3.35	3.47	3.68	3.73	− 0.30	− 7.44
Sm(III)-A-L^1	3.64	3.76	4.04	4.10	− 0.21	− 4.87
Y(III)-A-L^1	3.73	3.85	4.15	4.34	− 0.25	− 5.45
La(III)-A-L^2	4.05	4.11	4.28	4.39	− 0.50	− 10.22
Ce(III)-A-L^2	4.32	4.49	4.56	4.61	− 0.49	− 9.61
Pr(III)-A-L^2	4.39	4.52	4.67	4.21	− 0.97	− 18.73
Nd(III)-A-L^2	4.78	4.83	4.93	4.99	− 0.39	− 7.25
Sm(III)-A-L^2	4.96	5.04	5.16	5.18	− 0.31	− 5.65
Y(III)-A-L^2	5.08	5.18	5.23	5.30	− 0.48	− 8.30
La(III)-A-L^3	2.11	2.27	2.39	2.54	− 1.01	− 28.45
Ce(III)-A-L^3	2.41	2.52	2.67	2.79	− 0.96	− 25.60
Pr(III)-A-L^3	2.52	2.69	2.81	2.96	− 0.92	− 23.71
Nd(III)-A-L^3	3.08	3.13	3.25	3.34	− 0.58	− 14.80
Sm(III)-A-L^3	3.25	3.35	3.49	3.59	− 0.60	− 14.32
Y(III)-A-L^3	3.45	3.59	3.70	3.86	− 0.60	− 13.45

$A = H_2EGTA^{2-}$, $L = L'$ (anthranilic acid) or L^2 (3-methyl anthranilic acid) or $L^3 =$ monosodium salt of 5-sulfoanthranilic acid)

$\Delta \log K = (\log K_{MAL}^{MA} - \log K_{ML}^{M})$

$(\%) \text{ R.S.} = \dfrac{\Delta \log K}{\log K_{ML}^{M}} \times 100$

The values of $\Delta \log K$ and (%) R.S. for all the ternary systems are found to be negative indicating that the secondary ligands (L) bind better to M(III) aqueous ions than to the binary [M-EGTA]$^-$ complex. Such lowering in the values of stability constants of 1:1:1 ternary complexes $\log K_{MAL}^{MA}$ compared to $\log K_{ML}^{M}$ of 1:1 binary complex can be attributed due to the larger size of the primary

ligand (EGTA), destabilization effect caused by the repulsion between $1:1$ binary $[M\text{-}EGTA]^-$ complex and L^-/L^{2-} ligands, coupled with the availability of lesser number of coordinating sites for coordination on $[M(III)\text{-}EGTA]^-$ binary complex compared to aquated M(III) metal ions. The orders of stability constants for $1:1$ binary and $1:1:1$ ternary complexes were found to be in accordance with basicity order of the secondary ligands.

$$MAA > AA > SAA$$

With respect to metal ions the stability order is $Y(III) > Sm(III) > Nd(III) > Pr(III) > Ce(III) > La(III)$ which is in order of increasing ionic potential of the metal ions.

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