Studies of some lanthanide quaternary complexes

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Formation constants of mixed ligand quaternary lanthanide complexes of the type M-A-B-L'/L″ where M = La^{3+}, Pr^{3+}, Nd^{3+}; A = ethylenediamine N, N, N′, N′-tetraacetic acid (EDTA); B = thiodiglycolic acid (TDA); L′ = iminodiacetic acid (IDA) and L″ = glycine (Gly) have been determined by pH-metric technique at $35 \pm 1°C$ in 0.1 mol dm^{-3} KNO$_3$. Stability constants reveal the orders: La(III) < Pr(III) < Nd(III) in terms of metal ions, binary < ternary < quaternary in terms of complex species, and IDA < Gly in terms of amino acids. The $\Delta \log K$ values are negative for all the ternary and quaternary systems. However, $\Delta \log K$ values are significantly positive indicating intramolecular hydrophobic ligand-ligand interactions.

Mixed ligand complexes of biological importance have been extensively studied[1a,b]. A linear relationship was reported[1c−e] between the basicities of the secondary ligands and the stability constants of mixed ligand complexes. Stability constants of ternary lanthanide complexes have been correlated with some fundamental properties of metal ions and ligand characteristics[2,3]. We observed during our studies on formation of quaternary species that the metal ions expand their coordination sphere and the resulting quarternary species were more stable than the ternary ones[4,5]. In the present note we report the results of our potentiometric studies on 1:1:1:1 M(III)-EDTA-TDA-IDA/Gly system.

Experimental

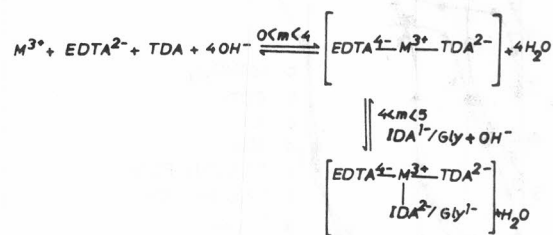Aqueous solutions of lanthanum(III) and praseodymium(III) and neodymium(III) nitrates were standardised by literature procedure[6,7]. The formation constants of equilibria were calculated by a modification[4] of the method of Santappa et al.[8] in the case of simultaneous addition of ligands to the metal ions and by the method of Thompson et al.[9]. for stepwise chelation of ligands.

Results and discussion

Curves from a to g (Fig. 1) have already been discussed earlier[5,10−13] Curve h represents the potentiometric titration of 1:1:1, M(III)-EDTA-IDA ternary system. Two inflections present at $m = 2$ and $m = 3$ show the formation of 1:1, M(III)-EDTA complex initially and the addition of IDA takes place later on. However, on curve i a well define inflection at $m = 4$ depicts the simultaneous chelation of EDTA and TDA to the metal ion resulting in the formation of 1:1:1, M(III)-EDTA-TDA species.

Curve j (Fig. 1) illustrates the titration of 1:1:1:1, M(III)-EDTA-TDA-IDA/Gly system. An inflection at $m = 4$ may be due to the titration of only four protons of the two ligands, two each from K$_2$EDTA and TDA, forming 1:1:1, M(III)-EDTA-TDA complex. This soluble complex appears to add IDA/Gly in the higher buffer region giving 1:1:1:1, M(III)-EDTA-TDA-IDA/Gly quatternary complex as shown by the presence of one more inflection at $m = 5$. The absence of any solid phase during the titration, the non-superimposable nature of the theoretical composite curve T (ref. 14) [drawn by adding the horizontal distance of curve i to the curve c(Fig. 1)] in the region of mixed-ligand complex formation and the evaluated values of stability constants support formation of quaternary complexes as follows:

$$M^{3+} + EDTA^{2-} + TDA + 4OH^- \xrightleftharpoons{\quad 0 < m < 4 \quad} \left[EDTA^{4-} - M^{3+} - TDA^{2-} \right] + 4H_2O$$

$$\Updownarrow \begin{array}{c} 4 < m < 5 \\ IDA^{1-}/Gly + OH^- \end{array}$$

$$\left[\begin{array}{c} EDTA^{4-} - M^{3+} - TDA^{2-} \\ IDA^{2-}/Gly^{1-} \end{array} \right] + H_2O$$

The stability constants (Table 1) have been found to follow the sequence, La(III) < Pr(III) < Nd(III), which is the order of increased occupancy of the 4f-orbitals of these lanthanides. The stability orders with regard to secondary and tertiary ligands follow the order of their basic strengths.

The negative values of $\Delta \log K$ (Table 1) are attributed to coulombic repulsions between negatively charge binary complex [M-EDTA]$^-$ and secondary ligand (L^{2-} or L^{1-}) during the formation of ternary complex.

A parameter "percentage relative stabilization" (% R.S.) $= (\log K_{MAL}^M - \log K_{ML}^M)/\log K_{ML}^M \times 100)$ has been introduced. The greater stabilization of the ternary and quaternary complexes may be explained on the basis of a cooperative effect (1f) between the primary, secondary and tertiary ligands in these cases. The existence of intramolecular hydrophobic inter-

Table 1—Metal-ligand stability constants of 1:1, binary, 1:1:1, ternary and 1:1:1:1, quaternary complexes and other related properties $\{[KNO_3] = 0.1$ mol dm^{-3}; temp.: $35 \pm 1°C$; pH-meter readability: 0.01; standardization: at $pH = 4$ & 9 $[KOH] = 0.1$ mol dm^{-3}; total volume: 50 dm^3; $T_M:T_A:T_B:T_L = 1:1:1:1$ or $T_M:T_A:T_B:T_L = 1:1:1:1\}$

M	A	B	L'	L''		pH range	La(III) log K	$-\Delta$ log K	$-(\%)$ R.S.	Pr(III) log K	$-\Delta$ log K	$-(\%)$ R.S.	Nd(III) log K	$-\Delta$ log K	$-(\%)$ R.S.
1	1	0	0	0	log K^M_{MA}	2 3-3.7	5.31	—	—	5.54	—	—	5.78	—	—
1	1	0	1	0	log $K^{MA}_{MAL'}$	7.4-10.2	4.10	1.21	10.67	4.65	0.89	6.25	5.01	0.77	4.21
1	1	0	0	1	log $K^{MA}_{MAL''}$	8.7-10.6	4.46	0.85	16.63	4.89	0.65	12.36	5.23	0.55	8.56
1	1	1	1	0	log $K^{MAB}_{MABL'}$	7.5-10.8	3.36	0.65	26.79	3.71	0.58	25.20	4.21	0.46	19.50
1	1	1	0	1	log $K^{MAB}_{MABL''}$	8.4-10.4	3.57	0.44	33.27	3.90	0.39	30.10	4.34	0.33	24.12
1	1	1	0	0	log K^M_{MAB}	2.5-5.1	9.32	—	—	9.83	—	—	10.45	—	—
1	1	0	1	0	log β_2	2.3-10.2	9.41	—	—	10.19	—	—	10.79	—	—
1	1	0	0	1	log β_3	2.3-10.6	9.77	—	—	10.43	—	—	11.01	—	—
1	1	1	1	0	log β_4	2.3-10.8	12.68	—	—	13.54	—	—	14.66	—	—
1	1	1	0	1	log β_5	2.3-10.4	12.89	—	—	13.73	—	—	14.79	—	—

dissociation constants of the ligands, calculated by Martell's method[15] and Albert's method[16],

A = K_2EDTA : $pK_1 = 5.58 \pm 0.02$, $pK_2 = 9.84 \pm 0.01$
B = TDA : $pK_1 = 2.98 \pm 0.10$, $pK_2 = 4.37 \pm 0.01$
L' = K_1IDA : $pK_1 = 9.13 \pm 0.02$
L'' = Gly : $pK_1 = 9.88 \pm 0.03$
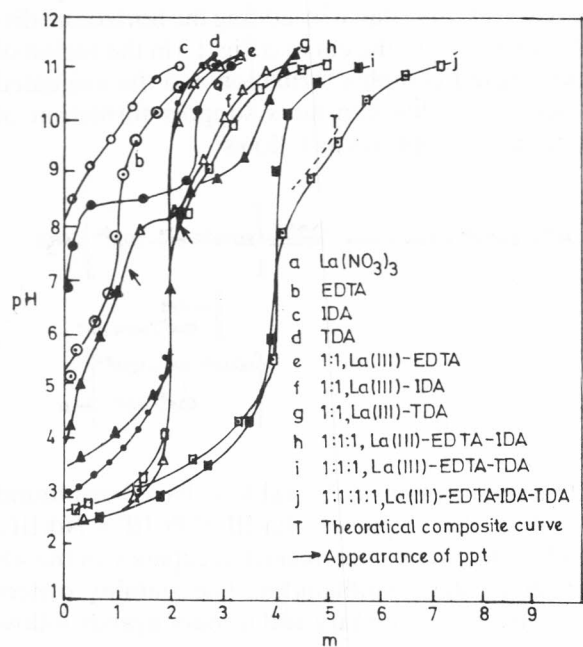
Fig. 1—Potentiometric titration curves for La(III)-EDTA-IDA-TDA system

Table 2—Possibility of occurrence of intramolecular hydrophobic ligand-ligand interaction in ternary and quaternary complexes

System	ΔLog K for metal ions		
	La(III)	Pr(III)	Nd(III)
1:1:1, M(III)-EDTA-IMDA/Gly	+ 0.36	+ 0.24	+ 0.22
1:1:1:1, M(III)-EDTA-TDA-IMDA/Gly	+ 0.21	+ 0.19	+ 0.13

of the association of secondary and tertiary ligands with MA^{-1} and MAB^{3-} ion in ternary and quaternary systems follows, in general, the same pattern as it does with aqueous ion, $M(H_2O)_n$.

actions may be examined by calculating the Δ log K values.

$$\Delta \log K = \log K_1 - \log K_2$$

Significantly positive values of Δ log K (Table 2) for ternary and quaternary complexes indicate hydrophobic interaction responsible for extrastabilization.

The linearity of log K^M_{MAB} versus log K^M_{MA}, and log K^{MAB}_{MABL}, versus log K^M_{MAB}, etc., shows that the affinity

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