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Stability Parameters of Some Lanthanide Mixed Ligand Complexes

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Stability constants of mixed ligand complexes of lanthanide metal ions *viz.* La(III), Pr(III) and Nd(III) with ethylene diamine-N,N,N′,N′-tetra-acetic acid (EDTA), pyridine-2,6-dicarboxylic acid (PDA), iminodiacetic acid (IDA) and glycine (GLY) as ligand have been studied potentiometrically at temperature 25±1°C and ionic strength 0.1 mol dm^{-3} KNO_3. A comparison of the stability constants in binary, ternary and quaternary complexes reveal the order, La(III) < Pr(III) < Nd(III) in terms of metal ions, binary < ternary < quaternary in terms of complex species and IDA < GLY in case of amino acids. The Δ log K values are negative for all the ternary and quaternary systems, however, $\Delta\Delta$ log K values are significantly positive. It shows the intramolecular hydrophobic ligand interaction.

INTRODUCTION

The factors affecting the stability of mixed ligand complexes are mainly directed towards the correlation of the characteristics of ligands and the mixed ligand complex stability. The work describing the effect of the nature of the ligand on the stability of the complex has been reviewed[1–4]. The effects of intramolecular interligand interactions[5–10] and non interacting substituents[11–16] in the ligands on the stability of the mixed ligand complexes are the major topics of current interest. The quaternary systems chosen for study are of type M–A–B–L/L′ where M = La(III), Pr(III) and Nd(III); A = EDTA; B = PDA; L = IDA and L′ = GLY, with a view to study their relative stability.

EXPERIMENTAL

The solution of all chemicals (AR, BDH, GR or E. Merck) used, were prepared in double distilled water. Standard solutions of rare earth nitrates were prepared and standardized by their oxalate method[17]. The amino acids (EDTA and IDA) were used in their monoprotonated form. The solution of PDA, GLY, potassium nitrate and potassium hydrogen phthalate were prepared by direct weighing method. The concentration of the ligand solutions was further checked by potentiometry.

pH Measurements were carried out with Toshniwal digital pH meter (accuracy ±0.01). The instrument was standardized against (0.05 M)

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potassium hydrogen phthalate solution for pH 4 at 25°C in the beginning of each titration. Each titration was repeated at least twice against (0.1 M) potassium hydroxide solution to ensure the reproducibility of the results, keeping the ionic strength of 0.1 mol dm^{-3} KNO_3 and total volume (50 dm^{-3}) constant in the beginning of each titration.

The dissociation constants of K_3EDTA ($pK_1 = 9.26$), PDA ($pK_1 = 2.57$) KIDA ($pK_1 = 9.05$) and GLY ($pK_1 = 9.77$) were calculated by the method of Chaberek and Martell[18]. Stability constants were evaluated by the method of Ramamoorthy and Santappa[19] for the simultaneous chelation of the ligands to the metal ion, however, in the case of stepwise addition of the ligands to the metal ion, Thompson and Loraas method[20] was applied. The calculations have been carried out on UPTRON PC-XT (20 MB Hard Disk) computer with Dot Matrix Printer PM 90001.

RESULTS AND DISCUSSION

Curves a to e, g and i (Figs. 1 and 2) have already been discussed[21-23]. Curve f (Figs. 1 and 2) represent the titration of 1 : 1, M(III)–PDA binary systems. The lowering in the initial pH followed by an inflection at m = 2 may be attributed to the formation of 1 : 1, M(III)–PDA binary complex. The other inflection at m ~ 3.5 may, however, be ascribed to the disproportionation of the initially formed 1 : 1 complex into 1 : 2, M(III)–PDA species and to the simultaneous precipitation of the remaining metal as metal hydroxide at higher pH.

Potentiometric titrations of 1 : 1 : 1, M(III)–EDTA–PDA ternary species (Figs. 1 and 2) have been exhibited by curve h. The lowering in the pH followed by an inflection at m = 3 on this curve may be ascribed to the simultaneous addition of both the ligands to the metal ion. Curve j illustrates the titration of 1 : 1 : 1 : 1, M(III)–EDTA–PDA–IDA/GLY system. This curve runs parallel to the curve h showing the titration of only three protons of the two ligand (EDTA and PDA) due to the initial formation of the 1 : 1 : 1, M(III)–EDTA–PDA complex. This soluble complex appears to add IDA/GLY in the higher buffer region giving 1 : 1 : 1 : 1, M(III)–EDTA–PDA–IDA/GLY quaternary complex as supported by the presence of one more inflection at m = 4.

$$M^{3+} + EDTA^{3-} + PDA + 3OH^- \overset{0<m<3}{\rightleftharpoons} [EDTA^{4-}—M^{3+}—PDA] + 3H_2O$$

$$3<m<4 \Downarrow IDA^{1-}/GLY\ OH^-$$

$$\left[\begin{matrix} EDTA^{4-}—M^{3+}—PDA \\ \quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad IDA^{2-}/GLY^{1-} \end{matrix}\right] + H_2O$$

The absence of any solid phase during the titration, the non-super-

impossible nature of theoretical composite curve T in the region of mixed ligand formation also support the above quaternary species[24].

The calculated values of the formation constants are recorded in Tables 1 and 2. The evaluated values of stability constants have been found to follow the trend : La(III) < Pr(III) < Nd(III) due to their decreasing size and increasing ionic potential (charge/radius ratio). The stability order has been found to be IDA < GLY in terms of amino acid.

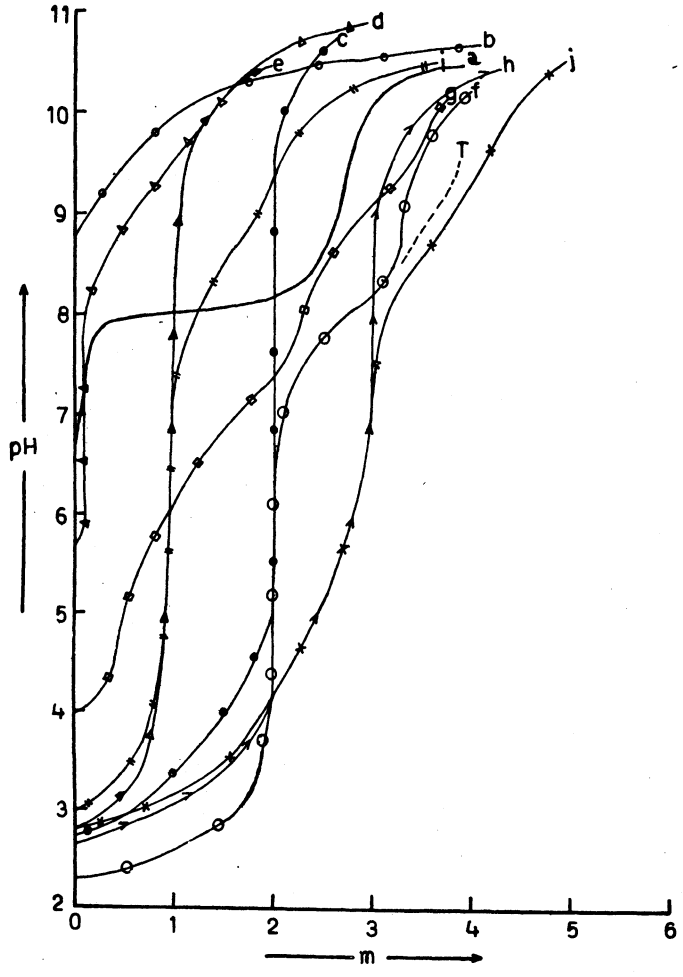

Fig. 1 1 : 1 : 1 : 1, La(III)-EDTA-PDA-IDA

(a) La(III) Nitrate, (b) EDTA, (c) PDA, (d) IMDA, (e) 1 : 1, La(III)-EDTA, (f) 1 : 1, La(1II)-PDA, (g) 1 : 1, La(III)-IDA, (h) 1 : 1 : 1, La(III)-EDTA-PDA, (i) 1 : 1 : 1, La(III)-EDTA-IDA, (j) 1 : 1 : 1, La(III)-EDTA-PDA-IDA, (t) Theoretical composite curve → Appearance of ppt.

Free energy of formation (Table 1) has been calculated and found to be negative in all the cases indicating complex formation almost spontaneous in nature.

The general order of stability for the complexes has been found to be $\log K^{M}_{MA} > \log K^{MA}_{MAL} > \log K^{MAB}_{MABL}$ and $\log K^{M}_{MA} > \log K^{MA}_{MAL}, > \log K^{MAB}_{MABL}$. But the overall stability of quaternary complexes is greater than

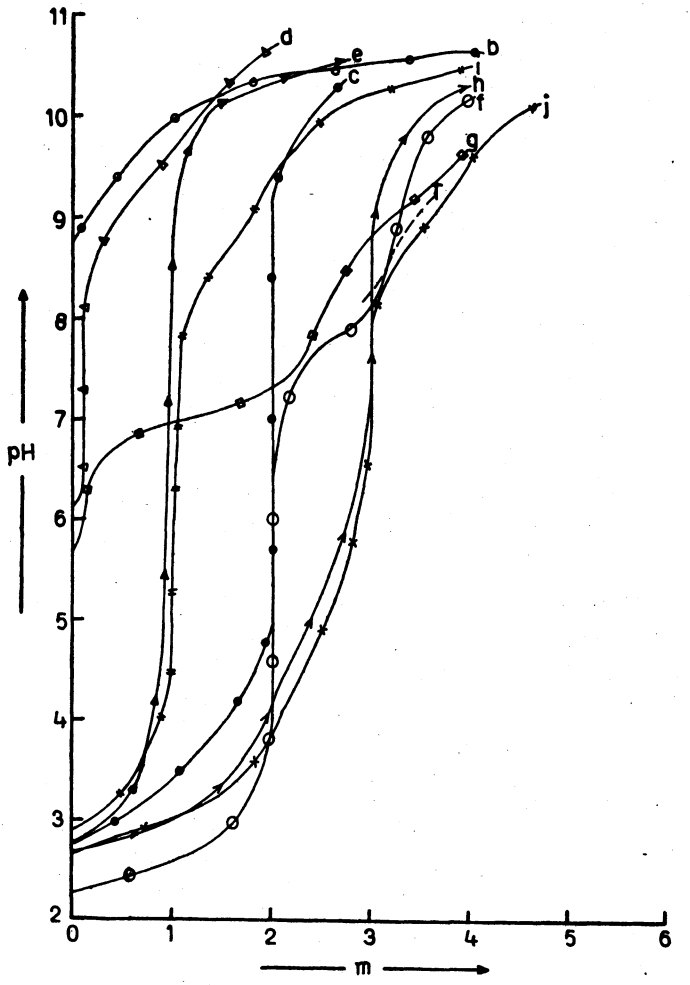

Fig. 2 1 : 1 : 1 : 1, La(III)-EDTA-PDA-GLY

(b) EDTA, (c) PDA, (d) GLY, (e) 1 : 1, La(III)-EDTA, (f) 1 : 1, La(III)-PDA, (g) 1 : 1, La(III)-GLY, (h) 1 : 1 : 1, La(III)-EDTA-PDA, (i) 1 : 1 : 1, La(III)-EDTA-GLY, (j) 1 : 1 : 1, La(III)-EDTA-PDA-GLY, (t) Theoretical composite curve → Appearance of ppt.

TABLE 1

STABILITY CONSTANTS OF 1 : 1, BINARY, 1 : 1 : 1, TERNARY AND 1 : 1 : 1 : 1, QUATERNARY COMPLEXES AND OTHER RELATED PARAMETERS

KNO_3 = 0.1 mol dm^{-3}; Temp. : 25±1°C; $T_M : T_A : T_B : T_L = 1 : 1 : 1 : 1$
KOH = 0.1 mol dm^{-3}; Total Volume : 50 dm^3; $T_M : T_A : T_B : T_L = 1 : 1 : 1 : 1$

System	Property	Value for Metal ion		
		La(III)	Pr(III)	Nd(III)
1 : 1,M(III)-EDTA	$\log K^{M}_{MA}$	5.21	5.41	5.68
	$-\Delta G$	7.13	7.38	7.75
1 : 1 : 1,M(III)-EDTA-IDA	$\log K^{MA}_{MAL}$	4.23	4.79	5.14
	$-\Delta G$	5.77	6.53	7.01
	$-\Delta \log K$	0.98	0.62	0.54
	−(%) R.S.	25.53	20.69	19.05
1 : 1 : 1,M(III)-EDTA-GLY	$\log K^{MA}_{MAL,}$	4.59	4.99	5.38
	$-\Delta G$	6.26	6.80	7.34
	$-\Delta \log K$	0.62	0.42	0.30
	−(%) R.S.	18.18	12.30	15.27
1 : 1 : 1 : 1,M(III)-EDTA-PDA-IDA	$\log K^{MAB}_{MABL}$	2.39	2.60	2.89
	$-\Delta G$	3.26	3.60	3.94
	$-\Delta \log K$	4.93	5.21	5.33
	−(%) R.S.	57.82	56.29	54.49
1 : 1 : 1 : 1,M(III)-EDTA-PDA-GLY	$\log K^{MAB}_{MABL,}$	3.45	3.62	3.76
	$-\Delta G$	4.70	4.94	5.13
	$-\Delta \log K$	3.87	4.23	4.46
	−(%) R.S.	38.50	36.38	35.39

for the ternary complexes and the overall stability of ternary complexes is greater than for the binary ones (Table 1) *i.e.* $\log K^{M}_{MA} < \log K^{M}_{MAB} < \log \beta_1 < \log \beta_2 < \log \beta_3 < \log \beta_4$. The lower values of $\log K^{MA}_{MAL}$ than $\log K^{M}_{MA}$ may be due to the coulombic repulsions between the negatively charged primary complex $[M—EDTA]^{1-}$ and the incoming ligand L^{2-} or L^{1-} during the formation of ternary complex. The $\Delta \log K$ values are consequently negative which should be primarily due to the electrostatic repulsion induced by the secondary or tertiary ligand. The statistically expected value of $\Delta \log K$ depends on the geometry of the complex and the denticity of the ligands[25]. In the present case, the—$\Delta \log K$ values are relatively smaller which indicate a greater stabilization of the mixed ligand complexes.

The $\Delta \log K$ values measure the relative case or difficulty in the formation of mixed ligand complexes as compared to the binary ones. In the

present case, only 1 : 1 binary, 1 : 1 : 1 ternary and 1 : 1 : 1 : 1 quaternary complexes have been studied with systems containing equal amount of metal and ligand. The values of Δ log K obtained for the mixed ligand complexes are recorded in Table 1, alongwith values of stability constants. It is notworthy that the magnitude of Δ log K cannot, however be compar-

TABLE 2
OVERALL STABILITY OF TERNARY AND QUATERNARY COMPLEXES

System	Property	Value for Metal ion		
		La(III)	Pr(III)	Nd(III)
1 : 1 : 1,M(III)-EDTA-PDA	$\log K^{M}_{MAB}$	7.32	7.85	8.22
1 : 1 : 1,M(III)-EDTA-IDA	$\log \beta_1$	9.68	10.46	11.05
1 : 1 : 1 : 1,M(III)-EDTA-PDA-IDA	$\log \beta_2$	9.71	10.49	11.11
1 : 1 : 1,M(III)-EDTA-GLY	$\log \beta_3$	10.04	10.66	11.29
1 : 1 : 1 : 1,M(III)-EDTA-PDA-GLY	$\log \beta_4$	10.77	11.47	11.98

ed for different mixed ligand complexes as its value depends on the log K^{M}_{ML} value. A parameter 'Percentage Relative Stabilization' (% R.S.) has been introduced for this purpose. A comparison of the relative stabilities of different mixed complexes can be more satisfactorily achieved on the basis of this parameter. The % R. S. for the ternary complex may be defined as:

$$(\%)\ \text{R.S.} = (\log K^{MA}_{MAL} - \log K^{M}_{ML})/\log K^{M}_{ML} \times 100$$

The greater stabilization of the ternary and quaternary complexes may tentatively be explained on the basis of a cooperative effect[26] between the primary, secondary and tertiary ligands in these cases. The possibilities of the stereoselectivity, indirect cooperative effect and intramolecular covalent bond formation being ruled out; the existence of intramolecular hydrophobic interactions may be examined by calculating $\Delta\Delta$ log K values.

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

Positive and significant values of $\Delta\Delta$ log K (Table 3) for the systems M-EDTA-IDA/GLY and M-EDTA-PDA/GLY may be regarded as an evidence of hydrophobic interaction responsible for the relatively greater stabilization of the mixed complexes.

For log log type of stability correlations[27], plots of

(a) $\log K^{MA}_{MAL}$ Vs $\log K^{M}_{MA}$ (b) $\log K^{MA}_{MAL}$, Vs $\log K^{M}_{MA}$
(c) $\log K^{M}_{MAB}$ Vs $\log K^{M}_{MA}$ (d) $\log K^{MA}_{MAL}$ Vs $\log K^{MA}_{MAL}$,
(e) $\log K^{MAB}_{MABL}$ Vs $\log K^{M}_{MAB}$ (f) $\log K^{MAB}_{MABL}$, Vs $\log K^{M}_{MAB}$

TPBLE 3

POSSIBILITY OF OCCURRENCE OF INTRAMOLECULAR HYDROPHOBIC LIGAND INTERACTION IN TERNARY AND QUATERNARY COMPLEXES

System	Value of $\Delta\Delta$ log K for Metal ion		
	La(III)	Pr(III)	Nd(III)
1 : 1 : 1,M(III)-EDTA-IDA/GLY	0.36	0.20	0.24
1 : 1 : 1 : 1,M(III)-EDTA-PDA-IDA/GLY	1.06	1.08	0.87

TABLE 4

SLOPE VALUE FOR THE LINEAR PLOTS REPRESENTING LOG LOG TYPE OF CORRELATION

Correlation*		Slope value
$\log K^{MA}_{MAL}$	Vs $\log K^{M}_{MA}$	2.066
$\log K^{MA}_{MAL'}$	Vs $\log K^{M}_{MA}$	1.666
$\log K^{M}_{MAB}$	Vs $\log K^{M}_{MA}$	1.956
$\log K^{MA}_{MAL}$	Vs $\log K^{MA}_{MAL'}$	1.233
$\log K^{MAB}_{MABL}$	Vs $\log K^{M}_{MAB}$	0.555
$\log K^{MAB}_{MABL'}$	Vs $\log K^{M}_{MAB}$	0.344

A = EDTA; B = PDA; L = IDA and L′ = GLY

have been studied. The slope values are given in Table 4. All plots are linear which shows that the affinity of the association of secondary and tertiary ligands to MA^{1-} ion in ternary and quaternary systems follows, in general, the same patterns as it does with aqueous metal ion.

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