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Note

Thermodynamic stability constants of gadolinium(III), dysprosium(III), erbium(III) and ytterbium(III) complexes with tyrosine

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Tyrosine is a biological important substance. Complexes of lanthanons with amino acids have been extensively studied[1,2], but little work appears to have been reported with tyrosine[3–7]. In this note, thermodynamic stability constants of Gd^{3+}, Dy^{3+}, Er^{3+} and Yb^{3+} with tyrosine are being reported.

EXPERIMENTAL

Standard carbonate free potassium hydroxide was used for pH metric titrations. All metal nitrates were of AnalaR grade and their solutions were standardized by EDTA method. The ligand solution was prepared in CO_2 free conductivity water immediately before use. The following two solutions (total volume 50 ml) were titrated against standard alkali at 35 ± 0.1 °C in a thermostat bath: (A) 20 ml of 0.625×10^{-2} M ligand; and (B) 20 ml of 0.625×10^{-2} M ligand $+5$ ml of 1×10^{-1} M metal nitrate. An ionic strength of 0.1, 0.2 and 0.3 M was maintained by the addition of a calculated amount of potassium nitrate solution (1 M). The pH was measured on a Photovolt Digicord pH meter having a sensitivity of ± 0.002. The plots of pH versus the volume of alkali added were plotted. The shapes of the titration curves were as usual. In the calculations, the concentrations were corrected for changes in volume produced by the addition of alkali during titration. The calculated error in stability constants is ± 0.01 log K.

RESULTS AND DISCUSSION

The protonation constant and successive formation constants were determined by the Calvin–Bjerrum pH titration technique[8,9], using relationships derived therein and employing various computational methods[10]. The values of the protonation constants of the ligand and metal–ligand stability constants at different ionic strengths are summarized in Table 1. The values of $\bar{n}$ obtained are of the order 2 between pH range 6.5 to 8.0. This suggests that Gd^{3+}, Dy^{3+}, Er^{3+} and Yb^{3+} form two types of complexes in the proportion 1:1 and 1:2 with tyrosine. Most amino acids are present as a single protonated form HL in the pH range 2.7 to 8.5. A few amino acids occur as

TABLE 1

VALUES OF THE PROTONATION CONSTANTS AND STABILITY CONSTANTS AT 35°C

Cation	*Constant*	*$\mu=0.1$*	*$\mu=0.2$*	*$\mu=0.3$*
	log $K5$	9.20	9.18	9.45
	(amino functional group)			
Gd^{3+}	log K_1	4.92	4.84	4.77
	log K_2	4.43	4.38	4.32
	log β_2	9.35	9.22	9.09
Dy^{3+}	log K_1	5.04	4.96	4.88
	log K_2	4.57	4.51	4.45
	log β_2	9.61	9.47	9.33
Er^{3+}	log K_1	5.15	5.07	4.99
	log K_2	4.80	4.75	4.70
	log β_2	9.95	9.82	9.69
Yb^{3+}	log K_1	5.35	5.27	5.19
	log K_2	5.00	4.94	4.88
	log β_2	10.35	10.21	10.07

TABLE 2

VALUES OF THERMODYNAMIC STABILITY CONSTANTS

	Gd^{3+}	*Dy^{3+}*	*Er^{3+}*	*Yb^{3+}*
log $K_1^{\mu=0}$	5.00	5.12	5.22	5.43
log $K_2^{\mu=0}$	4.49	4.63	4.85	5.06
log $\beta_2^{\mu=0}$	9.48	9.75	10.08	10.49

H_2L, H_2L^+ form over the whole range. This is true for tyrosine where protons of phenolic groups are not released. A comparison of metal–ligand stability constants values of tyrosine with those of serine permits the conclusion that the unionised hydroxy group is not participating in the complex formation[4,11,12]. The co-ordination appears to be only through amino nitrogen and carboxylic oxygen. The difference in log K_1 and log K_2 is less than 1.5, indicating the simultaneous formation of two types of complexes. The value of step formation constants at various ionic strengths, extrapolated to zero ionic strength gave step thermodynamic formation constants[10]. Likewise the values of overall thermodynamic stability constants were obtained and are summarized in Table 2. The values of log K_1, log K_2 and log β_2 decrease with an increase in ionic strength. The order of overall stability constant for these complexes is $Yb^{3+} > Er^{3+} > Dy^{3+} > Gd^{3+}$ as expected from their electronic configuration.

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